LECTURE NOTES ON INTERMEDIATE THERMODYNAMICS

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Contents

Preface

These are lecture notes for AME 50531 Intermediate Thermodynamics (AME 54531 for students in our London Programme), the second of two undergraduate courses in thermodynamics taught in the Department of Aerospace and Mechanical Engineering at the University of Notre Dame. Most of the students in this course are juniors or seniors majoring in aerospace or mechanical engineering. The objective of the course is to survey both practical and theoretical problems in classical thermodynamics.

The notes draw heavily on the text specified for the course, Borgnakke and Sonntag's (BS) *Fundamentals of Thermodynamics*, Eighth Edition, John Wiley, New York, 2013, especially Chapters 8-14. In general the nomenclature of BS is used, and much of the notes follow a similar structure as that text. In addition, Abbott and van Ness's *Thermodynamics*, McGraw-Hill, New York, 1972, has been used to guide some of the mathematical developments. Many example problems have been directly taken from BS and other texts; specific citations are given where they arise. Many of the unique aspects of these notes, which focus on thermodynamics of reactive gases with detailed finite rate kinetics, have arisen due to the author's involvement in research supported by the National Science Foundation under Grant No. CBET-0650843. The author is grateful for the support. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the National Science Foundation.

These notes emphasize both problem-solving as well as some rigorous undergraduate-level development of the underlying classical theory. It should also be remembered that practice is essential to the learning process; the student would do well to apply the techniques presented here by working as many problems as possible.

The notes, along with information on the course, can be found on the world wide web at `https://www3.nd.edu/~powers/ame.50531`. At this stage, anyone is free to make copies for their own use. I would be happy to hear from you about suggestions for improvement.

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Chapter 1

Review

Review BS, Chapters 1-7.

Here is a brief review of some standard concepts from a first course in thermodynamics.

- PROPERTY: characterizes the thermodynamics state of the system
  - EXTENSIVE: proportional to system's extent, upper case variables
    - V: total volume, SI-based units are m^3,
    - U: total internal energy, SI-based units are kJ,
    - H: total enthalpy, SI-based units are kJ,
    - S: total entropy, SI-based units are kJ/K.
  - INTENSIVE: independent of system's extent, lower case variables (exceptions are temperature T and pressure P, which are intensive). Intensive properties can be on a mass basis or a molar basis:
    - v: specific volume, SI-based units are m^3/kg,
    - u: specific internal energy, SI-based units are kJ/kg,
    - h: specific enthalpy, SI-based units are kJ/kg,
    - s: specific entropy, SI-based units are $kJ/kg/K$.
    - $\overline{v}$: molar specific volume, SI-based units are $m^3/kmole$,
    - $\overline{u}$: molar specific internal energy, SI-based units are $kJ/kmole$,
    - $\overline{h}$: molar specific enthalpy, SI-based units are $kJ/kmole$,
    - $\overline{s}$: molar specific entropy, SI-based units are $kJ/kmole/K$.
- DENSITY: $\rho = 1/v$, mass per unit volume, SI-based units are kg/m^3.
- EQUATIONS OF STATE: relate properties
  - CALORICALLY PERFECT IDEAL GAS (CPIG) has $Pv = RT$ and $u - u_o = c_v(T - T_o)$,

  - CALORICALLY IMPERFECT IDEAL GAS (CIIG) has $Pv = RT$ and $u - u_o = \int_{T_o}^{T} c_v(\hat{T})\, d\hat{T}$.
  - NON-IDEAL STATE EQUATIONS have $P = P(T, v)$, $u = u(T, v)$.

- Any intensive thermodynamic property can be expressed as a function of at most *two* other intensive thermodynamic properties (for simple compressible systems).
  - $P = RT/v$: thermal equation of state for ideal gas, SI-based units are kPa.
  - $c = \sqrt{kPv}$: sound speed for CPIG, SI-based units are m/s; $k = c_P/c_v$, the ratio of specific heats.
- ENERGY: $E = U + (1/2)m(\mathsf{v} \cdot \mathsf{v}) + mgz$, total energy = internal+kinetic+potential.
- FIRST LAW: $dE = \delta Q - \delta W$; if kinetic and potential are ignored, $dU = \delta Q - \delta W$; with $\delta Q = TdS$ and $\delta W = PdV$, we get the Gibbs equation $dU = TdS - PdV$.
- SECOND LAW: $dS \geq \delta Q/T$.
- PROCESS: moving from one state to another, in general with accompanying heat transfer and work.
- CYCLE: process which returns to initial state.
- SPECIFIC REVERSIBLE WORK: ${}_1w_2 = \int_1^2 Pdv$; $\delta w = Pdv$.
- SPECIFIC REVERSIBLE HEAT TRANSFER: ${}_1q_2 = \int_1^2 Tds$; $\delta q = Tds$.

Figure 1.1 gives an example of an isothermal thermodynamic process going from state 1 to state 2 in various thermodynamic planes. Figure 1.2 gives a sketch of a thermodynamic cycle.

Example 1.1

Consider an ideal gas in the $T - s$ plane. Compare the slope of an isochore to that of an isobar at a given point.

Recall the Gibbs equation for a simple compressible substance:

$$\boxed{Tds = du + Pdv.} \tag{1.1}$$

We have for the ideal gas

$$\boxed{du = c_v dT,} \qquad \text{if ideal gas.} \tag{1.2}$$

This holds for all ideal gases, be they calorically perfect or imperfect. Thus, the Gibbs equation can be rewritten as

$$Tds = \underbrace{c_v dT}_{=du} + Pdv. \tag{1.3}$$

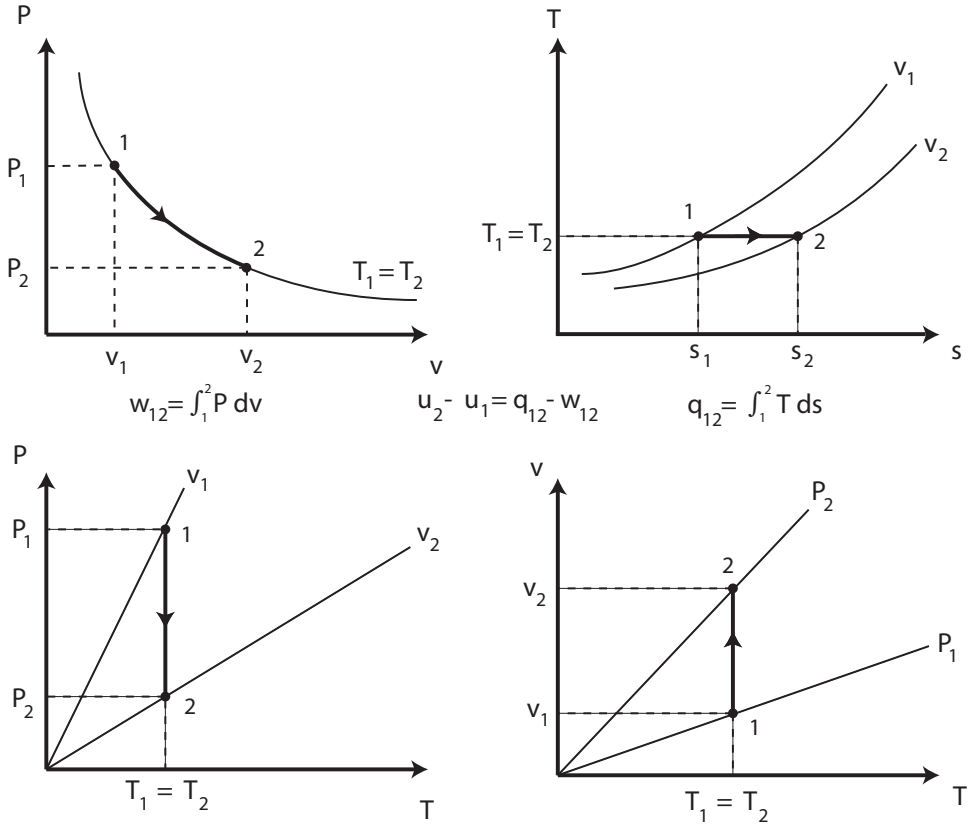

Figure 1.1: Sketch of isothermal thermodynamic process.

On an isochore, v is constant, so $dv = 0$. So on an isochore, we have

$$Tds = c_v dT, \qquad \text{on an isochore.} \tag{1.4}$$

or, using the partial derivative notation,

$$\boxed{\left.\frac{\partial T}{\partial s}\right|_v = \frac{T}{c_v}.} \tag{1.5}$$

Next recall the definition of enthalpy, h:

$$h = u + Pv. \tag{1.6}$$

We can differentiate Eq. (1.6) to get

$$dh = du + Pdv + vdP. \tag{1.7}$$

Substitute Eq. (1.7) into the Gibbs equation, (1.1), to eliminate du in favor of dh to get

$$Tds = \underbrace{dh - Pdv - vdP}_{=du} + Pdv, \tag{1.8}$$

$$= dh - vdP. \tag{1.9}$$

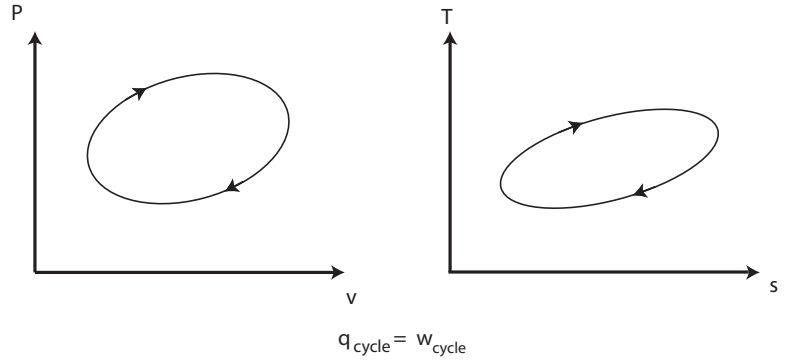

Figure 1.2: Sketch of thermodynamic cycle.

For an ideal gas, $dh = c_P dT$, where c_P is at most a function of T, so

$$Tds = \underbrace{c_P dT}_{=dh} - vdP. \tag{1.10}$$

Now for the isobar, $dP = 0$. Thus on an isobar, we have

$$Tds = c_P dT, \qquad \text{on an isobar.} \tag{1.11}$$

And so the slope on an isobar in the $T - s$ plane is

$$\boxed{\left.\frac{\partial T}{\partial s}\right|_P = \frac{T}{c_P}.} \tag{1.12}$$

Since $c_P > c_v$, (recall for an ideal gas that $c_P(T) - c_v(T) = R > 0$), we can say that the slope of the isochore is steeper than the isobar in the $T - s$ plane.

Example 1.2

Consider the following isobaric process for air, modeled as a CPIG, from state 1 to state 2. $P_1 = 100\ kPa$, $T_1 = 300\ K$, $T_2 = 400\ K$. Show the second law is satisfied.

Since the process is isobaric, $P = 100\ kPa$ describes a straight line in the $P - v$ and $P - T$ planes and $P_2 = P_1 = 100\ kPa$. Since we have an ideal gas, we have for the $v - T$ plane:

$$v = \left(\frac{R}{P}\right) T, \qquad \text{straight lines!} \tag{1.13}$$

$$v_1 = \frac{RT_1}{P_1} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(300\ K)}{100\ kPa} = 0.861\ \frac{m^3}{kg}, \tag{1.14}$$

$$v_2 = \frac{RT_2}{P_2} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(400\ K)}{100\ kPa} = 1.148\ \frac{m^3}{kg}. \tag{1.15}$$

Since the gas is ideal:

$$du = c_v dT. \tag{1.16}$$

Since our ideal gas is also calorically perfect, c_v is a constant, and we get

$$\begin{aligned}
\int_{u_1}^{u_2} du &= c_v \int_{T_1}^{T_2} dT, && (1.17)\\
u_2 - u_1 &= c_v (T_2 - T_1), && (1.18)\\
&= \left(0.7175 \ \frac{kJ}{kg \ K}\right)(400 \ K - 300 \ K), && (1.19)\\
&= 71.750 \ \frac{kJ}{kg}. && (1.20)
\end{aligned}$$

Also we have

$$\begin{aligned}
Tds &= du + Pdv, && (1.21)\\
Tds &= c_v dT + Pdv, && (1.22)\\
\text{from ideal gas}: \quad v &= \frac{RT}{P}: \qquad dv = \frac{R}{P}dT - \frac{RT}{P^2}dP, && (1.23)\\
Tds &= c_v dT + RdT - \frac{RT}{P}dP, && (1.24)\\
ds &= (c_v + R)\frac{dT}{T} - R\frac{dP}{P}, && (1.25)\\
&= (c_v + c_P - c_v)\frac{dT}{T} - R\frac{dP}{P}, && (1.26)\\
&= c_P \frac{dT}{T} - R\frac{dP}{P}, && (1.27)\\
\int_{s_1}^{s_2} ds &= c_P \int_{T_1}^{T_2} \frac{dT}{T} - R\int_{P_1}^{P_2} \frac{dP}{P}, && (1.28)\\
s_2 - s_1 &= c_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right). && (1.29)\\
& && (1.30)
\end{aligned}$$

Now since P is a constant,

$$\begin{aligned}
s_2 - s_1 &= c_P \ln\left(\frac{T_2}{T_1}\right), && (1.31)\\
&= \left(1.0045 \ \frac{kJ}{kg \ K}\right)\ln\left(\frac{400 \ K}{300 \ K}\right), && (1.32)\\
&= 0.2890 \ \frac{kJ}{kg \ K}. && (1.33)
\end{aligned}$$

Then one finds

$$\begin{aligned}
{}_1w_2 &= \int_{v_1}^{v_2} Pdv = P\int_{v_1}^{v_2} dv, && (1.34)\\
&= P(v_2 - v_1), && (1.35)\\
&= (100 \ kPa)\left(1.148 \ \frac{m^3}{kg} - 0.861 \ \frac{m^3}{kg}\right), && (1.36)\\
&= 28.700 \ \frac{kJ}{kg}. && (1.37)
\end{aligned}$$

Now

$$
\begin{aligned}
du &= \delta q - \delta w, && (1.38)\\
\delta q &= du + \delta w, && (1.39)\\
\int_1^2 \delta q &= \int_1^2 du + \int_1^2 \delta w, && (1.40)\\
{}_1q_2 &= (u_2 - u_1) + {}_1w_2, && (1.41)\\
{}_1q_2 &= 71.750\ \frac{kJ}{kg} + 28.700\ \frac{kJ}{kg}, && (1.42)\\
{}_1q_2 &= 100.450\ \frac{kJ}{kg}. && (1.43)
\end{aligned}
$$

Now in this process the gas is heated from 300 K to 400 K. One would expect at a minimum that the surroundings were at 400 K. Check for second law satisfaction.

$$
\begin{aligned}
s_2 - s_1 &\geq \frac{{}_1q_2}{T_{surr}}? && (1.44)\\
0.2890\ \frac{kJ}{kg\ K} &\geq \frac{100.450\ kJ/kg}{400\ K}? && (1.45)
\end{aligned}
$$

$$
\boxed{0.2890\ \frac{kJ}{kg\ K} \geq 0.2511\ \frac{kJ}{kg\ K},} \qquad \text{yes.} \qquad (1.46)
$$

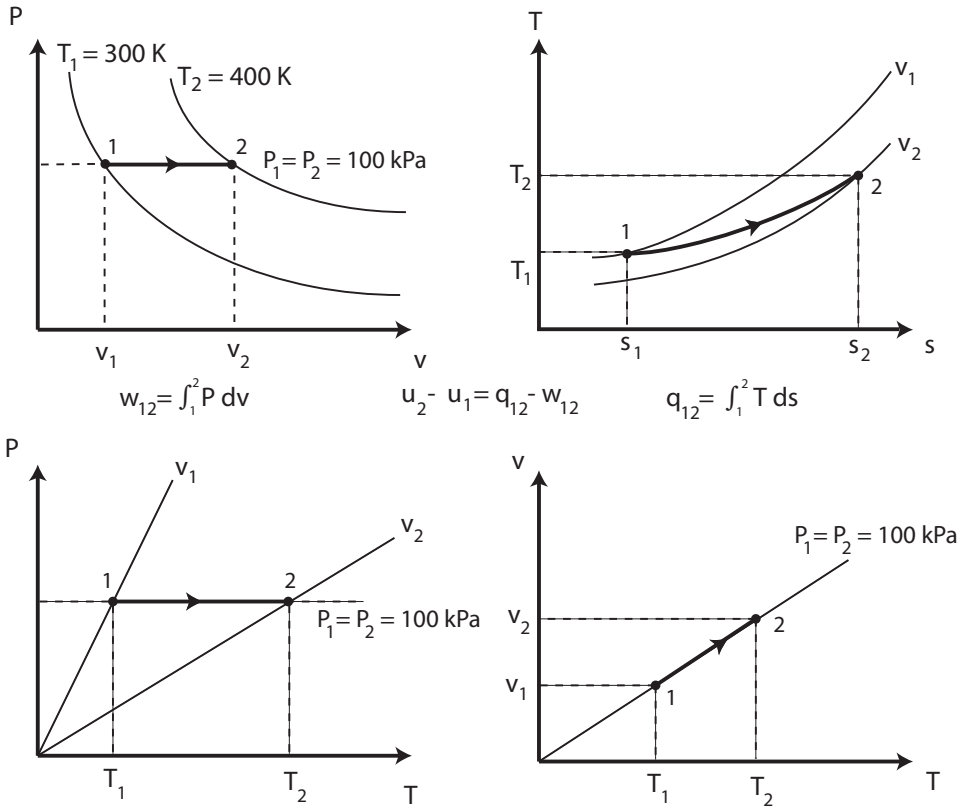

Figure 1.3: Sketch for isobaric example problem.

Chapter 2

Cycle analysis

Read BS, Chapters 5, 8, 9, 10.

2.1 Carnot

The Carnot cycle is the most well-known thermodynamic cycle. It is a useful idealization, but is difficult to realize in practice. Its real value lies in serving as a standard to which other cycles can be compared. These are usually fully covered in introductory courses. The cycle can be considered as follows

- $1 \rightarrow 2$: isentropic compression,
- $2 \rightarrow 3$: isothermal expansion,
- $3 \rightarrow 4$: isentropic expansion, and
- $4 \rightarrow 1$: isothermal compression.

This forms a rectangle in the $T - s$ plane The $P - v$ plane is more complicated. Both are shown in Figure 2.1.

2.1.1 Analysis for a calorically perfect ideal gas

For this discussion, consider a calorically perfect ideal gas. The isotherms are then straightforward and are hyperbolas described by

$$P = RT\frac{1}{v}. \tag{2.1}$$

The slope of the isotherms in the $P - v$ plane is found by differentiation:

$$\left.\frac{\partial P}{\partial v}\right|_T = -RT\frac{1}{v^2}, \tag{2.2}$$

$$= -\frac{P}{v}. \tag{2.3}$$

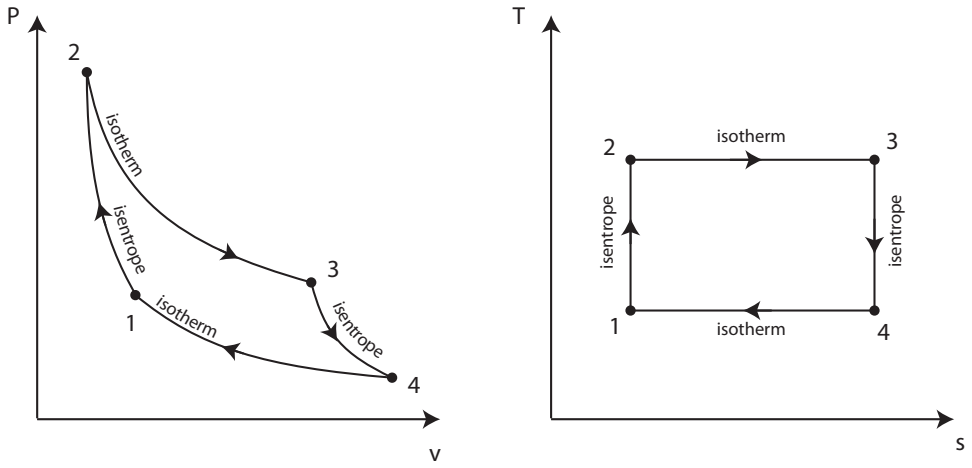

Figure 2.1: Sketch of $P - v$ and $T - s$ planes for a CPIG in a Carnot cycle.

The slope of the isentrope is found in the following way. Consider first the Gibbs equation, Eq. (1.1):

$$Tds = du + Pdv. \tag{2.4}$$

Because the gas is calorically perfect, one has

$$du = c_v dT, \tag{2.5}$$

so the Gibbs equation, Eq. (2.4), becomes

$$Tds = c_v dT + Pdv. \tag{2.6}$$

Now for the ideal gas, one has

$$\begin{aligned} Pv &= RT, && (2.7)\\ Pdv + vdP &= RdT, && (2.8)\\ \frac{Pdv + vdP}{R} &= dT. && (2.9) \end{aligned}$$

So then

$$Tds = c_v \underbrace{\left(\frac{Pdv + vdP}{R}\right)}_{=dT} + Pdv, \tag{2.10}$$

$$Tds = \left(\frac{c_v}{R} + 1\right) Pdv + \frac{c_v}{R} vdP, \qquad \text{Take } ds = 0, \tag{2.11}$$

$$0 = \left(\frac{c_v}{R} + 1\right) P + \frac{c_v}{R} v \left.\frac{\partial P}{\partial v}\right|_s, \tag{2.12}$$

$$\left.\frac{\partial P}{\partial v}\right|_s = -\frac{\frac{c_v}{R} + 1}{\frac{c_v}{R}} \frac{P}{v}, \tag{2.13}$$

$$= -\frac{\frac{c_v}{c_P - c_v} + 1}{\frac{c_v}{c_P - c_v}} \frac{P}{v}, \tag{2.14}$$

$$= -\frac{c_v + c_P - c_v}{c_v} \frac{P}{v}, \tag{2.15}$$

$$= -\frac{c_P}{c_v} \frac{P}{v}, \tag{2.16}$$

$$= -k \frac{P}{v}. \tag{2.17}$$

Since $k > 1$, the magnitude of the slope of the isentrope is greater than the magnitude of the slope of the isotherm:

$$\left|\left.\frac{\partial P}{\partial v}\right|_s\right| > \left|\left.\frac{\partial P}{\partial v}\right|_T\right|. \tag{2.18}$$

Example 2.1

(Adapted from BS, 7.94, p. 274) Consider an ideal gas Carnot cycle with air in a piston cylinder with a high temperature of 1200 K and a heat rejection at 400 K. During the heat addition, the volume triples. The gas is at 1.00 m^3/kg before the isentropic compression. Analyze.

Take state 1 to be the state before the compression. Then

$$T_1 = 400\ K, \quad v_1 = 1.00\ \frac{m^3}{kg}. \tag{2.19}$$

By the ideal gas law

$$P_1 = \frac{RT_1}{v_1} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(400\ K)}{1.00\ \frac{m^3}{kg}} = 1.148 \times 10^2\ kPa. \tag{2.20}$$

Now isentropically compress to state 2. By the standard relations for a CPIG, one finds

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}. \tag{2.21}$$

So

$$v_2 = v_1 \left(\frac{T_1}{T_2}\right)^{\frac{1}{k-1}} = \left(1.00\ \frac{m^3}{kg}\right)\left(\frac{400\ K}{1200\ K}\right)^{\frac{1}{1.4-1}} = 0.06415\ \frac{m^3}{kg}. \tag{2.22}$$

Note that $v_2 < v_1$ as is typical in a compression. The isentropic relation between pressure and volume can be rearranged to give the standard

$$P_2 v_2^k = P_1 v_1^k. \tag{2.23}$$

Thus, one finds that

$$P_2 = P_1 \left(\frac{v_1}{v_2}\right)^k = (1.148 \times 10^2\ kPa)\left(\frac{1.00\ \frac{m^3}{kg}}{0.06415\ \frac{m^3}{kg}}\right)^{1.4} = 5.36866 \times 10^3\ kPa. \tag{2.24}$$

Note the pressure has increased in the isentropic compression. Check to see if the ideal gas law is satisfied at state 2:

$$P_2 = \frac{RT_2}{v_2} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(1200\ K)}{0.06415\ \frac{m^3}{kg}} = 5.36866 \times 10^3\ kPa. \tag{2.25}$$

This matches. Now the expansion from state 2 to 3 is isothermal. This is the heat addition step in which the volume triples. So one gets

$$v_3 = 3v_2 = 3\left(0.06415\ \frac{m^3}{kg}\right) = 0.19245\ \frac{m^3}{kg}. \tag{2.26}$$

$$T_3 = T_2 = 1200\ K. \tag{2.27}$$

The ideal gas law then gives

$$P_3 = \frac{RT_3}{v_3} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(1200\ K)}{0.19245\ \frac{m^3}{kg}} = 1.78955 \times 10^3\ kPa. \tag{2.28}$$

Process 3 to 4 is an isentropic expansion back to 400 K. Using the isentropic relations for the CPIG, one gets

$$v_4 = v_3 \left(\frac{T_3}{T_4}\right)^{\frac{1}{k-1}} = \left(0.19245\ \frac{m^3}{kg}\right)\left(\frac{1200\ K}{400\ K}\right)^{\frac{1}{1.4-1}} = 3.000\ \frac{m^3}{kg}. \tag{2.29}$$

$$P_4 = P_3 \left(\frac{v_3}{v_4}\right)^k = (1.78955 \times 10^3\ kPa)\left(\frac{0.19245\ \frac{m^3}{kg}}{3.000\ \frac{m^3}{kg}}\right)^{1.4} = 3.82667 \times 10^1\ kPa. \tag{2.30}$$

Check:

$$P_4 = \frac{RT_4}{v_4} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(400\ K)}{3.000\ \frac{m^3}{kg}} = 3.82667 \times 10^1\ kPa. \tag{2.31}$$

A summary of the states is given in Table 2.1.

Now calculate the work, heat transfer and efficiency. Take the adiabatic exponent for air to be $k = 1.4$. Now since

$$k = \frac{c_P}{c_v}, \qquad c_P - c_v = R, \tag{2.32}$$

	$T\ (K)$	$P\ (kPa)$	$v\ (\frac{m^3}{kg})$
1	400	1.148×10^2	1.000
2	1200	5.36886×10^3	0.06415
3	1200	1.78955×10^3	0.19245
4	400	3.82667×10^2	3.000

Table 2.1: State properties for Carnot cycle.

one gets

$$\begin{aligned} k &= \frac{R + c_v}{c_v}, && (2.33)\\ kc_v &= R + c_v, && (2.34)\\ c_v(k-1) &= R, && (2.35)\\ c_v &= \frac{R}{k-1} = \frac{0.287\ \frac{kJ}{kg\ K}}{1.4-1} = 0.7175\ \frac{kJ}{kg\ K}. && (2.36) \end{aligned}$$

Recall the first law:

$$u_2 - u_1 = {}_1q_2 - {}_1w_2. \tag{2.37}$$

Recall also the caloric equation of state for a CPIG:

$$u_2 - u_1 = c_v(T_2 - T_1). \tag{2.38}$$

Now process $1 \rightarrow 2$ is isentropic, so it is also adiabatic, hence ${}_1q_2 = 0$, so one has

$$\begin{aligned} u_2 - u_1 &= \underbrace{{}_1q_2}_{=0} - {}_1w_2, && (2.39)\\ c_v(T_2 - T_1) &= -{}_1w_2, && (2.40)\\ \left(0.7175\ \frac{kJ}{kg\ K}\right)(1200\ K - 400\ K) &= -{}_1w_2, && (2.41)\\ {}_1w_2 &= -5.7400 \times 10^2\ \frac{kJ}{kg}. && (2.42) \end{aligned}$$

The work is negative as work is being done *on* the system in the compression process.

Process $2 \rightarrow 3$ is isothermal, so there is no internal energy change. The first law gives

$$
\begin{aligned}
u_3 - u_2 &= {}_2q_3 - {}_2w_3, && (2.43)\\
\underbrace{c_v(T_3 - T_2)}_{=0} &= {}_2q_3 - {}_2w_3, && (2.44)\\
0 &= {}_2q_3 - {}_2w_3, && (2.45)\\
{}_2q_3 &= {}_2w_3 = \int_{v_2}^{v_3} P\, dv, && (2.46)\\
&= \int_{v_2}^{v_3} \frac{RT}{v}\, dv, && (2.47)\\
&= RT_2 \int_{v_2}^{v_3} \frac{dv}{v}, && (2.48)\\
&= RT_2 \ln \frac{v_3}{v_2}, && (2.49)\\
&= \left(0.287\ \frac{kJ}{kg\ K}\right)(1200\ K) \ln \frac{0.19245\ \frac{m^3}{kg}}{0.06415\ \frac{m^3}{kg}}, && (2.50)\\
&= 3.78362 \times 10^2\ \frac{kJ}{kg}. && (2.51)
\end{aligned}
$$

The work is positive, which is characteristic of the expansion process.

Process $3 \rightarrow 4$ is adiabatic so ${}_3q_4 = 0$. The first law analysis gives then

$$
\begin{aligned}
u_4 - u_3 &= \underbrace{{}_3q_4}_{=0} - {}_3w_4, && (2.52)\\
c_v(T_4 - T_3) &= -{}_3w_4, && (2.53)\\
\left(0.7175\ \frac{kJ}{kg\ K}\right)(400\ K - 1200\ K) &= -{}_3w_4, && (2.54)\\
{}_3w_4 &= 5.74000 \times 10^2\ \frac{kJ}{kg}. && (2.55)
\end{aligned}
$$

Process $4 \rightarrow 1$ is isothermal. Similar to the other isothermal process, one finds

$$
\begin{aligned}
u_1 - u_4 &= {}_4q_1 - {}_4w_1, && (2.56)\\
\underbrace{c_v(T_1 - T_4)}_{=0} &= {}_4q_1 - {}_4w_1, && (2.57)\\
0 &= {}_4q_1 - {}_4w_1, && (2.58)\\
{}_4q_1 &= {}_4w_1 = \int_{v_4}^{v_1} P\, dv, && (2.59)\\
&= \int_{v_4}^{v_1} \frac{RT}{v}\, dv, && (2.60)\\
&= RT_4 \ln \frac{v_1}{v_4}, && (2.61)\\
&= \left(0.287\ \frac{kJ}{kg\ K}\right)(400\ K) \ln \frac{1.0000\ \frac{m^3}{kg}}{3.0000\ \frac{m^3}{kg}}, && (2.62)\\
&= -1.26121 \times 10^2\ \frac{kJ}{kg}. && (2.63)
\end{aligned}
$$

Process	$\Delta u \ \left(\frac{kJ}{kg}\right)$	$q \ \left(\frac{kJ}{kg}\right)$	$w \ \left(\frac{kJ}{kg}\right)$
$1 \rightarrow 2$	5.74000×10^2	0	-5.74000×10^2
$2 \rightarrow 3$	0	3.78362×10^2	3.78362×10^2
$3 \rightarrow 4$	-5.74000×10^2	0	5.74000×10^2
$4 \rightarrow 1$	0	-1.26121×10^2	-1.26121×10^2
Total	0	2.52241×10^2	2.52241×10^2

Table 2.2: First law parameters for Carnot cycle.

Table 2.2 summarizes the first law considerations. The cycle work is found by adding the work of each individual process:

$$w_{cycle} = {}_1w_2 + {}_2w_3 + {}_3w_4 + {}_4w_1, \tag{2.64}$$

$$= (-5.74 + 3.78362 + 5.74 - 1.26121) \times 10^2 = 2.52241 \times 10^2 \ \frac{kJ}{kg}. \tag{2.65}$$

The cycle heat transfer is

$$q_{cycle} = {}_1q_2 + {}_2q_3 + {}_3q_4 + {}_4q_1, \tag{2.66}$$

$$= (0 + 3.78362 + 0 - 1.26121) \times 10^2 = 2.52241 \times 10^2 \ \frac{kJ}{kg}. \tag{2.67}$$

Note that

$$w_{cycle} = q_{cycle}. \tag{2.68}$$

Check now for the cycle efficiency. Recall that the thermal efficiency is

$$\boxed{\eta = \frac{\text{what you want}}{\text{what you pay for}} = \frac{w_{cycle}}{q_{in}}.} \tag{2.69}$$

Here this reduces to

$$\eta = \frac{w_{cycle}}{{}_2q_3} = \frac{2.52241 \times 10^2 \ \frac{kJ}{kg}}{3.78362 \times 10^2 \ \frac{kJ}{kg}} = 0.6667. \tag{2.70}$$

Recall that the efficiency for any Carnot cycle should be

$$\boxed{\eta = 1 - \frac{T_{low}}{T_{high}}.} \tag{2.71}$$

So general Carnot theory holds that the efficiency should be

$$\eta = 1 - \frac{400 \ K}{1200 \ K} = \frac{2}{3} \sim 0.6667. \tag{2.72}$$

Recall further that for a Carnot cycle, one has

$$\boxed{\frac{q_{low}}{q_{high}} = \frac{T_{low}}{T_{high}}.} \tag{2.73}$$

For this problem then one has

$$\frac{-_4q_1}{_2q_3} = \frac{T_{low}}{T_{high}}, \tag{2.74}$$

$$\frac{1.26121 \times 10^2 \ \frac{kJ}{kg}}{3.78362 \times 10^2 \ \frac{kJ}{kg}} = \frac{400 \ K}{1200 \ K}, \tag{2.75}$$

$$\frac{1}{3} = \frac{1}{3}. \tag{2.76}$$

Indeed, the appropriate relation holds.

2.1.2 Exergy

Here we will introduce the concept of *exergy*, which relies on a Carnot cycle for its motivation. This concept is widely used in some industrial design applications; its use in the fundamental physics literature is not extensive, likely because it is not a thermodynamic property of a material, but also includes mechanical properties. This system quantity is one measure of how much useful work can be extracted from a system which is brought into equilibrium with a so-called reference rest state.

First let us imagine that the surroundings are at a reference temperature of T_o and a reference pressure of P_o. This yields a reference enthalpy of h_o and a reference entropy of s_o. We also take the surroundings to be at rest with a velocity of $\mathsf{v} = 0$, and a reference height of z_o.

Consider the sketch of Fig. 2.2. Let us consider a steady flow into and out of a control volume. The conservation of mass equation yields

$$\frac{dm_{cv}}{dt} = \dot{m}_{in} - \dot{m}_{out}. \tag{2.77}$$

For steady flow conditions, we have $d/dt = 0$, so we recover

$$\dot{m}_{in} = \dot{m}_{out} = \dot{m}. \tag{2.78}$$

The first law of thermodynamics for the control volume yields

$$\begin{aligned} \frac{dE_{cv}}{dt} &= \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_{in}\left(h_{in} + \frac{1}{2}\mathsf{v}_{in} \cdot \mathsf{v}_{in} + gz_{in}\right) \\ &\quad -\dot{m}_{out}\left(h_{out} + \frac{1}{2}\mathsf{v}_{out} \cdot \mathsf{v}_{out} + gz_{out}\right). \end{aligned} \tag{2.79}$$

We will soon relate $\dot{Q}_{cv}/\dot{m}$ to $q_{H,Carnot}$ as sketched in Fig. 2.2; this will introduce a sign convention problem. For now, we will maintain the formal sign convention associated with $\dot{Q}_{cv}$ connoting heat transfer into the control volume. For steady flow conditions, we get

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}\left(h_{in} - h_{out} + \frac{1}{2}(\mathsf{v}_{in} \cdot \mathsf{v}_{in} - \mathsf{v}_{out} \cdot \mathsf{v}_{out}) + g(z_{in} - z_{out})\right). \tag{2.80}$$

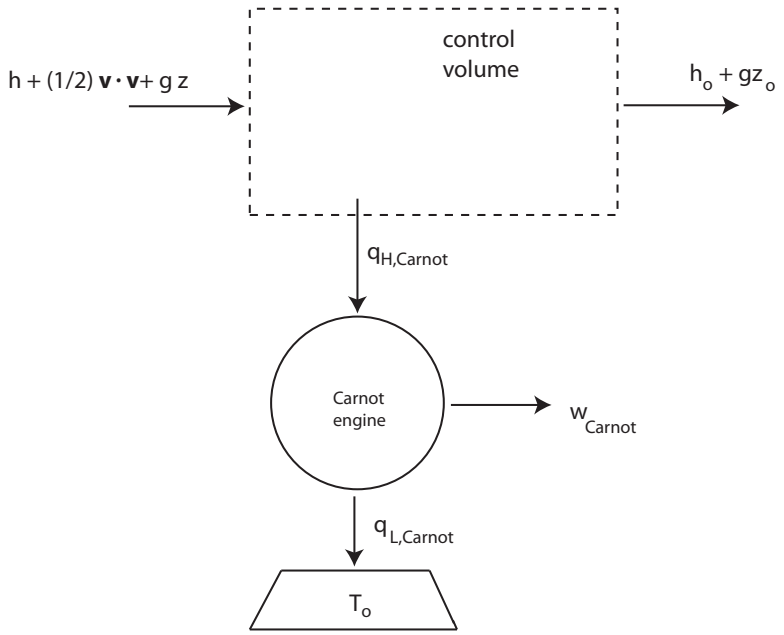

Figure 2.2: Sketch of control volume balance for exergy discussion.

Now take the "in" state to be simply a generic state with no subscript, and the "out" state to be the reference state, so

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}\left(h - h_o + \frac{1}{2}(\mathsf{v}\cdot\mathsf{v}) + g(z - z_o)\right). \tag{2.81}$$

Let us next scale by $\dot{m}$ so as to get

$$0 = q_{cv} - w_{cv} + h - h_o + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o). \tag{2.82}$$

Here we have taken $q_{cv} \equiv \dot{Q}_{cv}/\dot{m}$ and $w_{cv} = \dot{W}_{cv}/\dot{m}$.

Now, let us insist that $w_{cv} = 0$, and solve for q_{cv} to get

$$q_{cv} = -\left(h - h_o + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o)\right). \tag{2.83}$$

Now, we imagine the working fluid to be at an elevated enthalpy, velocity, and height relative to its rest state. Thus in the process of bringing it to its rest state, we will induce $q_{cv} < 0$. By our standard sign convention, this means that thermal energy is leaving the system. This energy which leaves the system can be harnessed, in the best of all possible worlds, by a Carnot engine in contact with a thermal reservoir at temperature T_o to generate useful work. It is this work which represents the available energy, also known as the exergy.

For the Carnot engine, we have

$$w_{Carnot} = q_{H,Carnot} - q_{L,Carnot}. \tag{2.84}$$

Note the standard sign convention for work and heat transfer is abandoned for the Carnot analysis! It is w_{Carnot} which gives the availability or exergy, which we define as ψ:

$$\psi = q_{H,Carnot} - q_{L,Carnot}. \tag{2.85}$$

Now let us require that the heat input to the Carnot engine be the heat associated with the heat transfer from the control volume. Because of the inconsistency in sign conventions, this requires that

$$q_{cv} = -q_{H,Carnot}. \tag{2.86}$$

Now for Carnot cycles, we know that

$$\begin{aligned} q_{H,Carnot} &= T(s - s_o), & (2.87)\\ q_{L,Carnot} &= T_o(s - s_o). & (2.88) \end{aligned}$$

So, by substituting Eqs. (2.86) and (2.88) into Eq. (2.85), the availability ψ is

$$\psi = -q_{cv} - T_o(s - s_o). \tag{2.89}$$

Now use Eq. (2.83) to eliminate q_{cv} from Eq. (2.89) to get

$$\psi = \left(h - h_o + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o)\right) - T_o(s - s_o), \tag{2.90}$$

$$\boxed{\psi = \left(h - T_o s + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + gz\right) - \left(h_o - T_o s_o + gz_o\right).} \tag{2.91}$$

So the exergy, that is, the ability to useful work, is enhanced by

- high enthalpy h, which for ideal gases implies high temperature T,
- high velocity v,
- high height z, and
- low entropy (or high order or structure) s.

Example 2.2

Find the exergy for a CPIG.

For a CPIG, we have

$$\begin{aligned} h - h_o &= c_P(T - T_o), & (2.92)\\ s - s_o &= c_P \ln\left(\frac{T}{T_o}\right) - R\ln\left(\frac{P}{P_o}\right). & (2.93) \end{aligned}$$

So we get

$$\boxed{\psi = c_P(T - T_o) - T_o\left(c_P \ln\left(\frac{T}{T_o}\right) - R\ln\left(\frac{P}{P_o}\right)\right) + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o).} \tag{2.94}$$

For $T \sim T_o$ $P \sim P_o$, we can use Taylor series to simplify this somewhat. First, we recall the general Taylor series for a log function near unity. Consider

$$y(x) = \ln x, \tag{2.95}$$

for $x \sim 1$. For a Taylor series near $x = 1$, we have

$$y(x) \sim y(1) + \left.\frac{dy}{dx}\right|_{x=1}(x-1) + \frac{1}{2}\left.\frac{d^2y}{dx^2}\right|_{x=1}(x-1)^2 + \ldots. \tag{2.96}$$

Now for $y = \ln x$, we have

$$\frac{dy}{dx} = \frac{1}{x}, \qquad \frac{d^2y}{dx^2} = -\frac{1}{x^2}, \tag{2.97}$$

and thus

$$y(1) = \ln(1) = 0, \qquad \left.\frac{dy}{dx}\right|_{x=1} = 1, \qquad \left.\frac{d^2y}{dx^2}\right|_{x=1} = -1 \tag{2.98}$$

So

$$y(x) = \ln x \sim 0 + (x-1) - \frac{1}{2}(x-1)^2 + \ldots \tag{2.99}$$

We then expand ψ via the following steps:

$$\begin{aligned}
\psi &= c_P(T - T_o) - c_P T_o \ln\left(\frac{T}{T_o}\right) + RT_o \ln\left(\frac{P}{P_o}\right) + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o), && (2.100)\\
&= c_P T_o\left(\left(\frac{T}{T_o} - 1\right) - \ln\left(\frac{T}{T_o}\right) + \frac{k-1}{k}\ln\left(\frac{P}{P_o}\right)\right) + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o), && (2.101)\\
&= c_P T_o\left(\left(\frac{T}{T_o} - 1\right) - \left(\left(\frac{T}{T_o} - 1\right) - \frac{1}{2}\left(\frac{T}{T_o} - 1\right)^2 + \ldots\right) + \frac{k-1}{k}\left(\frac{P}{P_o} - 1 + \ldots\right)\right)\\
&\quad + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o), && (2.102)\\
&= c_P T_o\left(\left(\frac{1}{2}\left(\frac{T}{T_o} - 1\right)^2 + \ldots\right) + \frac{k-1}{k}\left(\frac{P}{P_o} - 1 + \ldots\right)\right) + \frac{1}{2}\mathsf{v}\cdot\mathsf{v} + g(z - z_o). && (2.103)
\end{aligned}$$

Note that in the neighborhood of the ambient state, relative pressure differences are more effective than relative temperature differences at inducing high exergy.

2.2 Rankine

2.2.1 Classical

The Rankine cycle forms the foundation for the bulk of power generating devices which utilize steam as a working fluid. The ideal cycle is described by

- $1 \rightarrow 2$: isentropic pumping process in the pump,
- $2 \rightarrow 3$: isobaric heat transfer in the boiler,
- $3 \rightarrow 4$: isentropic expansion in the turbine, and
- $4 \rightarrow 1$: isobaric heat transfer in the condenser.

Note that to increase cycle efficiency one can

- lower the condenser pressure (increases liquid water in turbine),
- superheat the steam, or
- increase the pressure during heat addition.

A schematic for the Rankine cycle and the associated path in the $T - s$ plane is shown in Figure 2.3.

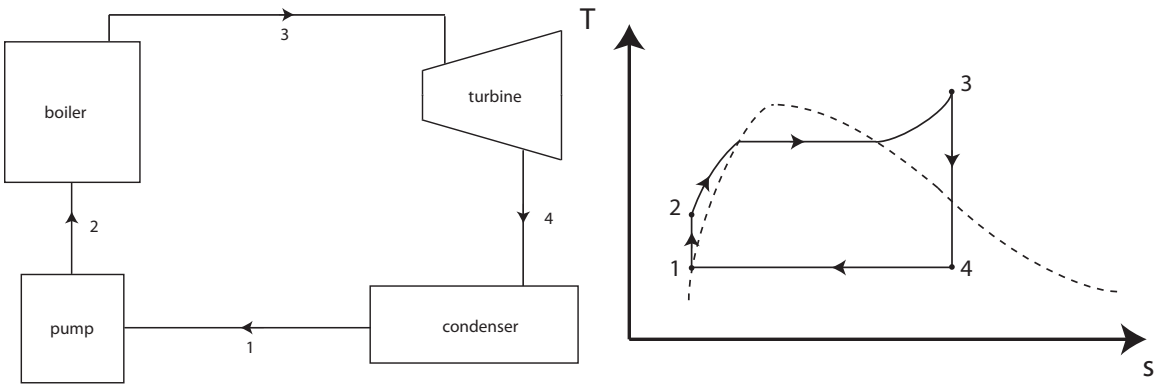

Figure 2.3: Schematic for Rankine cycle and the associated $T - s$ plane.

Example 2.3

(adopted from Moran and Shapiro, p. 312) Consider steam in an ideal Rankine cycle. Saturated vapor enters the turbine at 8.0 MPa. Saturated liquid exits the condenser at $P = 0.008$ MPa. The net power output of the cycle is 100 MW. Find

- thermal efficiency

- back work ratio
- mass flow rate of steam
- rate of heat transfer $\dot{Q}_{in}$ to the fluid in the boiler
- rate of heat transfer $\dot{Q}_{out}$ in the condenser
- mass flow rate of condenser cooling water if the cooling water enters at 15 $^\circ C$ and exits at 35 $^\circ C$.

Use the steam tables to fix the state. At the turbine inlet, one has $P_3 = 8.0\ MPa$, and $x_3 = 1$ (saturated steam). This gives two properties to fix the state, so that

$$h_3 = 2758\ \frac{kJ}{kg}, \qquad s_3 = 5.7432\ \frac{kJ}{kg\ K}. \tag{2.104}$$

State 4 has $P_4 = 0.008\ MPa$ and $s_4 = s_3 = 5.7432\ kJ/kg/K$, so the state is fixed. From the saturation tables, it is found then that

$$x_4 = \frac{s_4 - s_f}{s_g - s_f} = \frac{\left(5.7432\ \frac{kJ}{kg\ K}\right) - \left(0.5926\ \frac{kJ}{kg\ K}\right)}{7.6361\ \frac{kJ}{kg\ K}} = 0.6745. \tag{2.105}$$

Note the quality is $0 \leq x_4 \leq 1$, as it must be. The enthalpy is then

$$h_4 = h_f + x_4 h_{fg} = \left(173.88\ \frac{kJ}{kg}\right) + (0.6745)\left(2403.1\ \frac{kJ}{kg}\right) = 1794.8\ \frac{kJ}{kg}. \tag{2.106}$$

State 1 is saturated liquid at 0.008 MPa, so $x_1 = 0$, $P_1 = 0.008\ MPa$. One then gets $h_1 = h_f = 173.88\ kJ/kg$, $v_1 = v_f = 0.0010084\ m^3/kg$.

Now state 2 is fixed by the boiler pressure and $s_2 = s_1$. But this requires use of the sparse compressed liquid tables. Alternatively, the pump work is easily approximated by assuming an incompressible fluid so that

$$h_2 = h_1 + \frac{\dot{W}}{\dot{m}} = h_1 + v_1(P_2 - P_1), \tag{2.107}$$

$$h_2 = \left(173.88\ \frac{kJ}{kg}\right) + \left(0.0010084\ \frac{m^3}{kg}\right)(8000\ kPa - 8\ kPa) = 181.94\ \frac{kJ}{kg}. \tag{2.108}$$

The net power is

$$\dot{W}_{cycle} = \dot{W}_t + \dot{W}_p. \tag{2.109}$$

Now the first law for the turbine and pump give

$$\frac{\dot{W}_t}{\dot{m}} = h_3 - h_4, \qquad \frac{\dot{W}_p}{\dot{m}} = h_1 - h_2. \tag{2.110}$$

The energy input that is paid for is

$$\frac{\dot{Q}_{in}}{\dot{m}} = h_3 - h_2. \tag{2.111}$$

The thermal efficiency is then found by

$$\eta = \frac{\dot{W}_t + \dot{W}_p}{\dot{Q}_{in}} = \frac{(h_3 - h_4) + (h_1 - h_2)}{h_3 - h_2}, \tag{2.112}$$

$$= \frac{\left(\left(2758\ \frac{kJ}{kg}\right) - \left(1794.8\ \frac{kJ}{kg}\right) + \left(173.88\ \frac{kJ}{kg}\right) - \left(181.94\ \frac{kJ}{kg}\right)\right)}{\left(\left(2758\ \frac{kJ}{kg}\right) - \left(181.94\ \frac{kJ}{kg}\right)\right)}, \tag{2.113}$$

$$= \boxed{0.371.} \tag{2.114}$$

By definition the back work ratio bwr is the ratio of pump work to turbine work:

$$\begin{aligned} bwr &= \left|\frac{\dot{W}_p}{\dot{W}_t}\right|, && (2.115)\\ &= \left|\frac{h_1 - h_2}{h_3 - h_4}\right|, && (2.116)\\ &= \left|\frac{\left(\left(173.88\ \frac{kJ}{kg}\right) - \left(181.94\ \frac{kJ}{kg}\right)\right)}{\left(\left(2758\ \frac{kJ}{kg}\right) - \left(1794.8\ \frac{kJ}{kg}\right)\right)}\right|, && (2.117)\\ &= \boxed{0.00837.} && (2.118) \end{aligned}$$

The desired mass flow can be determined since we know the desired net power. Thus

$$\begin{aligned} \dot{m} &= \frac{\dot{W}_{cycle}}{(h_3 - h_4) + (h_1 - h_2)}, && (2.119)\\ &= \frac{100 \times 10^3\ kW}{\left(\left(2758\ \frac{kJ}{kg}\right) - \left(1794.8\ \frac{kJ}{kg}\right) + \left(173.88\ \frac{kJ}{kg}\right) - \left(181.94\ \frac{kJ}{kg}\right)\right)}, && (2.120)\\ &= 104.697\ \frac{kg}{s}, && (2.121)\\ &= \left(104.697\ \frac{kg}{s}\right)\left(3600\ \frac{s}{hr}\right) = \boxed{3.769 \times 10^5\ \frac{kg}{hr}.} && (2.122) \end{aligned}$$

The necessary heat transfer rate in the boiler is then

$$\begin{aligned} \dot{Q}_{in} &= \dot{m}(h_3 - h_2), && (2.123)\\ &= \left(104.697\ \frac{kg}{s}\right)\left(\left(2758\ \frac{kJ}{kg}\right) - \left(181.94\ \frac{kJ}{kg}\right)\right), && (2.124)\\ &= 269706\ kW, && (2.125)\\ &= \boxed{269.7\ MW.} && (2.126) \end{aligned}$$

In the condenser, one finds

$$\begin{aligned} \dot{Q}_{out} &= \dot{m}(h_1 - h_4), && (2.127)\\ &= \left(104.697\ \frac{kg}{s}\right)\left(\left(173.88\ \frac{kJ}{kg}\right) - \left(1794.8\ \frac{kJ}{kg}\right)\right), && (2.128)\\ &= -169705\ kW, && (2.129)\\ &= \boxed{-169.7\ MW.} && (2.130) \end{aligned}$$

Note also for the cycle that one should find

$$\dot{W}_{cycle} = \dot{Q}_{in} + \dot{Q}_{out} = (269.7\ MW) - (169.7\ MW) = 100\ MW. \quad (2.131)$$

For the condenser mass flow rate now perform a mass balance:

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \underbrace{\dot{Q}_{cv}}_{=0} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}_c(h_{in} - h_{out}) + \dot{m}(h_4 - h_1), \tag{2.132}$$

$$0 = \dot{m}_c(h_{in} - h_{out}) + \dot{m}(h_4 - h_1), \tag{2.133}$$

$$\dot{m}_c = -\frac{\dot{m}(h_4 - h_1)}{h_{in} - h_{out}}, \tag{2.134}$$

$$= -\frac{\left(104.697\ \frac{kg}{s}\right)\left(\left(1794.8\ \frac{kJ}{kg}\right) - \left(173.88\ \frac{kJ}{kg}\right)\right)}{\left(\left(62.99\ \frac{kJ}{kg}\right) - \left(146.68\ \frac{kJ}{kg}\right)\right)}, \tag{2.135}$$

$$= 2027.79\ \frac{kg}{s}, \tag{2.136}$$

$$= \left(2027.79\ \frac{kg}{s}\right)\left(\frac{3600\ s}{hr}\right), \tag{2.137}$$

$$= \boxed{7.3 \times 10^6\ \frac{kg}{hr}.} \tag{2.138}$$

The enthalpy for the cooling water was found by assuming values at the saturated state at the respective temperatures of 15 $^\circ C$ and 35 $^\circ C$.

Example 2.4

Compute the exergy at various points in the flow of a Rankine cycle as considered in the previous example problem. For that example, we had at state 1, the pump inlet that

$$h_1 = 173.88\ \frac{kJ}{kg}, \qquad s_1 = 0.5926\ \frac{kJ}{kg\ K}. \tag{2.139}$$

After the pump, at state 2, we have

$$h_2 = 181.94\ \frac{kJ}{kg}, \qquad s_2 = 0.5926\ \frac{kJ}{kg\ K}. \tag{2.140}$$

After the boiler, at state 3, we have

$$h_3 = 2758\ \frac{kJ}{kg}, \qquad s_3 = 5.7432\ \frac{kJ}{kg\ K}. \tag{2.141}$$

After the turbine, at state 4, we have

$$h_4 = 1794.8\ \frac{kJ}{kg}, \qquad s_4 = 5.7432\ \frac{kJ}{kg\ K}. \tag{2.142}$$

Now for this example, kinetic and potential energy contributions to the exergy are negligible, so we can say in general that

$$\psi = (h - T_o s) - (h_o - T_o s_o). \tag{2.143}$$

Now for this problem, we have $T_o = 298.15\ K$, $h_o = 104.89\ kJ/kg$, $s_o = 0.3674\ kJ/kg/K$. We have estimated h_o and s_o as the enthalpy and entropy of a saturated liquid at $25\ ^\circ C = 298.15\ K$.

So the exergies are as follows. At the pump entrance, we get

$$\begin{aligned}
\psi_1 &= (h_1 - T_o s_1) - (h_o - T_o s_o)\,, && (2.144)\\
&= \left(\left(173.88\ \frac{kJ}{kg}\right) - (298.15\ K)\left(0.5926\ \frac{kJ}{kg\ K}\right)\right) \\
&\quad - \left(\left(104.89\ \frac{kJ}{kg}\right) - (298.15\ K)\left(0.3674\ \frac{kJ}{kg\ K}\right)\right), && (2.145)\\
&= \boxed{1.84662\ \frac{kJ}{kg}.} && (2.146)
\end{aligned}$$

After the pump, just before the boiler, we have

$$\begin{aligned}
\psi_2 &= (h_2 - T_o s_2) - (h_o - T_o s_o)\,, && (2.147)\\
&= \left(\left(181.94\ \frac{kJ}{kg}\right) - (298.15\ K)\left(0.5926\ \frac{kJ}{kg\ K}\right)\right) \\
&\quad - \left(\left(104.89\ \frac{kJ}{kg}\right) - (298.15\ K)\left(0.3674\ \frac{kJ}{kg\ K}\right)\right), && (2.148)\\
&= \boxed{9.90662\ \frac{kJ}{kg}.} && (2.149)
\end{aligned}$$

So the exergy has gone up. Note here that $\psi_2 - \psi_1 = h_2 - h_1$ because the process is isentropic. Here $\psi_2 - \psi_1 = h_2 = h_1 = 181.94 - 173.88 = 8.06\ kJ/kg$.

After the boiler, just before the turbine, we have

$$\begin{aligned}
\psi_3 &= (h_3 - T_o s_3) - (h_o - T_o s_o)\,, && (2.150)\\
&= \left(\left(2758\ \frac{kJ}{kg}\right) - (298.15\ K)\left(5.7432\ \frac{kJ}{kg\ K}\right)\right) \\
&\quad - \left(\left(104.89\ \frac{kJ}{kg}\right) - (298.15\ K)\left(0.3674\ \frac{kJ}{kg\ K}\right)\right), && (2.151)\\
&= \boxed{1050.32\ \frac{kJ}{kg}.} && (2.152)
\end{aligned}$$

Relative to the pump, the boiler has added much more exergy to the fluid. After the turbine, just before the condenser, we have

$$\begin{aligned}
\psi_4 &= (h_4 - T_o s_4) - (h_o - T_o s_o)\,, && (2.153)\\
&= \left(\left(1794.8\ \frac{kJ}{kg}\right) - (298.15\ K)\left(5.7432\ \frac{kJ}{kg\ K}\right)\right) \\
&\quad - \left(\left(104.89\ \frac{kJ}{kg}\right) - (298.15\ K)\left(0.3674\ \frac{kJ}{kg\ K}\right)\right), && (2.154)\\
&= \boxed{87.1152\ \frac{kJ}{kg}.} && (2.155)
\end{aligned}$$

Note that $\psi_4 - \psi_3 = h_4 - h_3$ because the process is isentropic. The actual exergy (or available work) at the exit of the turbine is relative low, even though the enthapy state at the turbine exit remains at an elevated value.

2.2.2 Reheat

In a Rankine cycle with reheat, the steam is extracted from an intermediate stage of the turbine and reheated in the boiler. It is then expanded through the turbine again to the condenser pressure. One also avoids liquid in the turbine with this strategy. This generally results in a gain in cycle efficiency. Geometrically, the behavior on a $T - s$ diagram looks more like a Carnot cycle. This is often covered in an introductory thermodynamics class, so no formal example will be given here. A schematic for the Rankine cycle with reheat and the associated $T - s$ diagram is shown in Figure 2.4.

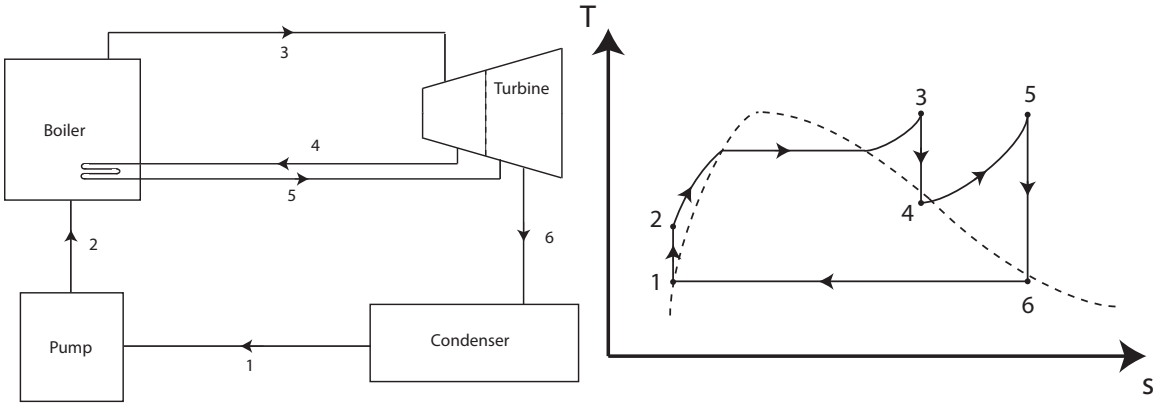

Figure 2.4: Schematic for Rankine cycle with reheat along with the relevant $T - s$ diagram.

2.2.3 Regeneration

In a Rankine cycle with regeneration, some steam is extracted from the turbine and used to pre-heat the liquid which is exiting the pump. This can lead to an increased thermal efficiency, all else being equal. The analysis is complicated by the need to take care of more complex mass and energy balances in some components. A schematic for the Rankine cycle with regeneration and open feedwater heating is shown in Figure 2.5.

Example 2.5

(BS, Ex. 11.4, pp. 438-440) Steam leaves boiler and enters turbine at 4 MPa, 400 $°C$. After expansion to 400 kPa, some stream is extracted for heating feedwater in an open feedwater heater. Pressure in feedwater heater is 400 kPa, and water leaves it at a saturated state at 400 kPa. The rest of the steam expands through the turbine to 10 kPa. Find the cycle efficiency.

- $1 \rightarrow 2$: compression through Pump $P1$,
- 2 & $6 \rightarrow 3$: mixing in open feedwater heater to saturated liquid state,
- $3 \rightarrow 4$: compression through Pump $P2$,
- $4 \rightarrow 5$: heating in boiler,

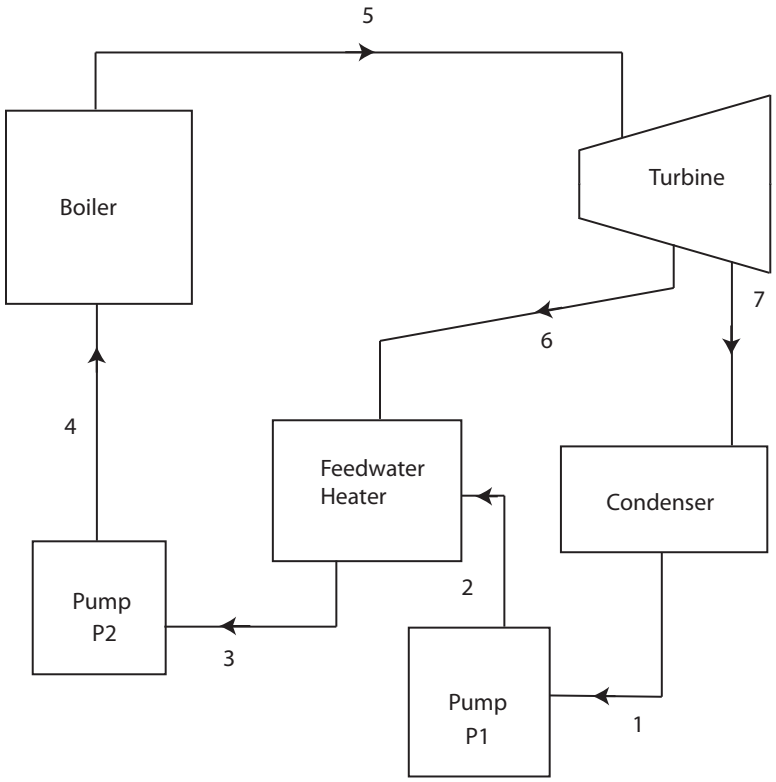

Figure 2.5: Schematic for Rankine cycle with regeneration and open feedwater heating.

- $5 \rightarrow 6$: partial expansion in turbine,
- $5 \rightarrow 7$: completion of turbine expansion, and
- $7 \rightarrow 1$: cooling in condenser.

From the tables, one can find

$$h_5 = 3213.6\ \frac{kJ}{kg}, \quad h_6 = 2685.6\ \frac{kJ}{kg}, \quad h_7 = 2144.1\ \frac{kJ}{kg}, \quad h_1 = 191.8\ \frac{kJ}{kg}, \quad h_3 = 604.73\ \frac{kJ}{kg},$$

$$v_1 = 0.00101\ \frac{m^3}{kg}, \qquad v_3 = 0.001084\ \frac{m^3}{kg}. \tag{2.156}$$

First consider the low pressure pump.

$$\begin{aligned} h_2 &= h_1 + v_1(P_2 - P_1), && (2.157)\\ &= \left(191.8\ \frac{kJ}{kg}\right) + \left(0.00101\ \frac{m^3}{kg}\right)\left((400\ kPa) - (10\ kPa)\right), && (2.158)\\ &= 192.194\ \frac{kJ}{kg} && (2.159) \end{aligned}$$

The pump work is

$$\begin{aligned} w_{P1} &= v_1(P_1 - P_2), && (2.160)\\ &= \left(0.00101\ \frac{m^3}{kg}\right)((10\ kPa) - (400\ kPa)), && (2.161)\\ &= -0.3939\ \frac{kJ}{kg}. && (2.162) \end{aligned}$$

Note, a sign convention consistent with work done by the fluid is used here. At this point the text abandons this sign convention instead.

Now consider the turbine

$$\begin{aligned} \underbrace{\frac{dm_{cv}}{dt}}_{=0} &= \dot{m}_5 - \dot{m}_6 - \dot{m}_7, && (2.163)\\ \dot{m}_5 &= \dot{m}_6 + \dot{m}_7, && (2.164)\\ 1 &= \frac{\dot{m}_6}{\dot{m}_5} + \frac{\dot{m}_7}{\dot{m}_5}, && (2.165)\\ \underbrace{\frac{dE_{cv}}{dt}}_{=0} &= \underbrace{\dot{Q}_{cv}}_{=0} - \dot{W}_{cv} + \dot{m}_5 h_5 - \dot{m}_6 h_6 - \dot{m}_7 h_7, && (2.166)\\ \dot{W}_{cv} &= \dot{m}_5 h_5 - \dot{m}_6 h_6 - \dot{m}_7 h_7. && (2.167) \end{aligned}$$

On a per mass basis, we get,

$$\begin{aligned} w_t &= \frac{\dot{W}_{cv}}{\dot{m}_5} = h_5 - \frac{\dot{m}_6}{\dot{m}_5} h_6 - \frac{\dot{m}_7}{\dot{m}_5} h_7, && (2.168)\\ &= h_5 - \frac{\dot{m}_6}{\dot{m}_5} h_6 - \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right) h_7, && (2.169)\\ &= h_5 - h_6 + h_6 - \frac{\dot{m}_6}{\dot{m}_5} h_6 - \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right) h_7, && (2.170)\\ &= h_5 - h_6 + h_6 \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right) - \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right) h_7, && (2.171)\\ &= h_5 - h_6 + \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right)(h_6 - h_7). && (2.172) \end{aligned}$$

Now consider the feedwater heater. The first law for this device gives

$$\begin{aligned} \underbrace{\frac{dE_{cv}}{dt}}_{=0} &= \underbrace{\dot{Q}_{cv}}_{=0} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}_2 h_2 + \dot{m}_6 h_6 - \dot{m}_3 h_3, && (2.173)\\ h_3 &= \frac{\dot{m}_2}{\dot{m}_3} h_2 + \frac{\dot{m}_6}{\dot{m}_3} h_6, && (2.174)\\ &= \frac{\dot{m}_7}{\dot{m}_5} h_2 + \frac{\dot{m}_6}{\dot{m}_5} h_6, && (2.175)\\ &= \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right) h_2 + \frac{\dot{m}_6}{\dot{m}_5} h_6, && (2.176)\\ \left(604.73\ \frac{kJ}{kg}\right) &= \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right)\left(192.194\ \frac{kJ}{kg}\right) + \frac{\dot{m}_6}{\dot{m}_5}\left(2685.6\ \frac{kJ}{kg}\right), && (2.177)\\ \frac{\dot{m}_6}{\dot{m}_5} &= 0.165451. && (2.178) \end{aligned}$$

Now get the turbine work

$$\begin{aligned} w_t &= h_5 - h_6 + \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right)(h_6 - h_7), && (2.179)\\ &= \left(3213.6\ \frac{kJ}{kg}\right) - \left(2685.6\ \frac{kJ}{kg}\right) \\ &\quad + (1 - 0.165451)\left(\left(2685.6\ \frac{kJ}{kg}\right) - \left(2144.1\ \frac{kJ}{kg}\right)\right), && (2.180)\\ &= 979.908\ \frac{kJ}{kg}. && (2.181) \end{aligned}$$

Now get the work for the high-pressure pump

$$\begin{aligned} w_{P2} &= v_3(P_3 - P_4), && (2.182)\\ &= \left(0.001084\ \frac{m^3}{kg}\right)((400\ kPa) - (4000\ kPa)), && (2.183)\\ &= -3.9024\ \frac{kJ}{kg}. && (2.184) \end{aligned}$$

Now

$$\begin{aligned} h_4 &= h_3 + v_3(P_4 - P_3), && (2.185)\\ &= \left(604.73\ \frac{kJ}{kg}\right) + \left(0.001084\ \frac{m^3}{kg}\right)((4000\ kPa) - (400\ kPa)), && (2.186)\\ &= 608.6\ \frac{kJ}{kg}. && (2.187) \end{aligned}$$

Now get the net work

$$\begin{aligned} \dot{W}_{net} &= \dot{m}_5 w_t + \dot{m}_1 w_{P1} + \dot{m}_5 w_{P2}, && (2.188)\\ w_{net} &= w_t + \frac{\dot{m}_1}{\dot{m}_5} w_{P1} + w_{P2}, && (2.189)\\ &= w_t + \frac{\dot{m}_7}{\dot{m}_5} w_{P1} + w_{P2}, && (2.190)\\ &= w_t + \left(1 - \frac{\dot{m}_6}{\dot{m}_5}\right) w_{P1} + w_{P2}, && (2.191)\\ &= \left(979.908\ \frac{kJ}{kg}\right) + (1 - 0.165451)\left(-0.3939\ \frac{kJ}{kg}\right) - \left(3.9024\ \frac{kJ}{kg}\right), && (2.192)\\ &= 975.677\ \frac{kJ}{kg}. && (2.193) \end{aligned}$$

Now for the heat transfer in the boiler, one has

$$\begin{aligned} q_h &= h_5 - h_4, && (2.194)\\ &= \left(3213.6\ \frac{kJ}{kg}\right) - \left(608.6\ \frac{kJ}{kg}\right), && (2.195)\\ &= 2605.0\ \frac{kJ}{kg}. && (2.196) \end{aligned}$$

Thus, the thermal efficiency is

$$\eta = \frac{w_{net}}{q_h} = \frac{975.677\ \frac{kJ}{kg}}{2605.0\ \frac{kJ}{kg}} = \boxed{0.375.} \qquad (2.197)$$

This does represent an increase of efficiency over a comparable Rankine cycle without regeneration, which happens to be 0.369.

2.2.4 Losses

- Turbine: These are typically the largest losses in the system. The turbine efficiency is defined by

$$\eta = \frac{w_t}{w_{ts}} = \frac{h_3 - h_4}{h_3 - h_{4s}}. \tag{2.198}$$

  Here h_{4s} and w_{ts} are the enthalpy and work the working fluid would have achieved had the process been isentropic. Note this is for a control volume.

- Pump: Pump losses are usually much smaller in magnitude than those for turbines. The pump efficiency for a control volume is defined by

$$\eta = \frac{w_{ps}}{w_p} = \frac{h_{2s} - h_1}{h_2 - h_1}. \tag{2.199}$$

- Piping: pressure drops via viscous and turbulent flow effects induce entropy gains in fluid flowing through pipes. There can also be heat transfer from pipes to the surroundings and vice versa.

- Condenser: Losses are relatively small here.

Losses will *always* degrade the overall thermal efficiency of the cycle.

2.2.5 Cogeneration

Often steam is extracted after the boiler for alternative uses. A good example is the Notre Dame power plant, where steam at high pressure and temperature is siphoned from the turbines to heat the campus in winter. The analysis for such a system is similar to that for a system with regeneration.

A schematic for cogeneration cycle is shown in Figure 2.6.

2.3 Air standard cycles

It is useful to model several real engineering devices by what is known as an air standard cycle. This is based on the following assumptions:

- CPIG,

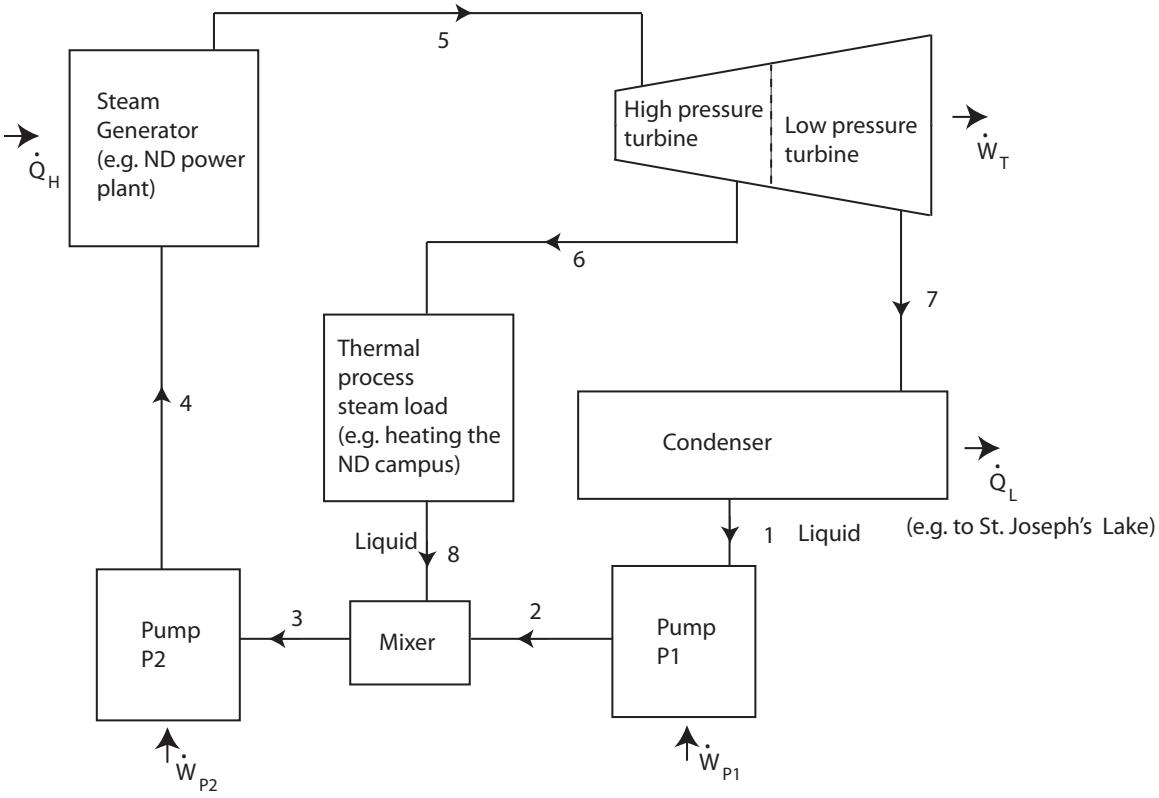

Figure 2.6: Schematic for Rankine cycle with cogeneration.

- no inlet or exhaust stages,
- combustion process replaced by heat transfer process,
- cycle completed by heat transfer to surroundings (not exhaust), and
- all process internally reversible.

In some cycles, it is common to model the working fluid as a *fixed mass*. In others, it is common to model the system as a *control volume*.

2.4 Brayton

2.4.1 Classical

The Brayton cycle is the air standard model for gas turbine engines. It is most commonly modeled on a control volume basis. It has the following components:

- $1 \rightarrow 2$: isentropic compression,

- $2 \rightarrow 3$: isobaric heat transfer to combustion chamber,
- $3 \rightarrow 4$: isentropic expansion through turbine, and
- $4 \rightarrow 1$: isobaric heat exchange with surroundings.

A schematic for the Brayton cycle is shown in Figure 2.7. Diagrams for $P - v$ and $T - s$ for

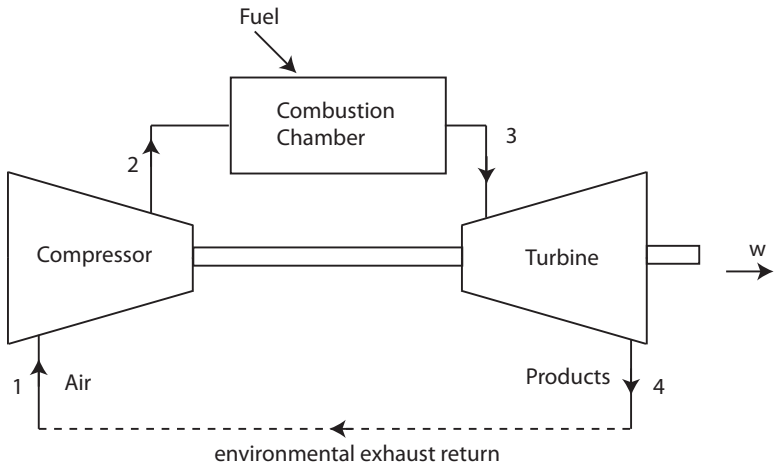

Figure 2.7: Schematic for Brayton cycle.

the Brayton cycle are shown in Figure 2.8.

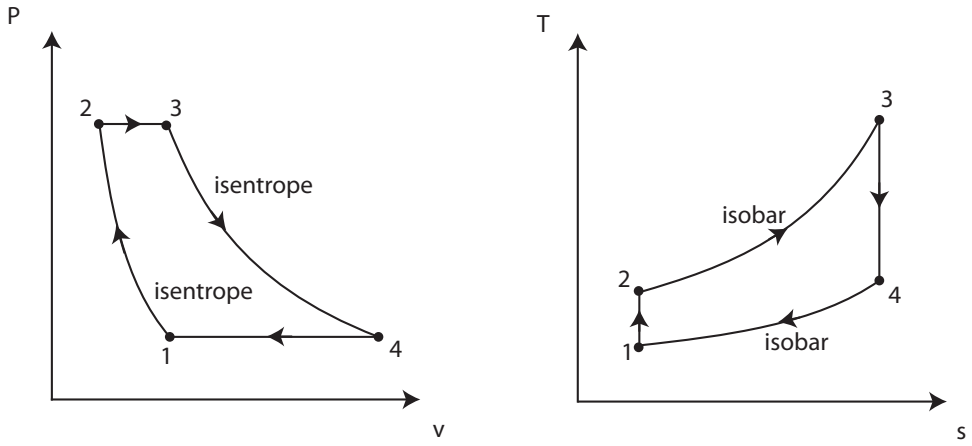

Figure 2.8: $P - v$ and $T - s$ diagrams for the Brayton cycle.

The efficiency of the air standard Brayton cycle is found as

$$\eta = \frac{w_{net}}{q_H}. \tag{2.200}$$

For the cycle, the first law holds that

$$w_{net} = q_{net} = q_H - q_L. \tag{2.201}$$

One notes for an isobaric control volume combustor that

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \dot{Q}_{cv} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}h_{in} - \dot{m}h_{out}. \tag{2.202}$$

So

$$\dot{Q}_{cv} = \dot{m}(h_{out} - h_{in}), \tag{2.203}$$

$$\frac{\dot{Q}_{cv}}{\dot{m}} = h_{out} - h_{in}, \tag{2.204}$$

$$q = h_{out} - h_{in}, \tag{2.205}$$

$$q = c_P(T_{out} - T_{in}). \tag{2.206}$$

So the thermal efficiency is

$$\eta = \frac{w_{net}}{q_H} = \frac{q_H - q_L}{q_H} = 1 - \frac{q_L}{q_H} = 1 - \frac{c_P(T_4 - T_1)}{c_P(T_3 - T_2)} = 1 - \frac{T_1\left(\frac{T_4}{T_1} - 1\right)}{T_2\left(\frac{T_3}{T_2} - 1\right)}. \tag{2.207}$$

Now because of the definition of the process, one also has

$$\frac{P_3}{P_4} = \frac{P_2}{P_1}. \tag{2.208}$$

And because $1 \rightarrow 2$ and $3 \rightarrow 4$ are isentropic, one has

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{k/(k-1)} = \frac{P_3}{P_4} = \left(\frac{T_3}{T_4}\right)^{k/(k-1)}. \tag{2.209}$$

So one then has

$$\frac{T_2}{T_1} = \frac{T_3}{T_4}. \tag{2.210}$$

Cross-multiplying, one finds

$$\frac{T_3}{T_2} = \frac{T_4}{T_1}. \tag{2.211}$$

Subtracting unity from both sides gives

$$\frac{T_3}{T_2} - 1 = \frac{T_4}{T_1} - 1. \tag{2.212}$$

So the thermal efficiency takes the form

$$\boxed{\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\frac{T_2}{T_1}} = 1 - \frac{1}{\left(\frac{P_2}{P_1}\right)^{(k-1)/k}}.} \tag{2.213}$$

Note that if a Carnot cycle were operating between the same temperature bounds that $\eta_{Carnot} = 1 - T_1/T_3$ would be greater than that for the Brayton cycle.

Relative to the Rankine cycle, the Brayton cycle has a large fraction of compressor work. So the backwork ratio *bwr* is larger.

One must also account for deviations from ideality. These effects are summarized in component efficiencies. The relevant efficiencies here, assuming a control volume approach, are

$$\eta_c = \frac{h_{2s} - h_1}{h_2 - h_1}, \tag{2.214}$$

$$\eta_t = \frac{h_3 - h_4}{h_3 - h_{4s}}. \tag{2.215}$$

For a CPIG, one gets then

$$\eta_c = \frac{T_{2s} - T_1}{T_2 - T_1}, \tag{2.216}$$

$$\eta_t = \frac{T_3 - T_4}{T_3 - T_{4s}}. \tag{2.217}$$

Example 2.6

(adopted from Moran and Shapiro, Example 9.6) Air enters the compressor of an air-standard Brayton cycle at 100 kPa, 300 K with a volumetric flow rate is 5 m^3/s. The pressure ratio in the compressor is 10. The turbine inlet temperature is 1400 K. Find the thermal efficiency, the back work ratio and the net power. Both the compressor and turbine have efficiencies of 0.8.

First calculate the state after the compressor if the compressor were isentropic.

$$\frac{P_2}{P_1} = \left(\frac{T_{2s}}{T_1}\right)^{k/(k-1)} = 10, \tag{2.218}$$

$$T_{2s} = T_1(10)^{(k-1)/k}, \tag{2.219}$$

$$= (300\ K)(10)^{(1.4-1)/1.4}, \tag{2.220}$$

$$= 579.209\ K. \tag{2.221}$$

Now

$$\eta_c = \frac{T_{2s} - T_1}{T_2 - T_1}, \tag{2.222}$$

$$T_2 = T_1 + \frac{T_{2s} - T_1}{\eta_c}, \tag{2.223}$$

$$= (300\ K) + \frac{(579.209\ K) - (300\ K)}{0.8}, \tag{2.224}$$

$$= 649.012\ K. \tag{2.225}$$

Now state three has $T_3 = 1400\ K$. Recall that $2 \rightarrow 3$ involves heat addition in a combustion chamber. Now calculate T_{4s} for the ideal turbine. Recall that the expansion is to the same pressure as the compressor inlet so that $P_3/P_4 = 10$. The isentropic relations give

$$\left(\frac{T_{4s}}{T_3}\right)^{k/(k-1)} = \frac{P_4}{P_3}, \tag{2.226}$$

$$T_{4s} = T_3 \left(\frac{P_4}{P_3}\right)^{(k-1)/k}, \tag{2.227}$$

$$= (1400\ K)\left(\frac{1}{10}\right)^{(1.4-1)/1.4}, \tag{2.228}$$

$$= 725.126\ K. \tag{2.229}$$

Now account for the actual behavior in the turbine:

$$\eta_t = \frac{T_3 - T_4}{T_3 - T_{4s}}, \tag{2.230}$$

$$T_4 = T_3 - \eta_t(T_3 - T_{4s}), \tag{2.231}$$

$$= (1400\ K) - (0.8)((1400\ K) - (725.126\ K)), \tag{2.232}$$

$$= 860.101\ K. \tag{2.233}$$

Now calculate the thermal efficiency of the actual cycle.

$$\eta = \frac{w_{net}}{q_H} = \frac{q_H - q_L}{q_H} = 1 - \frac{q_L}{q_H} = 1 - \frac{c_P(T_4 - T_1)}{c_P(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2}, \tag{2.234}$$

$$= 1 - \frac{860.101\ K - 300\ K}{1400\ K - 649.012\ K}, \tag{2.235}$$

$$= \boxed{0.254181.} \tag{2.236}$$

If the cycle were ideal, one would have

$$\eta_{ideal} = \frac{w_{net}}{q_H} = \frac{q_H - q_L}{q_H} = 1 - \frac{q_L}{q_H} = 1 - \frac{c_P(T_{4s} - T_1)}{c_P(T_3 - T_{2s})} = 1 - \frac{T_{4s} - T_1}{T_3 - T_{2s}}, \tag{2.237}$$

$$= 1 - \frac{(725.126\ K) - (300\ K)}{(1400\ K) - (579.209\ K)}, \tag{2.238}$$

$$= 0.482053. \tag{2.239}$$

Note also that for the ideal cycle one also has

$$\eta_{ideal} = 1 - \frac{T_1}{T_{2s}} = 1 - \frac{300\ K}{579.209\ K} = 0.482053. \tag{2.240}$$

The back work ratio is

$$bwr = \frac{w_{comp}}{w_{turb}}, \tag{2.241}$$

$$= \frac{c_P(T_2 - T_1)}{c_P(T_3 - T_4)}, \tag{2.242}$$

$$= \frac{T_2 - T_1}{T_3 - T_4}, \tag{2.243}$$

$$= \frac{(649.012\ K) - (300\ K)}{(1400\ K) - (860.101\ K)}, \tag{2.244}$$

$$= \boxed{0.646439.} \tag{2.245}$$

If the process were ideal, the back work ratio would have been

$$\begin{aligned} bwr_{ideal} &= \frac{w_{comp}}{w_{turb}}, && (2.246)\\ &= \frac{c_P(T_{2s}-T_1)}{c_P(T_3-T_{4s})}, && (2.247)\\ &= \frac{T_{2s}-T_1}{T_3-T_{4s}}, && (2.248)\\ &= \frac{(579.209\ K)-(300\ K)}{(1400\ K)-(725.126\ K)}, && (2.249)\\ &= 0.413721. && (2.250) \end{aligned}$$

Now get the net work. First get the mass flow rate from the volume flow rate. This requires the specific volume.

$$v_1 = \frac{RT_1}{P_1} = \frac{\left(0.287\ \frac{kJ}{kg\ K}\right)(300\ K)}{100\ kPa} = 0.861\ \frac{m^3}{kg}. \quad (2.251)$$

Now

$$\dot{m} = \rho_1 \dot{V} = \frac{\dot{V}}{v_1} = \frac{5\ \frac{m^3}{s}}{0.861\ \frac{m^3}{kg}} = 5.8072\ \frac{kg}{s}. \quad (2.252)$$

Recall $c_P = kc_v = 1.4(717.5\ J/kg/K) = 1004.5\ J/kg/K = 1.0045\ kJ/kg/K$. Now

$$\begin{aligned} \dot{W}_{cycle} &= \dot{m}c_P((T_3-T_4)-(T_2-T_1), && (2.253)\\ &= \left(5.8072\ \frac{kg}{s}\right)\left(1.0045\ \frac{kJ}{kg\ K}\right)((1400\ K)-(860.101\ K)-(649.012\ K)+(300\ K)), && (2.254)\\ &= \boxed{1113.51\ kW.} && (2.255) \end{aligned}$$

If the cycle were ideal, one would have

$$\begin{aligned} \dot{W}_{ideal} &= \dot{m}c_P((T_3-T_{4s})-(T_{2s}-T_1), && (2.256)\\ &= \left(5.8072\ \frac{kg}{s}\right)\left(1.0045\ \frac{kJ}{kg\ K}\right)((1400\ K)-(725.126\ K)-(579.209\ K)+(300\ K)), && (2.257)\\ &= 2308.04\ kW. && (2.258) \end{aligned}$$

Note that the inefficiencies had a significant effect on both the back work ratio and the net work of the engine.

2.4.2 Regeneration

One can improve cycle efficiency by regeneration. The hot gas in the turbine is used to preheat the gas exiting the compressor before it enters the combustion chamber. In this cycle, one takes

- $1 \rightarrow 2$: compression,
- $2 \rightarrow x$: compression exit gas goes through regenerator (heat exchanger),

- $x \rightarrow 3$: combustion chamber,
- $3 \rightarrow 4$: expansion in turbine, and
- $4 \rightarrow y$: turbine exit gas goes through regenerator (heat exchanger).

A schematic for the Brayton cycle is shown in Figure 2.9.

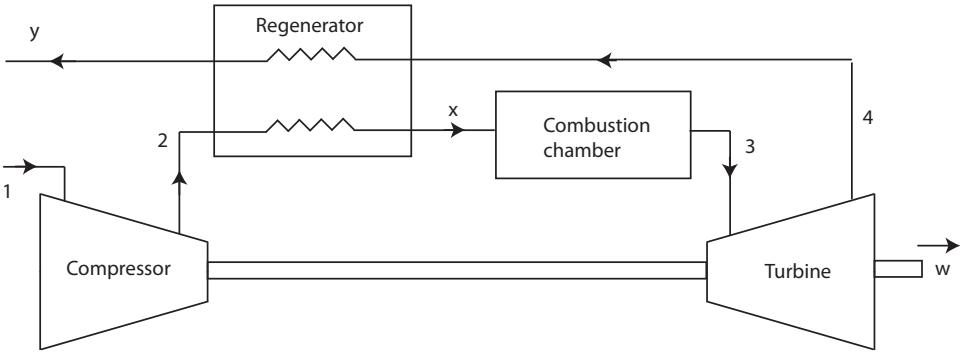

Figure 2.9: Schematic for Brayton cycle with regeneration.

For this to work, the gas at the turbine exit must have a higher temperature than the gas at the compressor exit. If the compression ratio is high, the compressor exit temperature is high, and there is little benefit to regeneration.

Now consider the regenerator, which is really a heat exchanger. The first law holds that

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \underbrace{\dot{Q}_{cv}}_{=0} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}h_2 - \dot{m}h_x + \dot{m}h_4 - \dot{m}h_y, \tag{2.259}$$

$$0 = h_2 - h_x + h_4 - h_y, \tag{2.260}$$

$$= c_P(T_2 - T_x) + c_P(T_4 - T_y), \tag{2.261}$$

$$= T_2 - T_x + T_4 - T_y. \tag{2.262}$$

Now consider the inlet temperatures to be known. Then the first law constrains the outlet temperatures such that

$$T_2 + T_4 = T_x + T_y. \tag{2.263}$$

If the heat exchanger were an ideal *co-flow heat exchanger*, one might expect the outlet temperatures to be the same, that is, $T_x = T_y$, and one would have $T_x = T_y = (1/2)(T_2 + T_4)$. But in fact one can do better. If a *counter-flow heat exchanger* is used, one could ideally expect to find

$$T_x = T_4, \qquad T_y = T_2. \tag{2.264}$$

The thermal efficiency is

$$\begin{aligned}
\eta &= \frac{w_{net}}{q_H}, && (2.265)\\
&= \frac{w_t - w_c}{q_H}, && (2.266)\\
&= \frac{c_P(T_3 - T_4) - c_P(T_2 - T_1)}{c_P(T_3 - T_x)}, && (2.267)\\
&= \frac{(T_3 - T_4) - (T_2 - T_1)}{T_3 - T_x}, && (2.268)\\
&= \frac{(T_3 - T_4) - (T_2 - T_1)}{T_3 - T_4}, && (2.269)\\
&= 1 - \frac{T_2 - T_1}{T_3 - T_4}, && (2.270)\\
&= 1 - \frac{T_1\left(\frac{T_2}{T_1} - 1\right)}{T_3\left(1 - \frac{T_4}{T_3}\right)}, && (2.271)\\
&= 1 - \frac{T_1\left(\left(\frac{P_2}{P_1}\right)^{(k-1)/k} - 1\right)}{T_3\left(1 - \left(\frac{P_4}{P_3}\right)^{(k-1)/k}\right)}, && (2.272)\\
&= 1 - \frac{T_1\left(\left(\frac{P_2}{P_1}\right)^{(k-1)/k} - 1\right)}{T_3\left(1 - \left(\frac{P_1}{P_2}\right)^{(k-1)/k}\right)}, && (2.273)\\
&= 1 - \frac{T_1}{T_3}\left(\frac{P_2}{P_1}\right)^{(k-1)/k} \frac{1 - \left(\frac{P_1}{P_2}\right)^{(k-1)/k}}{1 - \left(\frac{P_1}{P_2}\right)^{(k-1)/k}}, && (2.274)\\
&= \boxed{1 - \frac{T_1}{T_3}\left(\frac{P_2}{P_1}\right)^{(k-1)/k}}. && (2.275)
\end{aligned}$$

Note this is the Carnot efficiency moderated by the pressure ratio. As the pressure ratio rises, the thermal efficiency declines.

The regenerator itself will not be perfect. To achieve the performance postulated here would require infinite time or an infinite area heat exchanger. As both increase, viscous losses increase, and so there is a trade-off. One can summarize the behavior of an actual regenerator by an efficiency defined as

$$\eta_{reg} = \frac{h_x - h_2}{h'_x - h_2} = \frac{\text{actual}}{\text{ideal}}. \qquad (2.276)$$

If we have a CPIG, then

$$\eta_{reg} = \frac{T_x - T_2}{T'_x - T_2}. \tag{2.277}$$

Example 2.7

(extension for Moran and Shapiro, Example 9.6) How would the addition of a regenerator affect the thermal efficiency of the isentropic version of the previous example problem?

One may take the rash step of trusting the analysis to give a prediction from Eq. (2.275) of

$$\eta = 1 - \frac{T_1}{T_3}\left(\frac{P_2}{P_1}\right)^{(k-1)/k}, \tag{2.278}$$

$$= 1 - \left(\frac{300\ K}{1400\ K}\right)(10)^{(1.4-1)/1.4} = \boxed{0.586279.} \tag{2.279}$$

Without regeneration, the thermal efficiency of the ideal Brayton cycle had a value of 0.482053. Had the engine used a Carnot cycle between the same temperature limits, the efficiency would have been 0.785714.

2.4.3 Ericsson Cycle

If one used isothermal compression and expansion, which is slow and impractical, in place of isentropic processes in the Brayton cycle, one would obtain the *Ericsson cycle*. Diagrams for $P - v$ and $T - s$ for the Ericsson cycle are shown in Figure 2.10.

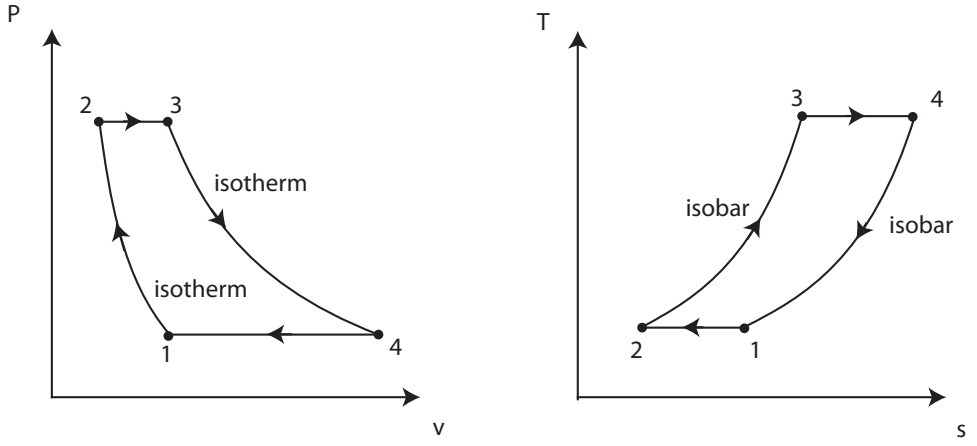

Figure 2.10: $P - v$ and $T - s$ diagram for the Ericsson cycle.

One can outline the Ericsson cycle as follows:

- $1 \rightarrow 2$: isothermal compression,
- $2 \rightarrow 3$: isobaric heating in the combustion chamber,
- $3 \rightarrow 4$: isothermal expansion in turbine, and
- $4 \rightarrow 1$: isobaric heat transfer in surroundings.

One also takes the *control volume* approach.

First consider the work in the isothermal compressor. For the control volume, one recalls that the work is given by the enthalpy difference, and that $dh = Tds + vdP = \delta q_c - \delta w_c$, with $\delta q_c = Tds$ and $\delta w_c = -vdP$, so

$$w_c = -\int_1^2 v\ dP = -RT_1 \int_1^2 \frac{dP}{P} = -RT_1 \ln \frac{P_2}{P_1}. \tag{2.280}$$

Note that $P_2/P_1 > 1$, so $w_c < 0$; work is done on the fluid in the compressor.

For the turbine, again for the control volume, the key is the enthalpy difference and $dh = Tds + vdP = \delta q_t - \delta w_t$, with $\delta q_t = Tds$ and $\delta w_t = -vdP$. The turbine work would be

$$w_t = -\int_3^4 v\ dP = -RT_3 \int_3^4 \frac{dP}{P} = -RT_3 \ln \frac{P_4}{P_3}. \tag{2.281}$$

But because $P_2 = P_3$ and $P_1 = P_4$, the turbine work is also

$$w_t = -RT_3 \ln \frac{P_1}{P_2} = RT_3 \ln \frac{P_2}{P_1}. \tag{2.282}$$

Note that because $P_2/P_1 > 1$, the turbine work is positive.

In the combustion chamber, one has from the first law

$$h_3 - h_2 = q_C \tag{2.283}$$

$$c_P(T_3 - T_2) = q_C. \tag{2.284}$$

For the isothermal turbine, one has $dh = c_P dT = 0 = q_t - w_t$, so $q_t = w_t$. The heat transfer necessary to keep the turbine isothermal is

$$q_t = w_t = RT_3 \ln \frac{P_2}{P_1}. \tag{2.285}$$

So the total heat that one pays for is

$$q_H = q_C + q_t = c_P(T_3 - T_1) + RT_3 \ln \frac{P_2}{P_1}. \tag{2.286}$$

So the thermal efficiency is

$$\eta = \frac{w_t + w_c}{q_H}, \tag{2.287}$$

$$\eta = \frac{R(T_3 - T_1)\ln\frac{P_2}{P_1}}{c_P(T_3 - T_1) + RT_3\ln\frac{P_2}{P_1}}, \tag{2.288}$$

$$= \frac{\left(1 - \frac{T_1}{T_3}\right)\ln\frac{P_2}{P_1}}{\frac{k}{k-1}\left(1 - \frac{T_1}{T_3}\right) + \ln\frac{P_2}{P_1}}, \tag{2.289}$$

$$= \frac{\left(1 - \frac{T_1}{T_3}\right)\ln\left(\frac{P_2}{P_1}\right)^{(k-1)/k}}{\left(1 - \frac{T_1}{T_3}\right) + \ln\left(\frac{P_2}{P_1}\right)^{(k-1)/k}}, \tag{2.290}$$

$$= \left(1 - \frac{T_1}{T_3}\right)\left(\frac{1}{1 + \frac{1 - \frac{T_1}{T_3}}{\ln\left(\frac{P_2}{P_1}\right)^{(k-1)/k}}}\right), \tag{2.291}$$

$$\sim \underbrace{\left(1 - \frac{T_1}{T_3}\right)}_{\text{Carnot}} \underbrace{\left(1 - \frac{1 - \frac{T_1}{T_3}}{\ln\left(\frac{P_2}{P_1}\right)^{(k-1)/k}} + \ldots\right)}_{\text{correction}}. \tag{2.292}$$

This is expressed as a Carnot efficiency modified by a correction which degrades the efficiency. Note the efficiency is less than that of a Carnot cycle. For high temperature ratios and high pressure ratios, the efficiency approaches that of a Carnot engine.

Now if one used multiple staged *intercooling* on the compressors and multiple staged expansions with reheat on the turbines, one can come closer to the isothermal limit, and better approximate the Carnot cycle.

2.4.4 Jet propulsion

If one modifies the Brayton cycle so that the turbine work is just sufficient to drive the compressor and the remaining enthalpy at the turbine exit is utilized in expansion in a nozzle to generate thrust, one has the framework for jet propulsion. Here the *control volume* approach is used. A schematic for a jet engine is shown in Figure 2.11. Diagrams for $P - v$ and $T - s$ for the jet propulsion Brayton cycle are shown in Figure 2.12. An important component of jet propulsion analysis is the kinetic energy of the flow. In the entrance region of the engine, the flow is decelerated, inducing a *ram compression* effect. For high velocity applications, this effect provides sufficient compression for the cycle and no compressor or turbine are needed! However, such a device, known as a ramjet, is not self-starting, and so is not practical for many applications.

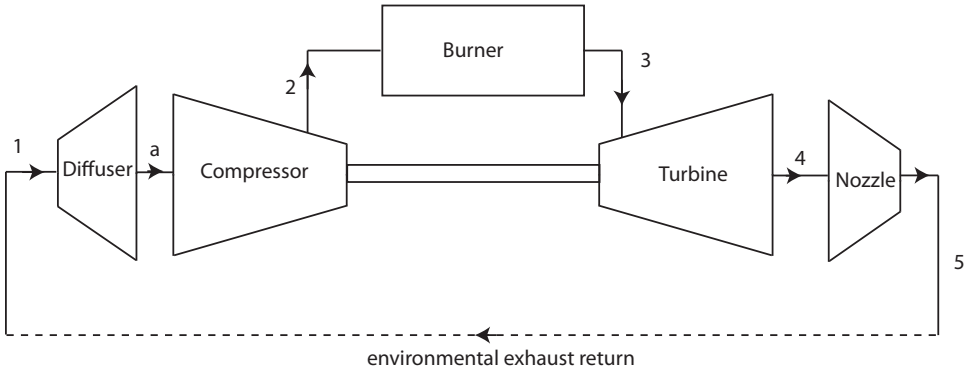

Figure 2.11: Schematic for jet propulsion.

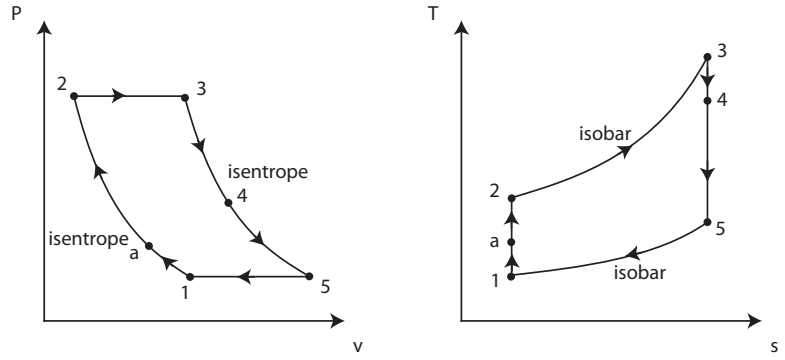

Figure 2.12: $P - v$ and $T - s$ diagrams for jet propulsion Brayton cycle.

One can outline the ideal jet propulsion cycle as follows:

- $1 \rightarrow a$: deceleration and ram compression in diffuser,
- $a \rightarrow 2$: isentropic compression in the compressor,
- $2 \rightarrow 3$: isobaric heating in the combustion chamber,
- $3 \rightarrow 4$: isentropic expansion in turbine,
- $4 \rightarrow 5$: isentropic conversion of thermal energy to kinetic energy in nozzle, and
- $5 \rightarrow 1$: isobaric heat transfer in surroundings.

The goal of the jet propulsion cycle is to produce a thrust force which is necessary to balance a fluid-induced aerodynamic drag force. When such a balance exists, the system is in steady state. One can analyze such a system in the reference frame in which the engine is stationary. In such a frame, Newton's second law gives

$$\underbrace{\frac{d}{dt}\left(m_{CV}\mathsf{v}_{CV}\right)}_{=0} = \underbrace{\mathbf{F}}_{\text{thrust force}} + \underbrace{P_1 A_1 \mathbf{i} - P_5 A_5 \mathbf{i}}_{\text{small}} + \dot{m}\mathsf{v}_1 - \dot{m}\mathsf{v}_5. \tag{2.293}$$

Solving for the thrust force, neglecting the small differences in pressure, one gets,

$$\mathbf{F} = \dot{m}\left(\mathsf{v}_5 - \mathsf{v}_1\right). \tag{2.294}$$

The work done by the thrust force is the product of this force and the air speed, v_1. This gives

$$|\dot{W}_p| = |\mathbf{F} \cdot \mathsf{v}_1| = |\dot{m}(\mathsf{v}_5 - \mathsf{v}_1) \cdot \mathsf{v}_1|. \tag{2.295}$$

Now the efficiency of the cycle is a bit different. The net work of the turbine and compressor is zero. Instead, the propulsive efficiency is defined as

$$\eta_p = \frac{\text{Propulsive Power}}{\text{Energy Input Rate}} = \frac{|\dot{W}_p|}{|\dot{Q}_H|}, \tag{2.296}$$

$$= \boxed{\frac{|\dot{m}\mathsf{v}_1 \cdot (\mathsf{v}_5 - \mathsf{v}_1)|}{\dot{m}|(h_3 - h_2)|}}. \tag{2.297}$$

Note the following unusual behavior for flight in an ideal inviscid atmosphere in which the flow always remains attached. In such a flow D'Alembert's paradox holds: there is no aerodynamic drag. Consequently there is no need for thrust generation in steady state operation. Thrust would only be needed to accelerate to a particular velocity. For such an engine then the exit velocity would equal the entrance velocity: $\mathsf{v}_5 = \mathsf{v}_1$ and $\mathbf{F} = 0$. Moreover, the propulsive efficiency is $\eta_p = 0$.

Example 2.8

(adopted from Çengal and Boles, p. 485). A turbojet flies with a velocity of 850 $\frac{ft}{s}$ at an altitude where the air is at 5 *psia* and -40 *F*. The compressor has a pressure ratio of 10, and the temperature at the turbine inlet is 2000 *F*. Air enters the compressor at a rate of $\dot{m} = 100$ $\frac{lbm}{s}$. Assuming an air standard with CPIG air, find the

- temperature and pressure at the turbine exit,
- velocity of gas at nozzle exit, and
- propulsive efficiency.

For the English units of this problem, one recalls that

$$1\ Btu = 777.5\ ft\ lbf, \qquad g_c = 32.2\ \frac{lbm\ ft}{lbf\ s^2}, \qquad 1\ \frac{Btu}{lbm} = 25037\ \frac{ft^2}{s^2}. \tag{2.298}$$

For air, one has

$$c_P = 0.240\ \frac{Btu}{lbm\ ^\circ R}, \qquad R = 53.34\ \frac{ft\ lbf}{lbm\ ^\circ R} = 1717.5\ \frac{ft^2}{s^2\ ^\circ R} = 0.0686\ \frac{Btu}{lbm\ ^\circ R}, \qquad k = 1.4. \tag{2.299}$$

First one must analyze the ram compression process. An energy balance gives

$$h_1 + \frac{\mathsf{v}_1 \cdot \mathsf{v}_1}{2} = h_a + \underbrace{\frac{\mathsf{v}_a \cdot \mathsf{v}_a}{2}}_{\text{small}}. \tag{2.300}$$

It is usually sufficient to neglect the kinetic energy of the fluid inside the engine. While it still has a non-zero velocity, it has been slowed enough so that enthalpy dominates kinetic energy inside the engine. So one takes

$$\begin{aligned} h_a &= h_1 + \frac{\mathsf{v}_1 \cdot \mathsf{v}_1}{2}, && (2.301)\\ 0 &= h_1 - h_a + \frac{\mathsf{v}_1 \cdot \mathsf{v}_1}{2}, && (2.302)\\ 0 &= c_P(T_1 - T_a) + \frac{\mathsf{v}_1 \cdot \mathsf{v}_1}{2}, && (2.303)\\ T_a &= T_1 + \frac{\mathsf{v}_1 \cdot \mathsf{v}_1}{2c_P}. && (2.304) \end{aligned}$$

The ambient temperature is

$$T_1 = -40 + 460 = 420\ ^\circ R. \tag{2.305}$$

So after ram compression, the temperature at the inlet to the compressor is

$$T_a = (420\ ^\circ R) + \frac{\left(850\ \frac{ft}{s}\right)^2}{2\left(0.240\ \frac{Btu}{lbm\ ^\circ R}\right)} \frac{1\ \frac{Btu}{lbm}}{25037\ \frac{ft^2}{s^2}} = 480\ ^\circ R. \tag{2.306}$$

Now get the pressure at the compressor inlet via the isentropic relations:

$$P_a = P_1 \left(\frac{T_a}{T_1}\right)^{k/(k-1)} = (5\ psia) \left(\frac{480\ ^\circ R}{420\ ^\circ R}\right)^{1.4/(1.4-1)} = 8.0\ psia. \tag{2.307}$$

Now consider the isentropic compressor.

$$P_2 = 10 P_a = 10(8.0\ psia) = 80\ psia. \tag{2.308}$$

Now get the temperature after passage through the compressor.

$$T_2 = T_a \left(\frac{P_2}{P_a}\right)^{(k-1)/k} = (480\ ^\circ R)\,(10)^{(1.4-1)/1.4} = 927\ ^\circ R. \tag{2.309}$$

The temperature at the entrance of the turbine is known to be $2000\ F = 2460\ ^\circ R$. Now the turbine work is equal to the compressor work, so

$$\begin{aligned} w_c &= w_t, && (2.310)\\ h_2 - h_a &= h_3 - h_4, && (2.311)\\ c_P(T_2 - T_a) &= c_P(T_3 - T_4), && (2.312)\\ T_2 - T_a &= T_3 - T_4, && (2.313)\\ T_4 &= T_3 - T_2 + T_a, && (2.314)\\ &= 2460\ ^\circ R - 927\ ^\circ R + 480\ ^\circ R, && (2.315)\\ &= \boxed{2013\ ^\circ R.} && (2.316) \end{aligned}$$

Use the isentropic relations to get P_4:

$$P_4 = P_3 \left(\frac{T_4}{T_3}\right)^{k/(k-1)} = (80\ psia) \left(\frac{2013\ ^\circ R}{2460\ ^\circ R}\right)^{1.4/(1.4-1)} = \boxed{39.7\ psia.} \tag{2.317}$$

Expansion through the nozzle completes the cycle. Assume an isentropic nozzle, therefore

$$\begin{aligned} T_5 &= T_4 \left(\frac{P_5}{P_4} \right)^{(k-1)/k}, && (2.318) \\ &= T_4 \left(\frac{P_1}{P_4} \right)^{(k-1)/k}, && (2.319) \\ &= = (2013\ ^\circ R) \left(\frac{5\ psia}{39.7\ psia} \right)^{(1.4-1)/1.4}, && (2.320) \\ &= 1114\ ^\circ R. && (2.321) \end{aligned}$$

Now consider the energy balance in the nozzle:

$$\begin{aligned} h_5 + \frac{\mathsf{v}_5 \cdot \mathsf{v}_5}{2} &= h_4 + \underbrace{\frac{\mathsf{v}_4 \cdot \mathsf{v}_4}{2}}_{\text{small}}, && (2.322) \\ 0 &= h_5 - h_4 + \frac{\mathsf{v}_5^2}{2}, && (2.323) \\ &= c_P(T_5 - T_4) + \frac{\mathsf{v}_5 \cdot \mathsf{v}_5}{2}, && (2.324) \\ \mathsf{v}_5 &= \sqrt{2c_P(T_4 - T_5)}, && (2.325) \\ &= \sqrt{2 \left(0.240\ \frac{Btu}{lbm\ ^\circ R} \right) (2013\ ^\circ R - 1114\ ^\circ R) \left(\frac{25037\ \frac{ft^2}{s^2}}{1 \frac{Btu}{lbm}} \right)}, && (2.326) \\ &= \boxed{3288\ \frac{ft}{s}.} && (2.327) \end{aligned}$$

Now find the thrust force magnitude

$$\begin{aligned} |\mathbf{F}| &= \dot{m}(\mathsf{v}_5 - \mathsf{v}_1) = \left(100\ \frac{lbm}{s} \right) \left(3288\ \frac{ft}{s} - 850\ \frac{ft}{s} \right) = 243800\ \frac{ft\ lbm}{s^2}, && (2.328) \\ &= \frac{243800\ \frac{ft\ lbm}{s^2}}{32.2\ \frac{lbm\ ft}{lbf\ s^2}}, && (2.329) \\ &= 7571.4\ lbf. && (2.330) \end{aligned}$$

The power is the product of the thrust force and the air speed, so

$$\begin{aligned} |\dot{W}_P| &= |\mathbf{F} \cdot \mathsf{v}_1| = (7571.4\ lbf) \left(850\ \frac{ft}{s} \right) \left(\frac{Btu}{777.5\ ft\ lbf} \right), && (2.331) \\ &= 8277\ \frac{Btu}{s}, && (2.332) \\ &= \left(8277\ \frac{Btu}{s} \right) \left(\frac{1.415\ hp}{\frac{Btu}{s}} \right), && (2.333) \\ &= 11711\ hp. && (2.334) \end{aligned}$$

Now for the heat transfer in the combustion chamber

$$\begin{aligned}
\dot{Q}_H &= \dot{m}(h_3 - h_2), && (2.335)\\
&= \dot{m}c_P(T_3 - T_2), && (2.336)\\
&= \left(100\ \frac{lbm}{s}\right)\left(0.240\ \frac{Btu}{lbm\ ^\circ R}\right)(2460\ ^\circ R - 927\ ^\circ R), && (2.337)\\
&= 36792\ \frac{Btu}{s}. && (2.338)
\end{aligned}$$

So the propulsion efficiency is

$$\eta_p = \frac{\dot{W}_P}{\dot{Q}_H} = \frac{8277\ \frac{Btu}{s}}{36792\ \frac{Btu}{s}} = \boxed{0.225.} \tag{2.339}$$

The remainder of the energy is excess kinetic energy and excess thermal energy, both of which ultimately dissipate so as to heat the atmosphere.

Other variants of the turbojet engine include the very important *turbofan engine* in which a large cowling is added to the engine and a an additional fan in front of the compressor forces a large fraction of the air to *bypass* the engine. The turbofan engine is used in most large passenger jets. Analysis reveals a significant increase in propulsive efficiency as well as a reduction in jet noise. Other important variants include the *turboprop*, *propfan*, *ramjet*, *scramjet*, jet with *afterburners*, and *rocket*.

2.5 Reciprocating engine power cycles

Here are some common notions for engines that depend on pistons driving in cylinders. The piston has a bore diameter B. The piston is connected to the crankshaft, and the stroke S of the piston is twice the radius of the crank, R_{crank}:

$$S = 2R_{crank}. \tag{2.340}$$

See Figure 2.13 for an illustration of this geometry for a piston-cylinder arrangement in two configurations. The total displacement for all the cylinders is

$$V_{displ} = N_{cyl}(V_{max} - V_{min}) = N_{cyl}A_{cyl}S. \tag{2.341}$$

Note that

$$A_{cyl} = \pi\frac{B^2}{4}. \tag{2.342}$$

The compression ratio is not the ratio of pressures; it is the ratio of volumes:

$$r_v = CR = \frac{V_{max}}{V_{min}}. \tag{2.343}$$

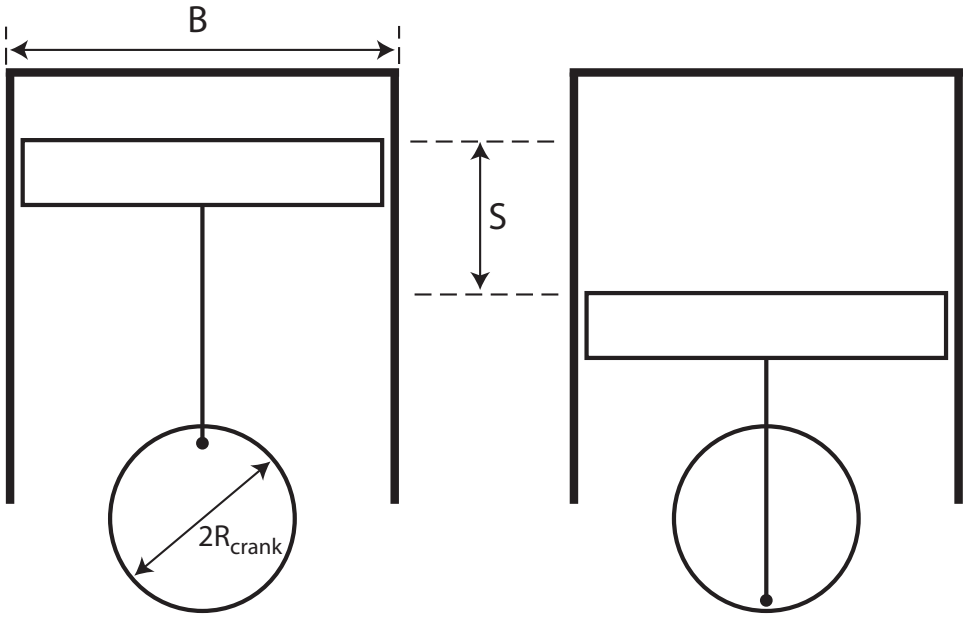

Figure 2.13: Piston-cylinder configurations illustrating geometric definitions.

For these engines the volumes are closed in expansion and compression, so the net work is

$$w_{net} = \oint P \, dv = P_{meff}(v_{max} - v_{min}). \tag{2.344}$$

Here one has defined a *mean effective pressure*: P_{meff}. The net work per cylinder per cycle is

$$W_{net} = m w_{net} = P_{meff} m (v_{max} - v_{min}) = P_{meff}(V_{max} - V_{min}). \tag{2.345}$$

Now consider the total power developed for all the cylinders. Assume the piston operates at a frequency of ν *cycles*$/s$:

$$\dot{W}_{net} = N_{cyl} P_{meff}(V_{max} - V_{min})\nu. \tag{2.346}$$

It is more common to express ν in revolutions per minute: $RPM = \nu(60 \, \frac{s}{min})$, so

$$\dot{W}_{net} = P_{meff} \underbrace{N_{cyl}(V_{max} - V_{min})}_{=V_{displ}} \frac{RPM}{60 \, \frac{s}{min}}, \tag{2.347}$$

$$= P_{meff} V_{displ} \frac{RPM}{60 \, \frac{s}{min}}. \tag{2.348}$$

This applies for a two-stroke engine. If the engine is a four stroke engine, the net power is reduced by a factor of 1/2.

2.6 Otto

The air-standard Otto cycle approximates the gasoline engine. It employs a *fixed mass* approach.

Diagrams for $P - v$ and $T - s$ for the Otto cycle are shown in Figure 2.14.

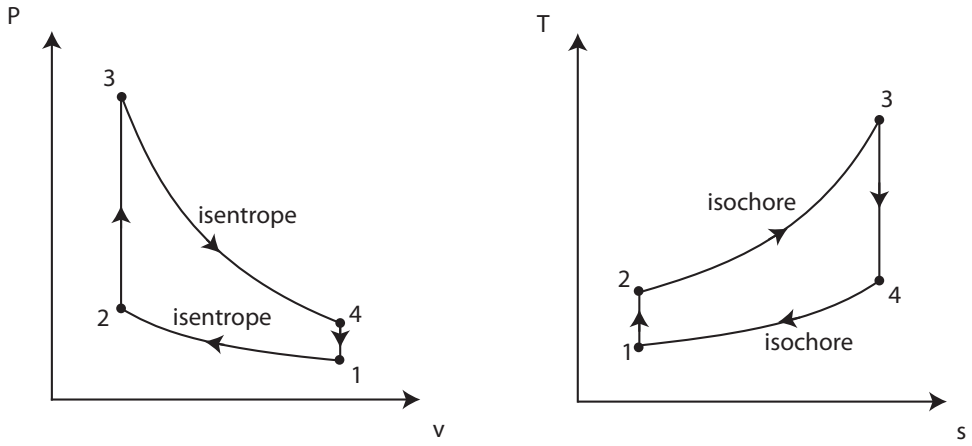

Figure 2.14: $P - v$ and $T - s$ diagrams for the Otto cycle.

One can outline the Otto cycle as follows:

- $1 \rightarrow 2$: isentropic compression in the compression stroke,
- $2 \rightarrow 3$: isochoric heating in the combustion stroke during spark ignition,
- $3 \rightarrow 4$: isentropic expansion in power stroke, and
- $4 \rightarrow 1$: isochoric rejection of heat to the surroundings.

Note for isochoric heating, such as $2 \rightarrow 3$, in a fixed mass environment, the first law gives

$$u_3 - u_2 = {}_2q_3 - {}_2w_3, \tag{2.349}$$

$$u_3 - u_2 = {}_2q_3 - \int_{v_2}^{v_3} P\, dv, \qquad \text{but } v_2 = v_3, \tag{2.350}$$

$$u_3 - u_2 = {}_2q_3 - \underbrace{\int_{v_2}^{v_2} P\, dv}_{=0}, \tag{2.351}$$

$${}_2q_3 = u_3 - u_2, \tag{2.352}$$

$${}_2q_3 = c_v(T_3 - T_2), \qquad \text{if CPIG.} \tag{2.353}$$

The thermal efficiency is found as follows:

$$\begin{aligned}
\eta &= \frac{w_{net}}{q_H}, && (2.354)\\
&= \frac{q_H - q_L}{q_H}, && (2.355)\\
&= 1 - \frac{q_L}{q_H}, && (2.356)\\
&= 1 - \frac{c_v(T_4 - T_1)}{c_v(T_3 - T_2)}, && (2.357)\\
&= 1 - \frac{T_4 - T_1}{T_3 - T_2}, && (2.358)\\
&= 1 - \frac{T_1\left(\frac{T_4}{T_1} - 1\right)}{T_2\left(\frac{T_3}{T_2} - 1\right)}. && (2.359)
\end{aligned}$$

Now one also has the isentropic relations:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1}, \quad (2.360)$$

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{k-1}. \quad (2.361)$$

But $V_4 = V_1$ and $V_2 = V_3$, so

$$\frac{T_3}{T_4} = \left(\frac{V_1}{V_2}\right)^{k-1} = \frac{T_2}{T_1}. \quad (2.362)$$

Cross multiplying the temperatures, one finds

$$\frac{T_3}{T_2} = \frac{T_4}{T_1}. \quad (2.363)$$

Thus the thermal efficiency reduces to

$$\boxed{\eta = 1 - \frac{T_1}{T_2}.} \quad (2.364)$$

In terms of the compression ratio $r_v = \frac{V_1}{V_2}$, one has

$$\boxed{\eta = 1 - r_v^{1-k} = 1 - \frac{1}{r_v^{k-1}}.} \quad (2.365)$$

Note if the compression ratio increases, the thermal efficiency increases. High compression ratios introduce detonation in the fuel air mixture. This induces strong pressure waves in the cylinder and subsequent engine *knock*. It can cause degradation of piston walls.

Some deviations of actual performance from that of the air-standard Otto cycle are as follows:

- specific heats actually vary with temperature,
- combustion may be incomplete (induces pollution and lowers fuel efficiency),
- work of inlet and exhaust ignored, and
- losses of heat transfer to engine walls ignored.

Example 2.9

(adopted from Moran and Shapiro, p. 363). The temperature at the beginning of the compression process of an air-standard Otto cycle with a compression ratio of 8 is 540 $^\circ R$, the pressure is 1 atm, and the cylinder volume is 0.02 ft^3. The maximum temperature is 3600 $^\circ R$. Find

- temperature and pressure at each stage of the process,
- thermal efficiency, and
- P_{meff} in atm.

For the isentropic compression,

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{k-1}, \tag{2.366}$$

$$= (540\ ^\circ R)(8)^{1.4-1}, \tag{2.367}$$

$$= \boxed{1240.69\ ^\circ R.} \tag{2.368}$$

One can use the ideal gas law to get the pressure at state 2:

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}, \tag{2.369}$$

$$P_2 = P_1 \frac{V_1}{V_2}\frac{T_2}{T_1}, \tag{2.370}$$

$$= (1\ atm)(8)\left(\frac{1240.69\ ^\circ R}{540\ ^\circ R}\right), \tag{2.371}$$

$$= \boxed{18.3792\ atm.} \tag{2.372}$$

Now $V_3 = V_2$ since the combustion is isochoric. And the maximum temperature is $T_3 = 3600\ ^\circ R$. This allows use of the ideal gas law to get P_3:

$$\frac{P_3 V_3}{T_3} = \frac{P_2 V_2}{T_2}, \tag{2.373}$$

$$P_3 = P_2 \underbrace{\frac{V_2}{V_3}}_{=1} \frac{T_3}{T_2}, \tag{2.374}$$

$$= (18.3792\ atm)(1)\left(\frac{3600\ ^\circ R}{1240.59\ ^\circ R}\right), \tag{2.375}$$

$$= \boxed{53.3333\ atm.} \tag{2.376}$$

One uses the isentropic relations for state 4:

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{k-1}, \tag{2.377}$$

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4}\right)^{k-1}, \tag{2.378}$$

$$T_4 = T_3\left(\frac{V_2}{V_1}\right)^{k-1}, \tag{2.379}$$

$$T_4 = T_3\left(\frac{V_1}{V_2}\right)^{1-k}, \tag{2.380}$$

$$= (3600\ ^\circ R)(8)^{1-1.4}, \tag{2.381}$$

$$= \boxed{1566.99\ ^\circ R.} \tag{2.382}$$

For the pressure at state 4, use the ideal gas law:

$$\frac{P_4V_4}{T_4} = \frac{P_3V_3}{T_3}, \tag{2.383}$$

$$P_4 = P_3\frac{V_3}{V_4}\frac{T_4}{T_3}, \tag{2.384}$$

$$= P_3\frac{V_2}{V_1}\frac{T_4}{T_3}, \tag{2.385}$$

$$= (53.3333\ atm)\left(\frac{1}{8}\right)\frac{1566.99\ ^\circ R}{3600\ ^\circ R}, \tag{2.386}$$

$$= \boxed{2.90184\ atm.} \tag{2.387}$$

The thermal efficiency is

$$\eta = 1 - \frac{1}{r_v^{k-1}}, \tag{2.388}$$

$$= 1 - \frac{1}{8^{1.4-1}}, \tag{2.389}$$

$$= \boxed{0.564725.} \tag{2.390}$$

Now get the mean effective pressure P_{meff}.

$$
\begin{aligned}
W_{net} &= P_{meff}(V_{max} - V_{min}), && (2.391)\\
P_{meff} &= \frac{W_{net}}{V_{max} - V_{min}}, && (2.392)\\
&= \frac{m(u_3 - u_4) + m(u_1 - u_2)}{V_1 - V_2}, && (2.393)\\
&= m\frac{c_v}{V_1}\frac{T_3 - T_4 + T_1 - T_2}{1 - \frac{V_2}{V_1}}, && (2.394)\\
&= \frac{P_1 V_1}{R T_1}\frac{c_v}{V_1}\frac{T_3 - T_4 + T_1 - T_2}{1 - \frac{V_2}{V_1}}, && (2.395)\\
&= \frac{P_1}{T_1}\frac{c_v}{R}\frac{T_3 - T_4 + T_1 - T_2}{1 - \frac{V_2}{V_1}}, && (2.396)\\
&= \frac{P_1}{T_1}\frac{1}{k-1}\frac{T_3 - T_4 + T_1 - T_2}{1 - \frac{V_2}{V_1}}, && (2.397)\\
&= \frac{1\ atm}{540\ ^\circ R}\frac{1}{1.4-1}\frac{3600\ ^\circ R - 1566.99\ ^\circ R + 540\ ^\circ R - 1240.59\ ^\circ R}{1 - \frac{1}{8}}, && (2.398)\\
&= \boxed{7.04981\ atm.} && (2.399)
\end{aligned}
$$

2.7 Diesel

The air standard Diesel cycle approximates the behavior of a Diesel engine. It is modeled as a *fixed mass* system. Here the compression is done before injection, so there is no danger of premature ignition due to detonation. No spark plugs are used. Diagrams for $P - v$ and $T - s$ for the Diesel cycle are shown in Figure 2.15. One can outline the Diesel cycle as follows:

- $1 \rightarrow 2$: isentropic compression in the compression stroke,
- $2 \rightarrow 3$: isobaric heating in the combustion stroke,
- $3 \rightarrow 4$: isentropic expansion in power stroke, and
- $4 \rightarrow 1$: isochoric rejection of heat to the surroundings.

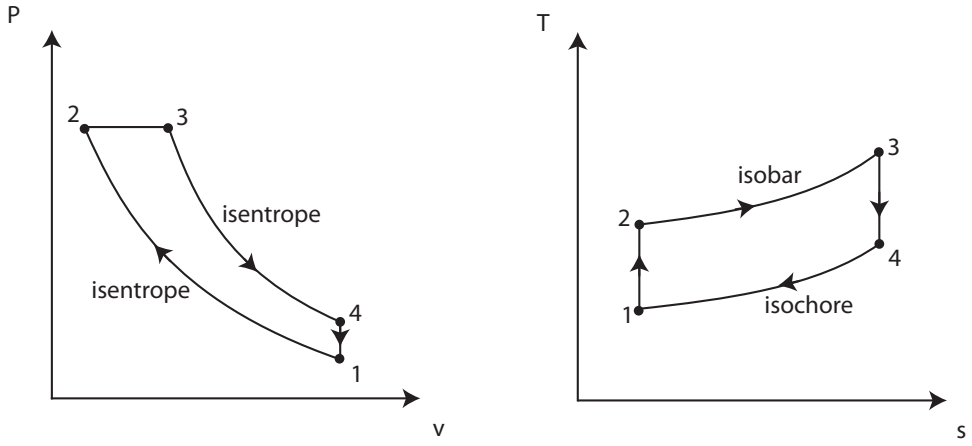

Figure 2.15: $P - v$ and $T - s$ diagrams for the Diesel cycle.

The thermal efficiency is found as follows:

$$\begin{aligned}
\eta &= \frac{w_{net}}{q_H}, && (2.400)\\
&= \frac{q_H - q_L}{q_H}, && (2.401)\\
&= 1 - \frac{q_L}{q_H}, && (2.402)\\
&= 1 - \frac{u_4 - u_1}{h_3 - h_2}, && (2.403)\\
&= 1 - \frac{c_v(T_4 - T_1)}{c_P(T_3 - T_2)}, && (2.404)\\
&= \boxed{1 - \frac{1}{k}\frac{T_1}{T_2}\frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1}.} && (2.405)
\end{aligned}$$

All else being equal, the Otto cycle will have higher efficiency than the Diesel cycle. However, the Diesel can operate at higher compression ratios because detonation is not as serious a problem in the compression ignition engine as it is in the spark ignition.

Example 2.10

(adopted from BS, Ex. 12.8 pp. 501-502). An air standard Diesel cycle has a compression ratio of 20, and the heat transferred to the working fluid has 1800 kJ/kg. Take air to be an ideal gas with *variable* specific heat. At the beginning of the compression process, $P_1 = 0.1\ MPa$, and $T_1 = 15\ ^\circ C$. Find

- Pressure and temperature at each point in the process,
- Thermal efficiency,
- P_{meff}, the mean effective pressure.

The enthalpies and entropies at the reference pressure for variable specific heat air are tabulated as functions of temperature in Table A7.1. Recall that

$$h(T) = h_{ref} + \int_{T_{ref}}^{T} c_P(\hat{T})\, d\hat{T}. \tag{2.406}$$

Recall further that

$$Tds = dh - vdP, \tag{2.407}$$

$$ds = \frac{dh}{T} - \frac{v}{T}dP. \tag{2.408}$$

Now for an ideal gas it can be shown that $dh = c_P(T)dT$; one also has $v/T = R/P$. Making these substitutions into Eq. (2.408) gives

$$ds = \frac{c_P(T)dT}{T} - R\frac{dP}{P}. \tag{2.409}$$

Integrating gives

$$s(T,P) = \underbrace{s_{ref} + \int_{T_{ref}}^{T} \frac{c_P(\hat{T})}{\hat{T}}\, d\hat{T}}_{=s_T^o} - R\ln\frac{P}{P_{ref}}, \tag{2.410}$$

$$s(T,P) = s_T^o(T) - R\ln\frac{P}{P_{ref}}. \tag{2.411}$$

Here the reference pressure is $P_{ref} = 0.1\ MPa$. Note that this happens to be the inlet state, which is a coincidence; so at the inlet there is no correction to the entropy for pressure deviation from its reference value. At the inlet, one has $T_1 = 15 + 273.15 = \boxed{288.15\ K.}$ One then gets from interpolating Table A7.1 that

$$h_1 = 288.422\ \frac{kJ}{kg}, \qquad s_{T_1}^o = s_1 = 6.82816\ \frac{kJ}{kg\ K}, \qquad u_1 = 205.756\ \frac{kJ}{kg}. \tag{2.412}$$

For the isentropic compression, one has

$$s_2 = s_1 = 6.82816\ \frac{kJ}{kg\ K}, \qquad V_2 = \frac{1}{20}V_1. \tag{2.413}$$

Now from the ideal gas law, one has

$$\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}, \tag{2.414}$$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1}\frac{V_1}{V_2}, \tag{2.415}$$

$$\frac{P_2}{P_{ref}} = 20\frac{T_2}{288\ K}. \tag{2.416}$$

Now

$$s_2(T_2,P_2) = s_{T_2}^o - R\ln\frac{P_2}{P_{ref}}, \tag{2.417}$$

$$\left(6.82816\ \frac{kJ}{kg\ K}\right) = s_{T_2}^o - \left(0.287\ \frac{kJ}{kg\ K}\right)\ln\left(20\frac{T_2}{288\ K}\right), \tag{2.418}$$

$$0 = s_{T_2}^o - \left(0.287\ \frac{kJ}{kg\ K}\right)\ln\left(20\frac{T_2}{288\ K}\right) - \left(6.82816\ \frac{kJ}{kg\ K}\right) \equiv F(T_2). \tag{2.419}$$

$T_2\ (K)$	$s^o_{T_2}\ \left(\frac{kJ}{kg\ K}\right)$	$F(T_2)\ \left(\frac{kJ}{kg\ K}\right)$
900	8.01581	8.57198×10^{-4}
1000	8.13493	8.97387×10^{-2}
800	7.88514	-9.60091×10^{-2}
850	7.95207	-4.64783×10^{-2}
899.347	8.01237	-2.37449×10^{-3}

Table 2.3: Iteration for T_2.

This then becomes a trial and error search in Table A7.1 for the T_2 which satisfies the previous equation. If one guesses $T_2 \sim 900\ K$, one gets $s^o_{T_2} = 8.01581\ kJ/kg/K$, and the right side evaluates to $0.000857198\ kJ/kg/K$. Performing a trial and error procedure, one finds the results summarized in Table 2.3. Take $T_2 = \boxed{900\ K}$ as close enough!

Then

$$P_2 = P_1 \frac{T_2}{T_1}\frac{V_1}{V_2}, \tag{2.420}$$

$$= (0.1\ MPa)\frac{900\ K}{288\ K}(20), \tag{2.421}$$

$$= \boxed{6.25\ MPa.} \tag{2.422}$$

Now at state 2, $T_2 = 900\ K$, one finds that

$$h_2 = 933.15\ \frac{kJ}{kg}, \qquad u_2 = 674.82\ \frac{kJ}{kg}. \tag{2.423}$$

The heat is added at constant pressure, so

$$q_H = h_3 - h_2, \tag{2.424}$$

$$h_3 = h_2 + q_H, \tag{2.425}$$

$$= \left(933.15\ \frac{kJ}{kg}\right) + \left(1800\ \frac{kJ}{kg}\right), \tag{2.426}$$

$$= 2733.15\ \frac{kJ}{kg}. \tag{2.427}$$

One can then interpolate Table A7.1 to find T_3 and $s^o_{T_3}$

$$T_3 = (2350\ K) + \frac{\left(2733.15\ \frac{kJ}{kg}\right) - \left(2692.31\ \frac{kJ}{kg}\right)}{\left(2755\ \frac{kJ}{kg}\right) - \left(2692.31\ \frac{kJ}{kg}\right)}((2400\ K) - (2350\ K)), \tag{2.428}$$

$$= \boxed{2382.17\ K,} \tag{2.429}$$

$$s^o_{T_3} = \left(9.16913\ \frac{kJ}{kg\ K}\right) + \frac{\left(2733.15\ \frac{kJ}{kg}\right) - \left(2692.31\ \frac{kJ}{kg}\right)}{\left(2755\ \frac{kJ}{kg}\right) - \left(2692.31\ \frac{kJ}{kg}\right)}\left(\left(9.19586\ \frac{kJ}{kg\ K}\right) - \left(9.16913\ \frac{kJ}{kg\ K}\right)\right), \tag{2.430}$$

$$= 9.18633\ \frac{kJ}{kg\ K}. \tag{2.431}$$

$T_4\ (K)$	$s^o_{T_4}\ \left(\frac{kJ}{kg\ K}\right)$	$F(T_4)\ \left(\frac{kJ}{kg\ K}\right)$
400	7.15926	-9.34561×10^{-1}
800	7.88514	-4.07614×10^{-1}
1400	8.52891	7.55464×10^{-2}
1200	8.34596	-6.31624×10^{-2}
1300	8.44046	8.36535×10^{-3}
1250	8.39402	-2.68183×10^{-2}
1288	8.42931	-1.23117×10^{-4}

Table 2.4: Iteration for T_4.

One also has $P_3 = P_2 = \boxed{6.25\ MPa.}$ Now get the actual entropy at state 3:

$$\begin{aligned} s_3(T_3, P_3) &= s^o_{T_3} - R \ln \frac{P_3}{P_{ref}}, && (2.432)\\ &= \left(9.18633\ \frac{kJ}{kg\ K}\right) - \left(0.287\ \frac{kJ}{kg\ K}\right) \ln\left(\frac{6.25\ MPa}{0.1\ MPa}\right), && (2.433)\\ &= 7.99954 \frac{kJ}{kg\ K}. && (2.434) \end{aligned}$$

Now $3 \rightarrow 4$ is an isentropic expansion to state 4, which has the same volume as state 1; $V_1 = V_4$. So the ideal gas law gives

$$\begin{aligned} \frac{P_4 V_4}{T_4} &= \frac{P_1 V_1}{T_1}, && (2.435)\\ \frac{P_4}{P_1} &= \frac{T_4}{T_1}\frac{V_1}{V_4}, && (2.436)\\ \frac{P_4}{P_{ref}} &= \frac{T_4}{T_1}\frac{V_1}{V_4}. && (2.437) \end{aligned}$$

Now consider the entropy at state 4, which must be the same as that at state 3:

$$\begin{aligned} s_4(T_4, P_4) &= s^o_{T_4} - R \ln \frac{P_4}{P_{ref}}, && (2.438)\\ s_3 &= s^o_{T_4} - R \ln \left(\frac{T_4}{T_1} \underbrace{\frac{V_1}{V_4}}_{=1} \right), && (2.439)\\ \left(7.99954\ \frac{kJ}{kg\ K}\right) &= s^o_{T_4} - \left(0.287\ \frac{kJ}{kg\ K}\right) \ln\left(\frac{T_4}{288\ K}\right), && (2.440)\\ 0 &= s^o_{T_4} - \left(0.287\ \frac{kJ}{kg\ K}\right) \ln\left(\frac{T_4}{288\ K}\right) - \left(7.99954\ \frac{kJ}{kg\ K}\right) = F(T_4). && (2.441) \end{aligned}$$

Using Table A7.1, this equation can be iterated until T_4 is found. So $T_4 = \boxed{1288\ K.}$ At this temperature, one has

$$h_4 = 1381.68\ \frac{kJ}{kg}, \qquad u_4 = 1011.98\ \frac{kJ}{kg}. \tag{2.442}$$

Now one can calculate the cycle efficiency:

$$\eta = 1 - \frac{u_4 - u_1}{h_3 - h_2}, \tag{2.443}$$

$$= 1 - \frac{\left(1011.98\ \frac{kJ}{kg}\right) - \left(205.756\ \frac{kJ}{kg}\right)}{\left(2733.15\ \frac{kJ}{kg}\right) - \left(933.15\ \frac{kJ}{kg}\right)}, \tag{2.444}$$

$$= \boxed{0.552098.} \tag{2.445}$$

Now one has

$$q_L = u_1 - u_4 = \left(205.756\ \frac{kJ}{kg}\right) - \left(1011.98\ \frac{kJ}{kg}\right) = -806.224\ \frac{kJ}{kg}. \tag{2.446}$$

So,

$$w_{net} = q_H + q_L = \left(1800\ \frac{kJ}{kg}\right) - \left(806.224\ \frac{kJ}{kg}\right) = 993.776\ \frac{kJ}{kg}. \tag{2.447}$$

So

$$P_{meff} = \frac{W_{net}}{V_{max} - V_{min}}, \tag{2.448}$$

$$= \frac{w_{net}}{v_{max} - v_{min}}, \tag{2.449}$$

$$= \frac{w_{net}}{v_1 - v_2}, \tag{2.450}$$

$$= \frac{w_{net}}{\frac{RT_1}{P_1} - \frac{RT_2}{P_2}}, \tag{2.451}$$

$$= \frac{993.776\ \frac{kJ}{kg}}{\left(0.287\ \frac{kJ}{kg\ K}\right)\left(\frac{288\ K}{100\ kPa} - \frac{900\ K}{6250\ kPa}\right)}, \tag{2.452}$$

$$= \boxed{1265.58\ kPa.} \tag{2.453}$$

2.8 Stirling

Another often-studied air-standard engine is given by the Stirling cycle. This is similar to the Otto cycle except the adiabatic processes are replaced by isothermal ones. The efficiency can be shown to be equal to that of a Carnot engine. Stirling engines are difficult to build. Diagrams for $P - v$ and $T - s$ for the Stirling cycle are shown in Figure 2.16.

One can outline the Stirling cycle as follows:

- $1 \rightarrow 2$: isothermal compression in the compression stroke,
- $2 \rightarrow 3$: isochoric heat transfer in the combustion stroke,
- $3 \rightarrow 4$: expansion in power stroke, and
- $4 \rightarrow 1$: isochoric rejection of heat to the surroundings.

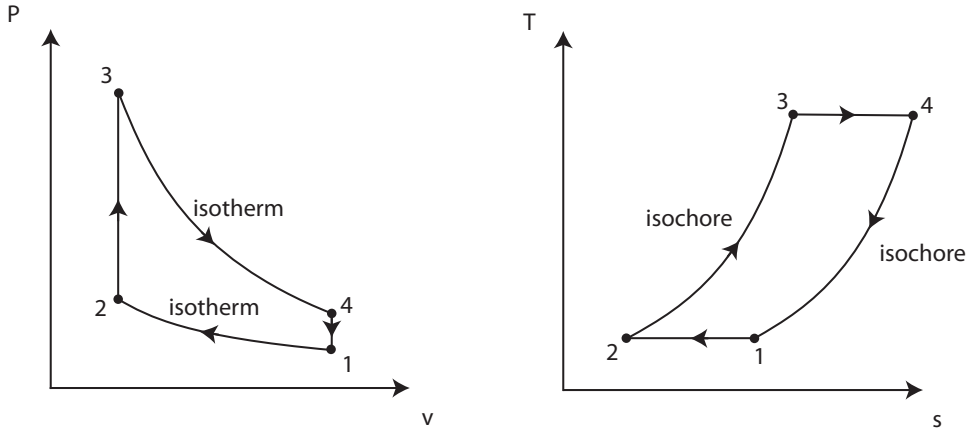

Figure 2.16: $P - v$ and $T - s$ diagrams for the Stirling cycle.

2.9 Refrigeration

A simple way to think of a refrigerator is a cyclic heat engine operating in reverse. Rather than extracting work from heat transfer from a high temperature source and rejecting heat to a low temperature source, the refrigerator takes a work input to move heat from a low temperature source to a high temperature source.

2.9.1 Vapor-compression

A common refrigerator is based on a vapor-compression cycle. This is a Rankine cycle in reverse. While one could employ a turbine to extract some work, it is often impractical. Instead the high pressure gas is simply irreversibly throttled down to low low pressure.

One can outline the vapor-compression refrigeration cycle as follows:

- $1 \rightarrow 2$: isentropic compression
- $2 \rightarrow 3$: isobaric heat transfer to high temperature reservoir in condenser,
- $3 \rightarrow 4$: adiabatic expansion in throttling valve, and
- $4 \rightarrow 1$: isobaric (and often isothermal) heat transfer to low temperature reservoir in evaporator.

A schematic for the vapor-compression refrigeration cycle is shown in Figure 2.17. A $T - s$ diagram for the vapor-compression refrigeration cycle is shown in Figure 2.18.

The efficiency does not make sense for a refrigerator as $0 \leq \eta \leq 1$. Instead a coefficient

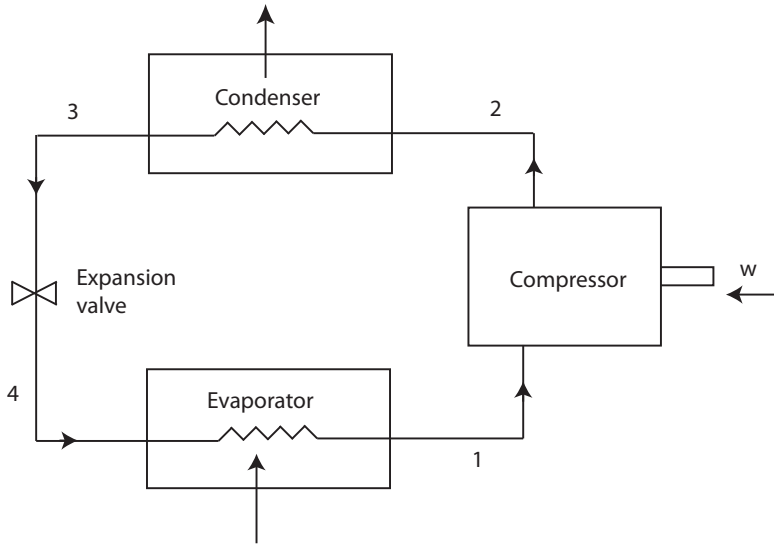

Figure 2.17: Schematic diagram for the vapor-compression refrigeration cycle.

of performance, β, is defined as

$$\beta = \frac{\text{what one wants}}{\text{what one pays for}}, \tag{2.454}$$

$$= \boxed{\frac{q_L}{w_c}.} \tag{2.455}$$

Note that a heat pump is effectively the same as a refrigerator, except one desires q_H rather than q_L. So for a heat pump, the coefficient of performance, β', is defined as

$$\boxed{\beta' = \frac{q_H}{w_c}.} \tag{2.456}$$

It is possible for both β and β' to be greater than unity.

Example 2.11

(from Moran and Shapiro, p. 442) $R-12$ is the working fluid in an ideal vapor-compression refrigeration cycle that communicates thermally with a cold region at 20 $°C$ and a warm region at 40 $°C$. Saturated vapor enters the compressor at 20 $°C$ and saturated liquid leaves the condenser at 40 $°C$. The mass flow rate of the refrigerant is 0.008 kg/s. Find

- compressor power in kW,
- refrigeration capacity in ton,
- coefficient of performance, and
- coefficient of performance of an equivalent Carnot cycle.

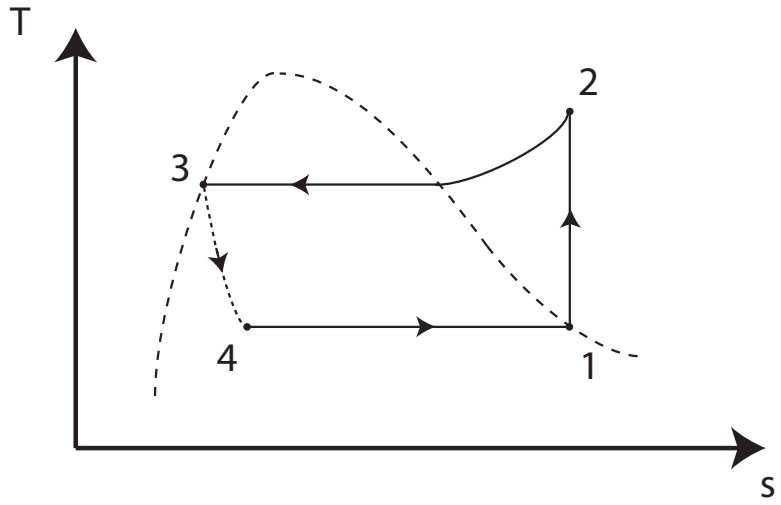

Figure 2.18: $T - s$ diagram for the vapor-compression refrigeration cycle.

At compressor inlet for the ideal cycle, one has a saturated vapor.

$$T_1 = 20\ ^\circ C, \qquad x_1 = 1. \tag{2.457}$$

The tables then give

$$h_1 = 195.78\ \frac{kJ}{kg}, \qquad s_1 = 0.6884\ \frac{kJ}{kg\ K}, \qquad P_1 = 5.6729\ bar. \tag{2.458}$$

Now at the end of the condenser (state 3), one has $T_3 = 40\ ^\circ C$. The condenser is on an isobar, so the pressure is the saturation pressure at the temperature, which is

$$P_3 = P_2 = 9.6065\ bar. \tag{2.459}$$

So, two properties at the end of the compression are known: pressure and entropy. The allows determination of the enthalpy at the end of compression via the tables:

$$h_2 = 205.1\ \frac{kJ}{kg}. \tag{2.460}$$

State 3 is at the end of the condenser, so $x_3 = 0$, and one finds the enthalpy from the tables to be

$$h_3 = 74.59\ \frac{kJ}{kg}. \tag{2.461}$$

Now the throttling device has constant enthalpy, so

$$h_4 = h_3 = 74.59\ \frac{kJ}{kg}. \tag{2.462}$$

However, the fluid has been throttled to a lower pressure: that of the evaporator, which is the same as state 1, the compressor inlet, so

$$P_4 = P_1 = 5.6729\ bar. \tag{2.463}$$

The compressor work is

$$\begin{aligned}
\dot{W}_c &= \dot{m}(h_2 - h_1), && (2.464)\\
&= \left(0.008\ \frac{kg}{s}\right)\left(\left(205.1\ \frac{kJ}{kg}\right) - \left(195.78\ \frac{kJ}{kg}\right)\right), && (2.465)\\
&= \boxed{0.075\ kW.} && (2.466)
\end{aligned}$$

Now one desires the heat which leaves the cold region to be high for a good refrigerator. This is the heat transfer at the low temperature part of the $T - s$ diagram, which here gives

$$\begin{aligned}
\dot{Q}_L &= \dot{m}(h_1 - h_4), && (2.467)\\
&= \left(0.008\ \frac{kg}{s}\right)\left(\left(195.78\ \frac{kJ}{kg}\right) - \left(74.59\ \frac{kJ}{kg}\right)\right), && (2.468)\\
&= 0.9695\ kW, && (2.469)\\
&= \left(0.9695\ \frac{kJ}{s}\right)\left(\frac{60\ s}{min}\right)\left(\frac{1\ ton}{211\ \frac{kJ}{min}}\right), && (2.470)\\
&= \boxed{0.276\ ton.} && (2.471)
\end{aligned}$$

The units *ton* is used for power and is common in the refrigeration industry. It is the power required to freeze one "short ton" of water at 0 $^\circ C$ in 24 hours. It is 12000 Btu/hr, 3.516853 kW, or 4.7162 hp. A short ton is a U.S ton, which is 2000 lbm. A long ton is British and is 2240 lbm. A metric ton is 1000 kg and is 2204 lbm.

The coefficient of performance is

$$\begin{aligned}
\beta &= \frac{\dot{Q}_L}{\dot{W}_c}, && (2.472)\\
&= \frac{0.9695\ kW}{0.075\ kW}, && (2.473)\\
&= \boxed{12.93.} && (2.474)
\end{aligned}$$

The equivalent Carnot refrigerator would have

$$\begin{aligned}
\beta_{max} &= \frac{\dot{Q}_L}{\dot{W}_c}, && (2.475)\\
&= \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L}, && (2.476)\\
&= \frac{1}{\frac{\dot{Q}_H}{\dot{Q}_L} - 1}, && (2.477)\\
&= \frac{1}{\frac{T_H}{T_L} - 1}, && (2.478)\\
&= \frac{T_L}{T_H - T_L}, && (2.479)\\
&= \frac{20 + 273.15}{40 + 273.15 - (20 + 273.15)}, && (2.480)\\
&= \boxed{14.6575.} && (2.481)
\end{aligned}$$

2.9.2 Air standard

This is effectively the inverse Brayton cycle. It is used in the liquefaction of air and other gases. It is also used in aircraft cabin cooling. It has the following components:

- $1 \rightarrow 2$: isentropic compression,
- $2 \rightarrow 3$: isobaric heat transfer to a high temperature environment
- $3 \rightarrow 4$: isentropic expansion through turbine, and
- $4 \rightarrow 1$: isobaric heat exchange with low temperature surroundings.

A schematic for the air standard refrigeration cycle is shown in Figure 2.19. A $T-s$ diagram

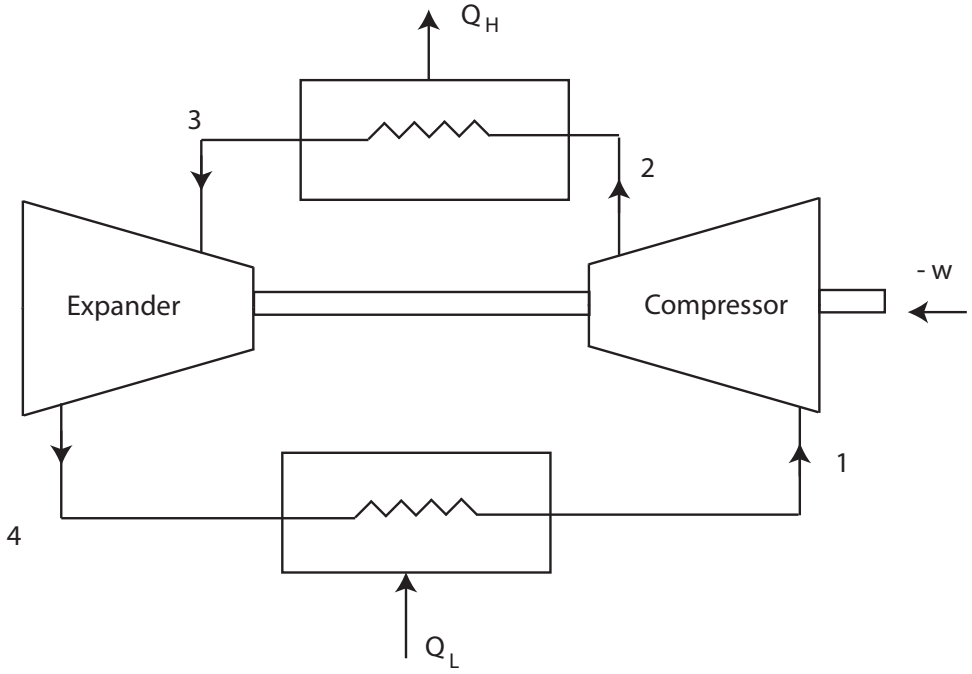

Figure 2.19: Schematic for air standard refrigeration cycle.

for the air standard refrigeration cycle is shown in Figure 2.20.

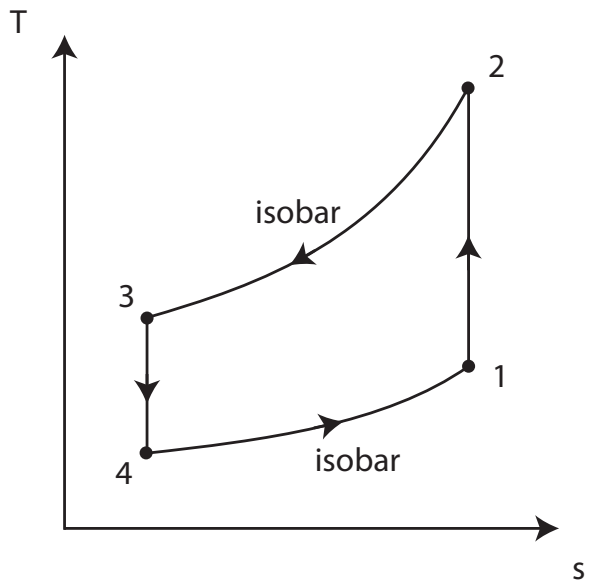

Figure 2.20: $T - s$ diagram for air standard refrigeration Brayton cycle.

Chapter 3

Gas mixtures

Read BS, Chapter 11.
See for background Sandler, Chapter 7.
See for background Smith, van Ness, and Abbott, Chapter 10.
See for background Tester and Modell.

One is often faced with mixtures of simple compressible substances, and it the thermodynamics of such mixtures upon which attention is now fixed. Here a discussion of some of the fundamentals of mixture theory will be given. In general, thermodynamics of mixtures can be a challenging topic about which much remains to be learned. In particular, these notes will focus on ideal mixtures of ideal gases, for which results are often consistent with intuition. The chemical engineering literature contains a full discussion of the many nuances associated with non-ideal mixtures of non-ideal materials.

3.1 Some general issues

Here the notation of BS will be used. There is no effective consensus on notation for mixtures. That of BS is more unusual than most; however, the ideas are correct, which is critical. Consider a mixture of N components, each a pure substance, so that the total mass and total number of moles are

$$\boxed{m = m_1 + m_2 + m_3 + \cdots + m_N = \sum_{i=1}^{N} m_i,} \qquad \text{mass, units= } kg, \tag{3.1}$$

$$\boxed{n = n_1 + n_2 + n_3 + \cdots + n_N = \sum_{i=1}^{N} n_i,} \qquad \text{moles, units= } kmole. \tag{3.2}$$

Recall 1 $mole = 6.02214179 \times 10^{23}$ $molecule$. The mass fraction of component i is defined as c_i:

$$\boxed{c_i \equiv \frac{m_i}{m},} \qquad \text{mass fraction, dimensionless.} \tag{3.3}$$

The mole fraction of component i is defined as y_i:

$$\boxed{y_i \equiv \frac{n_i}{n},} \qquad \text{mole fraction, dimensionless.} \tag{3.4}$$

Now the molecular mass of species i is the mass of a mole of species i. It units are typically $g/mole$. This is an identical unit to $kg/kmole$. Molecular mass is sometimes called "molecular weight," but this is formally incorrect, as it is a mass measure, not a force measure. Mathematically the definition of M_i corresponds to

$$\boxed{M_i \equiv \frac{m_i}{n_i},} \qquad \left(\frac{kg}{kmole} = \frac{g}{mole}\right). \tag{3.5}$$

Then one gets mass fraction in terms of mole fraction as

$$\begin{aligned}
c_i &= \frac{m_i}{m}, && (3.6)\\
&= \frac{n_i M_i}{m}, && (3.7)\\
&= \frac{n_i M_i}{\sum_{j=1}^{N} m_j}, && (3.8)\\
&= \frac{n_i M_i}{\sum_{j=1}^{N} n_j M_j}, && (3.9)\\
&= \frac{\frac{n_i M_i}{n}}{\frac{1}{n}\sum_{j=1}^{N} n_j M_j}, && (3.10)\\
&= \frac{\frac{n_i M_i}{n}}{\sum_{j=1}^{N} \frac{n_j M_j}{n}}, && (3.11)\\
&= \frac{y_i M_i}{\sum_{j=1}^{N} y_j M_j}. && (3.12)
\end{aligned}$$

Similarly, one finds mole fraction in terms of mass fraction by the following:

$$\begin{aligned}
y_i &= \frac{n_i}{n}, && (3.13)\\
&= \frac{\frac{m_i}{M_i}}{\sum_{j=1}^{N} \frac{m_j}{M_j}}, && (3.14)\\
&= \frac{\frac{m_i}{M_i m}}{\sum_{j=1}^{N} \frac{m_j}{M_j m}}, && (3.15)\\
&= \frac{\frac{c_i}{M_i}}{\sum_{j=1}^{N} \frac{c_j}{M_j}}. && (3.16)
\end{aligned}$$

The mixture itself has a mean molecular mass:

$$M \equiv \frac{m}{n}, \tag{3.17}$$

$$= \frac{\sum_{i=1}^{N} m_i}{n}, \tag{3.18}$$

$$= \sum_{i=1}^{N} \frac{n_i M_i}{n}, \tag{3.19}$$

$$= \sum_{i=1}^{N} y_i M_i. \tag{3.20}$$

Example 3.1

Air is often modeled as a mixture in the following molar ratios:

$$O_2 + 3.76 N_2. \tag{3.21}$$

Find the mole fractions, the mass fractions, and the mean molecular mass of the mixture.

Take O_2 to be species 1 and N_2 to be species 2. Consider the number of moles of O_2 to be

$$n_1 = 1 \ kmole, \tag{3.22}$$

and N_2 to be

$$n_2 = 3.76 \ kmole. \tag{3.23}$$

The molecular mass of O_2 is $M_1 = 32 \ kg/kmole$. The molecular mass of N_2 is $M_2 = 28 \ kg/kmole$. The total number of moles is

$$n = 1 \ kmole + 3.76 \ kmole = 4.76 \ kmole. \tag{3.24}$$

So the mole fractions are

$$y_1 = \frac{1 \ kmole}{4.76 \ kmole} = \boxed{0.2101,} \tag{3.25}$$

$$y_2 = \frac{3.76 \ kmole}{4.76 \ kmole} = \boxed{0.7899.} \tag{3.26}$$

Note that

$$\sum_{i=1}^{N} y_i = 1. \tag{3.27}$$

That is to say $y_1 + y_2 = 0.2101 + 0.7899 = 1$. Now for the masses, one has

$$m_1 = n_1 M_1 = (1 \ kmole) \left(32 \ \frac{kg}{kmole} \right) = 32 \ kg, \tag{3.28}$$

$$m_2 = n_2 M_2 = (3.76 \ kmole) \left(28 \ \frac{kg}{kmole} \right) = 105.28 \ kg. \tag{3.29}$$

So one has

$$m = m_1 + m_2 = 32 \ kg + 105.28 \ kg = 137.28 \ kg. \tag{3.30}$$

The mass fractions then are

$$c_1 = \frac{m_1}{m} = \frac{32\ kg}{137.28\ kg} = \boxed{0.2331,} \tag{3.31}$$

$$c_2 = \frac{m_2}{m} = \frac{105.28\ kg}{137.28\ kg} = \boxed{0.7669.} \tag{3.32}$$

Note that

$$\sum_{i=1}^{N} c_i = 1. \tag{3.33}$$

That is $c_1 + c_2 = 0.2331 + 0.7669 = 1$. Now for the mixture molecular mass, one has

$$M = \frac{m}{n} = \frac{137.28\ kg}{4.76\ kmole} = \boxed{28.84\ \frac{kg}{kmole}.} \tag{3.34}$$

Check against another formula.

$$M = \sum_{i=1}^{N} y_i M_i = y_1 M_1 + y_2 M_2 = (0.2101)\left(32\ \frac{kg}{kmole}\right) + (0.7899)\left(28\ \frac{kg}{kmole}\right) = 28.84\ \frac{kg}{kmole}. \tag{3.35}$$

Now postulates for mixtures are not as well established as those for pure substances. The literature has much controversial discussion of the subject. A strong advocate of the axiomatic approach, C. A. Truesdell, proposed the following "metaphysical principles" for mixtures, which are worth considering.

1. *All properties of the mixture must be mathematical consequences of properties of the constituents.*

2. *So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.*

3. *The motion of the mixture is governed by the same equations as is a single body.*

Most important for the present discussion is the first principle. When coupled with fluid mechanics, the second two take on additional importance. The approach of mixture theory is to divide and conquer. One typically treats each of the constituents as a single material and then devises appropriate average or mixture properties from those of the constituents.

The best example of this is air, which is not a single material, but is often treated as such.

3.2 Ideal and non-ideal mixtures

A general extensive property, such as U, for an N-species mixture will be such that

$$\boxed{U = U(T, P, n_1, n_2, \ldots, n_N).} \tag{3.36}$$

A *partial molar property* is a generalization of an intensive property, and is defined such that it is the *partial derivative of an extensive property with respect to number of moles, with T and P held constant*. For internal energy, then the partial molar internal energy is

$$\boxed{\overline{u}_i \equiv \left.\frac{\partial U}{\partial n_i}\right|_{T,P,n_j,i\neq j}.} \tag{3.37}$$

Pressure and temperature are held constant because those are convenient variables to control in an experiment. One also has the partial molar volume

$$\boxed{\overline{\mathrm{v}}_i = \left.\frac{\partial V}{\partial n_i}\right|_{T,P,n_j,i\neq j}.} \tag{3.38}$$

It shall be soon seen that there are other natural ways to think of the volume per mole.

Now in general one would expect to find

$$\overline{u}_i = \overline{u}_i(T, P, n_1, n_2, \ldots, n_N), \tag{3.39}$$
$$\overline{\mathrm{v}}_i = \overline{\mathrm{v}}_i(T, P, n_1, n_2, \ldots, n_N). \tag{3.40}$$

This is the case for what is known as a *non-ideal mixture*. An *ideal mixture* is defined as a mixture for which the partial molar properties $\overline{u}_i$ and $\overline{\mathrm{v}}_i$ are not functions of the composition, that is

$$\overline{u}_i = \overline{u}_i(T, P), \qquad \text{if ideal mixture,} \tag{3.41}$$
$$\overline{\mathrm{v}}_i = \overline{\mathrm{v}}_i(T, P), \qquad \text{if ideal mixture.} \tag{3.42}$$

An ideal mixture also has the property that $\overline{h}_i = \overline{h}_i(T, P)$, while for a non-ideal mixture $\overline{h}_i = \overline{h}_i(T, P, n_1, \ldots, n_N)$. Though not obvious, it will turn out that some properties of an ideal mixture will depend on composition. For example, the entropy of a constituent of an ideal mixture will be such that

$$\overline{s}_i = \overline{s}_i(T, P, n_1, n_2, \ldots, n_N). \tag{3.43}$$

3.3 Ideal mixtures of ideal gases

The most straightforward mixture to consider is an ideal mixture of ideal gases. Even here, there are assumptions necessary that remain difficult to verify absolutely.

3.3.1 Dalton model

The most common model for a mixture of ideal gases is the *Dalton model*. Key assumptions define this model

- Each constituent shares a common temperature.
- Each constituent occupies the entire volume.
- Each constituent possesses a *partial pressure* which sums to form the total pressure of the mixture.

The above characterize a Dalton model for any gas, ideal or non-ideal. One also takes for convenience

- Each constituent behaves as an ideal gas.
- The mixture behaves as a single ideal gas.

It is more convenient to deal on a molar basis for such a theory. For the Dalton model, additional useful quantities, the species mass concentration ρ_i, the mixture mass concentration ρ, the species molar concentration $\overline{\rho}_i$, and the mixture molar concentration $\overline{\rho}$, can be defined. As will be seen, these definitions for concentrations are useful; however, they are not in common usage. Following BS, the bar notation, $\bar{\cdot}$, will be reserved for properties which are mole-based rather than mass-based. As mentioned earlier, the notion of a partial molal property is discussed extensively in the chemical engineering literature and has implications beyond those considered here. For the Dalton model, in which each component occupies the same volume, one has

$$\boxed{V_i = V.} \tag{3.44}$$

The mixture mass concentration, also called the density is simply

$$\boxed{\rho = \frac{m}{V},} \qquad \left(\frac{kg}{m^3}\right). \tag{3.45}$$

The mixture molar concentration is

$$\boxed{\overline{\rho} = \frac{n}{V},} \qquad \left(\frac{kmole}{m^3}\right). \tag{3.46}$$

For species i, the equivalents are

$$\rho_i = \frac{m_i}{V}, \qquad \left(\frac{kg}{m^3}\right), \tag{3.47}$$

$$\overline{\rho}_i = \frac{n_i}{V}, \qquad \left(\frac{kmole}{m^3}\right). \tag{3.48}$$

One can find a convenient relation between species molar concentration and species mole fraction by the following operations

$$\begin{aligned} \overline{\rho}_i &= \frac{n_i}{V}\frac{n}{n}, && (3.49)\\ &= \frac{n_i}{n}\frac{n}{V}, && (3.50)\\ &= y_i\overline{\rho}. && (3.51) \end{aligned}$$

A similar relation exists between species molar concentration and species mass fraction via

$$\begin{aligned} \overline{\rho}_i &= \frac{n_i}{V}\frac{m}{m}\frac{M_i}{M_i}, && (3.52)\\ &= \frac{m}{V}\frac{\overbrace{n_i M_i}^{=m_i}}{mM_i}, && (3.53)\\ &= \rho\,\frac{\overbrace{m_i}^{=c_i}}{m}\,\frac{1}{M_i}, && (3.54)\\ &= \rho\frac{c_i}{M_i}. && (3.55) \end{aligned}$$

The specific volumes, mass and molar, are similar. One takes

$$\begin{aligned} v &= \frac{V}{m}, \qquad \overline{v} = \frac{V}{n}, && (3.56)\\ v_i &= \frac{V}{m_i}, \qquad \overline{v}_i = \frac{V}{n_i}. && (3.57) \end{aligned}$$

Note that this definition of molar specific volume is *not* the partial molar volume defined in the chemical engineering literature, which takes the form $\overline{\mathrm{v}}_i = \partial V/\partial n_i|_{T,P,n_j,i\neq j}$.

For the partial pressure of species i, one can say for the Dalton model

$$\boxed{P = \sum_{i=1}^{N} P_i.} \tag{3.58}$$

For species i, one has

$$\begin{aligned} P_i V &= n_i \overline{R} T, && (3.59)\\ P_i &= \frac{n_i \overline{R} T}{V}, && (3.60)\\ \underbrace{\sum_{i=1}^{N} P_i}_{=P} &= \sum_{i=1}^{N} \frac{n_i \overline{R} T}{V}, && (3.61)\\ P &= \frac{\overline{R}T}{V}\underbrace{\sum_{i=1}^{N} n_i}_{=n}. && (3.62) \end{aligned}$$

So, for the mixture, one has

$$PV = n\overline{R}T. \tag{3.63}$$

One could also say

$$P = \underbrace{\frac{n}{V}}_{=\overline{\rho}} \overline{R}T = \overline{\rho}\overline{R}T. \tag{3.64}$$

Here n is the total number of moles in the system. Additionally $\overline{R}$ is the universal gas constant with value

$$\overline{R} = 8.314472 \ \frac{kJ}{kmole \ K} = 8.314472 \ \frac{J}{mole \ K}. \tag{3.65}$$

Sometimes this is expressed in terms of k_B, the *Boltzmann constant*, and $\mathcal{N}$, Avogadro's number:

$$\overline{R} = k_B \mathcal{N}, \tag{3.66}$$

$$\mathcal{N} = 6.02214179 \times 10^{23} \ \frac{molecule}{mole}, \tag{3.67}$$

$$k_B = 1.380650 \times 10^{-23} \ \frac{J}{K \ molecule}. \tag{3.68}$$

Example 3.2

Compare the molar specific volume defined here with the partial molar volume from the chemical engineering literature.

The partial molar volume $\overline{\mathrm{v}}_i$, is given by

$$\overline{\mathrm{v}}_i = \left.\frac{\partial V}{\partial n_i}\right|_{T,P,n_j,i\neq j}. \tag{3.69}$$

For the ideal gas, one has

$$PV = \overline{R}T\sum_{k=1}^{N} n_k, \tag{3.70}$$

$$V = \frac{\overline{R}T\sum_{k=1}^{N} n_k}{P}, \tag{3.71}$$

$$\left.\frac{\partial V}{\partial n_i}\right|_{T,P,n_j,i\neq j} = \frac{\overline{R}T\sum_{k=1}^{N} \frac{\partial n_k}{\partial n_i}}{P}, \tag{3.72}$$

$$= \frac{\overline{R}T\sum_{k=1}^{N} \delta_{ki}}{P}, \tag{3.73}$$

$$= \frac{\overline{R}T\left(\overbrace{\delta_{1i}}^{=0} + \overbrace{\delta_{2i}}^{=0} + \cdots + \overbrace{\delta_{ii}}^{=1} + \cdots + \overbrace{\delta_{Ni}}^{=0}\right)}{P}, \tag{3.74}$$

$$\overline{\mathrm{v}}_i = \frac{\overline{R}T}{P}, \tag{3.75}$$

$$= \frac{V}{\sum_{k=1}^{N} n_k}, \tag{3.76}$$

$$= \frac{V}{n}. \tag{3.77}$$

Here the so-called Kronecker delta function has been employed, which is much the same as the identity matrix:

$$\delta_{ki} = 0, \qquad k \neq i, \tag{3.78}$$

$$\delta_{ki} = 1, \qquad k = i. \tag{3.79}$$

Contrast this with the earlier adopted definition of molar specific volume

$$\overline{v}_i = \frac{V}{n_i}. \tag{3.80}$$

So, why is there a difference? The molar specific volume is a simple definition. One takes the instantaneous volume V, which is shared by all species in the Dalton model, and scales it by the instantaneous number of moles of species i, and acquires a natural definition of molar specific volume consistent with the notion of a mass specific volume. On the other hand, the partial molar volume specifies how the volume changes if the number of moles of species i changes, *while holding T and P and all other species mole numbers constant*. One can imagine adding a mole of species i, which would necessitate a change in V in order to guarantee the P remain fixed.

3.3.1.1 Binary mixtures

Consider now a *binary mixture* of two components A and B. This is easily extended to a general mixture of N components. First the total number of moles is the sum of the parts:

$$n = n_A + n_B. \tag{3.81}$$

Now, write the ideal gas law for each component:

$$P_A V_A = n_A \overline{R} T_A, \tag{3.82}$$
$$P_B V_B = n_B \overline{R} T_B. \tag{3.83}$$

But by the assumptions of the Dalton model, $V_A = V_B = V$, and $T_A = T_B = T$, so

$$P_A V = n_A \overline{R} T, \tag{3.84}$$
$$P_B V = n_B \overline{R} T. \tag{3.85}$$

One also has

$$PV = n\overline{R}T. \tag{3.86}$$

Solving for n, n_A and n_B, one finds

$$n = \frac{PV}{\overline{R}T}, \tag{3.87}$$
$$n_A = \frac{P_A V}{\overline{R}T}, \tag{3.88}$$
$$n_B = \frac{P_B V}{\overline{R}T}. \tag{3.89}$$

Now $n = n_A + n_B$, so one has

$$\frac{PV}{\overline{R}T} = \frac{P_A V}{\overline{R}T} + \frac{P_B V}{\overline{R}T}. \tag{3.90}$$
$$P = P_A + P_B. \tag{3.91}$$

That is the total pressure is the sum of the partial pressures. This is a mixture rule for pressure

One can also scale each constituent ideal gas law by the mixture ideal gas law to get

$$\frac{P_A V}{PV} = \frac{n_A \overline{R} T}{n \overline{R} T}, \tag{3.92}$$
$$\frac{P_A}{P} = \frac{n_A}{n}, \tag{3.93}$$
$$= y_A, \tag{3.94}$$
$$P_A = y_A P. \tag{3.95}$$

Likewise

$$P_B = y_B P. \tag{3.96}$$

Now, one also desires rational mixture rules for energy, enthalpy, and entropy. Invoke Truesdell's principles on a mass basis for internal energy. Then the total internal energy U (with

units J) for the binary mixture must be

$$\begin{aligned} U = mu &= m_A u_A + m_B u_B, && (3.97)\\ &= m\left(\frac{m_A}{m}u_A + \frac{m_B}{m}u_B\right), && (3.98)\\ &= m\left(c_A u_A + c_B u_B\right), && (3.99)\\ u &= c_A u_A + c_B u_B. && (3.100) \end{aligned}$$

For the enthalpy, one has

$$\begin{aligned} H = mh &= m_A h_A + m_B h_B, && (3.101)\\ &= m\left(\frac{m_A}{m}h_A + \frac{m_B}{m}h_B\right), && (3.102)\\ &= m\left(c_A h_A + c_B h_B\right), && (3.103)\\ h &= c_A h_A + c_B h_B. && (3.104) \end{aligned}$$

It is easy to extend this to a mole fraction basis rather than a mass fraction basis. One can also obtain a gas constant for the mixture on a mass basis. For the mixture, one has

$$\begin{aligned} PV &= n\overline{R}T \equiv mRT, && (3.105)\\ \frac{PV}{T} \equiv mR &= n\overline{R}, && (3.106)\\ &= (n_A + n_B)\overline{R}, && (3.107)\\ &= \left(\frac{m_A}{M_A} + \frac{m_B}{M_B}\right)\overline{R}, && (3.108)\\ &= \left(m_A\frac{\overline{R}}{M_A} + m_B\frac{\overline{R}}{M_B}\right), && (3.109)\\ &= \left(m_A R_A + m_B R_B\right), && (3.110)\\ R &= \left(\frac{m_A}{m}R_A + \frac{m_B}{m}R_B\right), && (3.111)\\ R &= \left(c_A R_A + c_B R_B\right). && (3.112) \end{aligned}$$

For the entropy, one has

$$\begin{aligned} S = ms = &= m_A s_A + m_B s_B, && (3.113)\\ &= m\left(\frac{m_A}{m}s_A + \frac{m_B}{m}s_B\right), && (3.114)\\ &= m\left(c_A s_A + c_B s_B\right), && (3.115)\\ s &= c_A s_A + c_B s_B. && (3.116) \end{aligned}$$

Note that s_A is evaluated at T and P_A, while s_B is evaluated at T and P_B. For a CPIG, one

has

$$s_A = \underbrace{s^o_{298,A} + c_{PA} \ln\left(\frac{T}{T_o}\right)}_{\equiv s^o_{T,A}} - R_A \ln\left(\frac{P_A}{P_o}\right), \tag{3.117}$$

$$= s^o_{298,A} + c_{PA} \ln\left(\frac{T}{T_o}\right) - R_A \ln\left(\frac{y_A P}{P_o}\right). \tag{3.118}$$

Likewise

$$s_B = \underbrace{s^o_{298,B} + c_{PB} \ln\left(\frac{T}{T_o}\right)}_{\equiv s^o_{T,B}} - R_B \ln\left(\frac{y_B P}{P_o}\right). \tag{3.119}$$

Here the "o" denotes some reference state. As a superscript, it typically means that the property is evaluated at a reference pressure. For example, $s^o_{T,A}$ denotes the portion of the entropy of component A that is evaluated at the reference pressure P_o and is allowed to vary with temperature T. Note also that $s_A = s_A(T, P, y_A)$ and $s_B = s_B(T, P, y_B)$, so the entropy of a single constituent depends on the composition of the mixture and not just on T and P. This contrasts with energy and enthalpy for which $u_A = u_A(T)$, $u_B = u_B(T)$, $h_A = h_A(T)$, $h_B = h_B(T)$ if the mixture is composed of ideal gases. Occasionally, one finds h^o_A and h^o_B used as a notation. This denotes that the enthalpy is evaluated at the reference pressure. However, if the gas is ideal, the enthalpy is not a function of pressure and $h_A = h^o_A$, $h_B = h^o_B$.

If one is employing a calorically imperfect ideal gas model, then one finds for species i that

$$s_i = s^o_{T,i} - R_i \ln\left(\frac{y_i P}{P_o}\right), \qquad i = A, B. \tag{3.120}$$

3.3.1.2 Entropy of mixing

Example 3.3

Initially calorically perfect ideal gases A and B are segregated within the same large volume by a thin frictionless, thermally conducting diaphragm. Thus, both are at the same initial pressure and temperature, P_1 and T_1. The total volume is thermally insulated and fixed, so there are no global heat or work exchanges with the environment. The diaphragm is removed, and A and B are allowed to mix. Assume A has mass m_A and B has mass m_B. The gases are allowed to have distinct molecular masses, M_A and M_B. Find the final temperature T_2, pressure P_2, and the change in entropy.

The ideal gas law holds that at the initial state

$$V_{A1} = \frac{m_A R_A T_1}{P_1}, \qquad V_{B1} = \frac{m_B R_B T_1}{P_1}. \tag{3.121}$$

At the final state one has

$$V_2 = V_{A2} = V_{B2} = V_{A1} + V_{B1} = (m_A R_A + m_B R_B)\frac{T_1}{P_1}. \tag{3.122}$$

Mass conservation gives

$$m_2 = m_1 = m_A + m_B. \tag{3.123}$$

One also has the first law

$$\begin{aligned}
U_2 - U_1 &= {}_1Q_2 - {}_1W_2, && (3.124)\\
U_2 - U_1 &= 0, && (3.125)\\
U_2 &= U_1, && (3.126)\\
m_2 u_2 &= m_A u_{A1} + m_B u_{B1}, && (3.127)\\
(m_A + m_B) u_2 &= m_A u_{A1} + m_B u_{B1}, && (3.128)\\
0 &= m_A(u_{A1} - u_2) + m_B(u_{B1} - u_2), && (3.129)\\
0 &= m_A c_{vA}(T_1 - T_2) + m_B c_{vB}(T_1 - T_2), && (3.130)\\
T_2 &= \frac{m_A c_{vA} T_1 + m_B c_{vB} T_1}{m_A c_{vA} + m_B c_{vB}}, && (3.131)\\
T_2 &= \boxed{T_1.} && (3.132)
\end{aligned}$$

The final pressure by Dalton's law then is

$$\begin{aligned}
P_2 &= P_{A2} + P_{B2}, && (3.133)\\
&= \frac{m_A R_A T_2}{V_2} + \frac{m_B R_B T_2}{V_2}, && (3.134)\\
&= \frac{m_A R_A T_1}{V_2} + \frac{m_B R_B T_1}{V_2}, && (3.135)\\
&= \frac{(m_A R_A + m_B R_B)\, T_1}{V_2}, && (3.136)\\
&\quad \text{substitute for } V_2 \text{ from Eq. (3.122)} && (3.137)\\
&= \frac{(m_A R_A + m_B R_B)\, T_1}{(m_A R_A + m_B R_B)\frac{T_1}{P_1}}, && (3.138)\\
&= \boxed{P_1.} && (3.139)
\end{aligned}$$

So the initial and final temperatures and pressures are identical.

Now the entropy change of gas A is

$$\begin{aligned}
s_{A2} - s_{A1} &= c_{PA} \ln\left(\frac{T_{A2}}{T_{A1}}\right) - R_A \ln\left(\frac{P_{A2}}{P_{A1}}\right), && (3.140)\\
&= c_{PA} \ln\left(\frac{T_2}{T_1}\right) - R_A \ln\left(\frac{y_{A2} P_2}{y_{A1} P_1}\right), && (3.141)\\
&= c_{PA} \underbrace{\ln\left(\frac{T_1}{T_1}\right)}_{=0} - R_A \ln\left(\frac{y_{A2} P_1}{y_{A1} P_1}\right), && (3.142)\\
&= -R_A \ln\left(\frac{y_{A2} P_1}{(1) P_1}\right), && (3.143)\\
&= -R_A \ln y_{A2}. && (3.144)
\end{aligned}$$

Likewise

$$s_{B2} - s_{B1} = -R_B \ln y_{B2}. \tag{3.145}$$

So the change in entropy of the mixture is

$$\begin{aligned}
\Delta S &= m_A(s_{A2} - s_{A1}) + m_B(s_{B2} - s_{B1}), && (3.146)\\
&= -m_A R_A \ln y_{A2} - m_B R_B \ln y_{B2}, && (3.147)\\
&= -\underbrace{(n_A M_A)}_{=m_A}\underbrace{\left(\frac{\overline{R}}{M_A}\right)}_{=R_A}\ln y_{A2} - \underbrace{(n_B M_B)}_{=m_B}\underbrace{\left(\frac{\overline{R}}{M_B}\right)}_{=R_B}\ln y_{B2}, && (3.148)\\
&= -\overline{R}(n_A \ln y_{A2} + n_B \ln y_{B2}), && (3.149)\\
&= \boxed{-\overline{R}\left(n_A \underbrace{\ln\left(\frac{n_A}{n_A+n_B}\right)}_{\leq 0} + n_B \underbrace{\ln\left(\frac{n_B}{n_A+n_B}\right)}_{\leq 0}\right)}, && (3.150)\\
&\geq 0. && (3.151)
\end{aligned}$$

We can also scale Eq. (3.149) by $\overline{R}n$ to get

$$\begin{aligned}
\frac{1}{\overline{R}}\underbrace{\frac{\Delta S}{n}}_{=\Delta\overline{s}} &= -\left(\underbrace{\frac{n_A}{n}}_{=y_{A2}}\ln y_{A2} + \underbrace{\frac{n_B}{n}}_{=y_{B2}}\ln y_{B2}\right), && (3.152)\\
\frac{\Delta\overline{s}}{\overline{R}} &= -\left(y_{A2}\ln y_{A2} + y_{B2}\ln y_{B2}\right), && (3.153)\\
&= -\left(\ln y_{A2}^{y_{A2}} + \ln y_{B2}^{y_{B2}}\right), && (3.154)\\
&= -\ln\left(y_{A2}^{y_{A2}} y_{B2}^{y_{B2}}\right). && (3.155)
\end{aligned}$$

For an N-component mixture, mixed in the same fashion such that P and T are constant, this extends to

$$\begin{aligned}
\Delta S &= -\overline{R}\sum_{k=1}^{N} n_k \ln y_k, && (3.156)\\
&= -\overline{R}\sum_{k=1}^{N} n_k \underbrace{\ln\left(\frac{n_k}{\sum_{i=1}^{N} n_i}\right)}_{\leq 0} \geq 0, && (3.157)\\
&= -\overline{R}\sum_{k=1}^{N} \frac{n_k}{n} n \ln y_k, && (3.158)\\
&= -\overline{R}n\sum_{k=1}^{N} \frac{n_k}{n}\ln y_k, && (3.159)\\
&= -\overline{R}\frac{m}{M}\sum_{k=1}^{N} y_k \ln y_k, && (3.160)
\end{aligned}$$

$$= -Rm \sum_{k=1}^{N} \ln y_k^{y_k}, \tag{3.161}$$

$$= -Rm \left(\ln y_1^{y_1} + \ln y_2^{y_2} + \cdots + \ln y_N^{y_N} \right), \tag{3.162}$$

$$= -Rm \ln \left(y_1^{y_1} y_2^{y_2} \ldots y_N^{y_N} \right), \tag{3.163}$$

$$= -Rm \ln \left(\prod_{k=1}^{N} y_k^{y_k} \right), \tag{3.164}$$

Dividing by m to recover an intensive property and R to recover a dimensionless property, we get

$$\boxed{\frac{\Delta s}{R} = \frac{\Delta \overline{s}}{\overline{R}} = -\ln \left(\prod_{k=1}^{N} y_k^{y_k} \right).} \tag{3.165}$$

Note that there is a fundamental dependency of the mixing entropy on the mole fractions. Since $0 \leq y_k \leq 1$, the product is guaranteed to be between 0 and 1. The natural logarithm of such a number is negative, and thus the entropy change for the mixture is guaranteed positive semi-definite. Note also that for the entropy of mixing, Truesdell's third principle is not enforced.

Now if one mole of pure N_2 is mixed with one mole of pure O_2, one certainly expects the resulting homogeneous mixture to have a higher entropy than the two pure components. But what if one mole of pure N_2 is mixed with another mole of pure N_2. Then we would expect no increase in entropy. However, if we had the unusual ability to distinguish N_2 molecules whose origin was from each respective original chamber, then indeed there would be an entropy of mixing. Increases in entropy thus do correspond to increases in disorder.

3.3.1.3 Mixtures of constant mass fraction

If the mass fractions, and thus the mole fractions, remain constant during a process, the equations simplify. This is often the case for common non-reacting mixtures. Air at moderate values of temperature and pressure behaves this way. In this case, all of Truesdell's principles can be enforced. For a CPIG, one would have

$$u_2 - u_1 = c_A c_{vA}(T_2 - T_1) + c_B c_{vB}(T_2 - T_1), \tag{3.166}$$

$$= c_v(T_2 - T_1). \tag{3.167}$$

where

$$c_v \equiv c_A c_{vA} + c_B c_{vB}. \tag{3.168}$$

Similarly for enthalpy

$$h_2 - h_1 = c_A c_{PA}(T_2 - T_1) + c_B c_{PB}(T_2 - T_1), \tag{3.169}$$

$$= c_P(T_2 - T_1). \tag{3.170}$$

where

$$c_P \equiv c_A c_{PA} + c_B c_{PB}. \tag{3.171}$$

For the entropy

$$\begin{aligned} s_2 - s_1 &= c_A(s_{A2} - s_{A1}) + c_B(s_{B2} - s_{B1}), && (3.172)\\ &= c_A\left(c_{PA}\ln\left(\frac{T_2}{T_1}\right) - R_A\ln\left(\frac{y_A P_2}{y_A P_1}\right)\right) + c_B\left(c_{PB}\ln\left(\frac{T_2}{T_1}\right) - R_B\ln\left(\frac{y_B P_2}{y_B P_1}\right)\right), && (3.173)\\ &= c_A\left(c_{PA}\ln\left(\frac{T_2}{T_1}\right) - R_A\ln\left(\frac{P_2}{P_1}\right)\right) + c_B\left(c_{PB}\ln\left(\frac{T_2}{T_1}\right) - R_B\ln\left(\frac{P_2}{P_1}\right)\right), && (3.174)\\ &= c_P\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right). \end{aligned}$$

The mixture behaves as a pure substance when the appropriate mixture properties are defined. One can also take

$$\boxed{k = \frac{c_P}{c_v}.} \tag{3.175}$$

3.3.2 Summary of properties for the Dalton mixture model

Listed here is a summary of mixture properties for an N-component mixture of ideal gases on a mass basis:

$$\begin{aligned} M &= \sum_{i=1}^{N} y_i M_i, && (3.176)\\ \rho &= \sum_{i=1}^{N} \rho_i, && (3.177)\\ v &= \frac{1}{\sum_{i=1}^{N}\frac{1}{v_i}} = \frac{1}{\rho}, && (3.178)\\ u &= \sum_{i=1}^{N} c_i u_i, && (3.179)\\ h &= \sum_{i=1}^{N} c_i h_i, && (3.180)\\ R &= \frac{\overline{R}}{M} = \sum_{i=1}^{N} c_i R_i = \sum_{i=1}^{N} \frac{y_i \overbrace{M_i R_i}^{=\overline{R}}}{\underbrace{\sum_{j=1}^{N} y_j M_j}_{=M}} = \frac{\overline{R}}{M}\underbrace{\sum_{i=1}^{N} y_i}_{=1}, && (3.181) \end{aligned}$$

$$c_v = \sum_{i=1}^{N} c_i c_{vi}, \tag{3.182}$$

$$c_v = c_P - R, \qquad \text{if ideal gas}, \tag{3.183}$$

$$c_P = \sum_{i=1}^{N} c_i c_{Pi}, \tag{3.184}$$

$$k = \frac{c_P}{c_v}, \tag{3.185}$$

$$s = \sum_{i=1}^{N} c_i s_i, \tag{3.186}$$

$$c_i = \frac{y_i M_i}{M}, \tag{3.187}$$

$$P_i = y_i P, \tag{3.188}$$

$$\rho_i = c_i \rho, \tag{3.189}$$

$$v_i = \frac{v}{c_i} = \frac{1}{\rho_i}, \tag{3.190}$$

$$V = V_i, \tag{3.191}$$

$$T = T_i, \tag{3.192}$$

$$h_i = h_i^o, \qquad \text{if ideal gas}, \tag{3.193}$$

$$h_i = u_i + \frac{P_i}{\rho_i} = u_i + P_i v_i = \underbrace{u_i + R_i T}_{\text{if ideal gas}}, \tag{3.194}$$

$$h_i = \underbrace{h_{298,i}^o + \int_{298}^{T} c_{Pi}(\hat{T})\, d\hat{T}}_{\text{if ideal gas}}, \tag{3.195}$$

$$s_i = \underbrace{\underbrace{s_{298,i}^o + \int_{298}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T}}_{=s_{T,i}^o} - R_i \ln\left(\frac{P_i}{P_o}\right)}_{\text{if ideal gas}}, \tag{3.196}$$

$$s_i = \underbrace{s_{T,i}^o - R_i \ln\left(\frac{y_i P}{P_o}\right)}_{\text{if ideal gas}} = \underbrace{s_{T,i}^o - R_i \ln\left(\frac{P_i}{P_o}\right)}_{\text{if ideal gas}}, \tag{3.197}$$

$$P_i = \underbrace{\rho_i R_i T = \rho R_i T c_i = \frac{R_i T}{v_i}}_{\text{if ideal gas}}, \tag{3.198}$$

$$P = \underbrace{\rho RT = \rho\overline{R}T\sum_{i=1}^{N}\frac{c_i}{M_i} = \frac{RT}{v}}_{\text{if ideal gas}}, \tag{3.199}$$

$$h = \underbrace{\sum_{i=1}^{N} c_i h^o_{298,i} + \int_{298}^{T} c_P(\hat{T})\, d\hat{T}}_{\text{if ideal gas}}, \tag{3.200}$$

$$h = u + \frac{P}{\rho} = u + Pv = \underbrace{u + RT}_{\text{if ideal gas}}, \tag{3.201}$$

$$s = \underbrace{\sum_{i=1}^{N} c_i s^o_{298,i} + \int_{298}^{T} \frac{c_P(\hat{T})}{\hat{T}}\, d\hat{T} - R\ln\left(\frac{P}{P_o}\right) - R\ln\left(\prod_{i=1}^{N} y_i^{y_i}\right)}_{\text{if ideal gas}}. \tag{3.202}$$

These relations are not obvious. A few are derived in examples here.

Example 3.4

Derive the expression $h = u + P/\rho$.

Start from the equation for the constituent h_i, multiply by mass fractions, sum over all species, and use properties of mixtures:

$$h_i = u_i + \frac{P_i}{\rho_i}, \tag{3.203}$$

$$c_i h_i = c_i u_i + c_i \frac{P_i}{\rho_i}, \tag{3.204}$$

$$\sum_{i=1}^{N} c_i h_i = \sum_{i=1}^{N} c_i u_i + \sum_{i=1}^{N} c_i \frac{P_i}{\rho_i}, \tag{3.205}$$

$$\underbrace{\sum_{i=1}^{N} c_i h_i}_{=h} = \underbrace{\sum_{i=1}^{N} c_i u_i}_{=u} + \sum_{i=1}^{N} c_i \frac{\rho_i R_i T}{\rho_i}, \tag{3.206}$$

$$h = u + T\underbrace{\sum_{i=1}^{N} c_i R_i}_{=R}, \tag{3.207}$$

$$= u + RT, \tag{3.208}$$

$$= \boxed{u + \frac{P}{\rho}.} \tag{3.209}$$

Example 3.5

Find the expression for mixture entropy of the ideal gas.

$$s_i = s^o_{298,i} + \int_{298}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T} - R_i \ln\left(\frac{P_i}{P_o}\right), \tag{3.210}$$

$$c_i s_i = c_i s^o_{298,i} + c_i \int_{298}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T} - c_i R_i \ln\left(\frac{P_i}{P_o}\right), \tag{3.211}$$

$$s = \sum_{i=1}^{N} c_i s_i = \sum_{i=1}^{N} c_i s^o_{298,i} + \sum_{i=1}^{N} c_i \int_{298}^{T} \frac{c_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T} - \sum_{i=1}^{N} c_i R_i \ln\left(\frac{P_i}{P_o}\right), \tag{3.212}$$

$$= \sum_{i=1}^{N} c_i s^o_{298,i} + \int_{298}^{T} \sum_{i=1}^{N} \frac{c_i c_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T} - \sum_{i=1}^{N} c_i R_i \ln\left(\frac{P_i}{P_o}\right), \tag{3.213}$$

$$= s^o_{298} + \int_{298}^{T} \frac{c_P(\hat{T})}{\hat{T}}\, d\hat{T} - \sum_{i=1}^{N} c_i R_i \ln\left(\frac{P_i}{P_o}\right). \tag{3.214}$$

All except the last term are natural extensions of the property for a single material. Consider now the last term involving pressure ratios.

$$-\sum_{i=1}^{N} c_i R_i \ln\left(\frac{P_i}{P_o}\right) = -\left(\sum_{i=1}^{N} c_i R_i \ln\left(\frac{P_i}{P_o}\right) + R\ln\frac{P}{P_o} - R\ln\frac{P}{P_o}\right), \tag{3.215}$$

$$= -R\left(\sum_{i=1}^{N} c_i \frac{R_i}{R} \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{3.216}$$

$$= -R\left(\sum_{i=1}^{N} c_i \frac{\overline{R}/M_i}{\sum_{j=1}^{N} c_j \overline{R}/M_j} \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{3.217}$$

$$= -R\left(\sum_{i=1}^{N} \underbrace{\left(\frac{c_i/M_i}{\sum_{j=1}^{N} c_j/M_j}\right)}_{=y_i} \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{3.218}$$

$$= -R\left(\sum_{i=1}^{N} y_i \ln\left(\frac{P_i}{P_o}\right) + \ln\frac{P}{P_o} - \ln\frac{P}{P_o}\right), \tag{3.219}$$

$$= -R\left(\sum_{i=1}^{N} \ln\left(\frac{P_i}{P_o}\right)^{y_i} - \ln\frac{P}{P_o} + \ln\frac{P}{P_o}\right), \tag{3.220}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{y_i}\right) + \ln\frac{P_o}{P} + \ln\frac{P}{P_o}\right), \tag{3.221}$$

$$= -R\left(\ln\left(\frac{P_o}{P}\prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{3.222}$$

$$= -R\left(\ln\left(\frac{P_o}{P^{\sum_{i=1}^{N} y_i}} \frac{1}{P_o^{\sum_{i=1}^{N} y_i}} \prod_{i=1}^{N} (P_i)^{y_i}\right) + \ln\frac{P}{P_o}\right), \tag{3.223}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}\left(\frac{P_i}{P}\right)^{y_i}\right)+\ln\frac{P}{P_o}\right), \tag{3.224}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}\left(\frac{y_iP}{P}\right)^{y_i}\right)+\ln\frac{P}{P_o}\right), \tag{3.225}$$

$$= -R\left(\ln\left(\prod_{i=1}^{N}y_i^{y_i}\right)+\ln\frac{P}{P_o}\right). \tag{3.226}$$

So the mixture entropy becomes

$$s = s^o_{298}+\int_{298}^{T}\frac{c_P(\hat{T})}{\hat{T}}\,d\hat{T}-R\left(\ln\left(\prod_{i=1}^{N}y_i^{y_i}\right)+\ln\frac{P}{P_o}\right), \tag{3.227}$$

$$= \boxed{\underbrace{s^o_{298}+\int_{298}^{T}\frac{c_P(\hat{T})}{\hat{T}}\,d\hat{T}-R\ln\frac{P}{P_o}}_{\text{classical entropy of a single body}}\underbrace{-R\ln\left(\prod_{i=1}^{N}y_i^{y_i}\right)}_{\text{non-Truesdellian}}}. \tag{3.228}$$

The extra entropy is not found in the theory for a single material, and in fact is not in the form suggested by Truesdell's postulates. While it is in fact possible to redefine the constituent entropy definition in such a fashion that the mixture entropy in fact takes on the classical form of a single material via the definition $s_i = s^o_{298,i}+\int_{298}^{T}\frac{c_{Pi}(\hat{T})}{\hat{T}}\,d\hat{T}-R_i\ln\left(\frac{P_i}{P_o}\right)+R_i\ln y_i$, this has the disadvantage of predicting *no entropy change* after mixing two pure substances. Such a theory would suggest that this obviously irreversible process is in fact reversible.

On a molar basis, one has the equivalents

$$\overline{\rho} = \sum_{i=1}^{N}\overline{\rho}_i=\frac{n}{V}=\frac{\rho}{M}, \tag{3.229}$$

$$\overline{v} = \frac{1}{\sum_{i=1}^{N}\frac{1}{\overline{v}_i}}=\frac{V}{n}=\frac{1}{\overline{\rho}}=vM, \tag{3.230}$$

$$\overline{u} = \sum_{i=1}^{N}y_i\overline{u}_i=uM, \tag{3.231}$$

$$\overline{h} = \sum_{i=1}^{N}y_i\overline{h}_i=hM, \tag{3.232}$$

$$\overline{c}_v = \sum_{i=1}^{N}y_i\overline{c}_{vi}=c_vM, \tag{3.233}$$

$$\overline{c}_v = \overline{c}_P-\overline{R}, \tag{3.234}$$

$$\overline{c}_P = \sum_{i=1}^{N}y_i\overline{c}_{Pi}=c_PM, \tag{3.235}$$

$$k = \frac{\overline{c}_P}{\overline{c}_v}, \tag{3.236}$$

$$\overline{s} = \sum_{i=1}^{N} y_i \overline{s}_i = sM, \tag{3.237}$$

$$\overline{\rho}_i = y_i \overline{\rho} = \frac{\rho_i}{M_i}, \tag{3.238}$$

$$\overline{v}_i = \frac{V}{n_i} = \frac{\overline{v}}{y_i} = \frac{1}{\overline{\rho}_i} = v_i M_i, \tag{3.239}$$

$$\overline{\mathrm{v}}_i = \left.\frac{\partial V}{\partial n_i}\right|_{P,T,n_j} = \underbrace{\frac{V}{n} = \overline{v} = vM}_{\text{if ideal gas}}, \tag{3.240}$$

$$P_i = y_i P, \tag{3.241}$$

$$P = \underbrace{\overline{\rho}\overline{R}T = \frac{\overline{R}T}{\overline{v}}}_{\text{if ideal gas}}, \tag{3.242}$$

$$P_i = \underbrace{\overline{\rho}_i\overline{R}T = \frac{\overline{R}T}{\overline{v}_i}}_{\text{if ideal gas}}, \tag{3.243}$$

$$\overline{h} = \overline{u} + \frac{P}{\overline{\rho}} = \overline{u} + P\overline{v} = \underbrace{\overline{u} + \overline{R}T}_{\text{if ideal gas}} = hM, \tag{3.244}$$

$$\overline{h}_i = \overline{h}_i^o, \qquad \text{if ideal gas}, \tag{3.245}$$

$$\overline{h}_i = \overline{u}_i + \frac{P_i}{\overline{\rho}_i} = \overline{u}_i + P_i\overline{v}_i = \overline{u}_i + P\overline{\mathrm{v}}_i = \underbrace{\overline{u}_i + \overline{R}T}_{\text{if ideal gas}} = h_i M_i, \tag{3.246}$$

$$\overline{h}_i = \underbrace{\overline{h}_{298,i}^o + \int_{298}^{T} \overline{c}_{Pi}(\hat{T})\, d\hat{T}}_{\text{if ideal gas}} = h_i M_i, \tag{3.247}$$

$$\overline{s}_i = \underbrace{\underbrace{\overline{s}_{298,i}^o + \int_{298}^{T} \frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}}\, d\hat{T}}_{=\overline{s}_{T,i}^o} - \overline{R}\ln\left(\frac{y_i P}{P_o}\right)}_{\text{if ideal gas}}, \tag{3.248}$$

$$\overline{s}_i = \underbrace{\overline{s}_{T,i}^o - \overline{R}\ln\left(\frac{y_i P}{P_o}\right)}_{\text{if ideal gas}} = s_i M_i, \tag{3.249}$$

$$\overline{s} = \underbrace{\sum_{i=1}^{N} y_i \overline{s}_{298,i}^o + \int_{298}^{T} \frac{\overline{c}_P(\hat{T})}{\hat{T}}\, d\hat{T} - \overline{R}\ln\left(\frac{P}{P_o}\right) - \overline{R}\ln\left(\prod_{i=1}^{N} y_i^{y_i}\right)}_{\text{if ideal gas}} = sM. \tag{3.250}$$

3.3.3 Amagat model

The Amagat model is an entirely different paradigm than the Dalton model. It is not used as often. In the Amagat model,

- all components share a common temperature T,
- all components share a common pressure P, and
- each component has a different volume.

Consider, for example, a binary mixture of calorically perfect ideal gases, A and B. For the mixture, one has

$$PV = n\overline{R}T, \tag{3.251}$$

with

$$n = n_A + n_B. \tag{3.252}$$

For the components one has

$$PV_A = n_A\overline{R}T, \tag{3.253}$$
$$PV_B = n_B\overline{R}T. \tag{3.254}$$

Then $n = n_A + n_B$ reduces to

$$\frac{PV}{\overline{R}T} = \frac{PV_A}{\overline{R}T} + \frac{PV_B}{\overline{R}T}. \tag{3.255}$$

Thus

$$V = V_A + V_B, \tag{3.256}$$
$$1 = \frac{V_A}{V} + \frac{V_B}{V}. \tag{3.257}$$

3.4 Gas-vapor mixtures

Next consider a mixture of ideal gases in which one of the components may undergo a phase transition to its liquid state. The most important practical example is an air-water mixture. Assume the following:

- The solid or liquid contains no dissolved gases.
- The gaseous phases are all well modeled as ideal gases.
- When the gas mixture and the condensed phase are at a given total pressure and temperature, the equilibrium between the condensed phase and its vapor is not influenced by the other component. So for a binary mixture of A and B where A could have both gas and liquid components $P_A = P_{sat}$. That is the partial pressure of A is equal to its saturation pressure at the appropriate temperature.

Considering an air water vapor mixture, one models the water vapor as an ideal gas and expresses the total pressure as

$$P = P_a + P_v. \tag{3.258}$$

Here v denotes vapor and a denotes air. A good model for the enthalpy of the water vapor is to take

$$h_v(T, \text{low}P) = h_g(T). \tag{3.259}$$

If T is given in degrees Celsius, a good model from the steam tables is

$$h_g(T) = 2501.3 \ \frac{kJ}{kg} + \left(1.82 \ \frac{kJ}{kg \ ^\circ C}\right) T. \tag{3.260}$$

Some definitions:

- *absolute humidity*: ω, the mass of water present in a unit mass of dry air, also called humidity ratio,

$$\begin{aligned}
\omega &\equiv \boxed{\frac{m_v}{m_a}}, && (3.261)\\
&= \frac{M_v n_v}{M_a n_a}, && (3.262)\\
&= \frac{M_v \frac{P_v V}{\bar{R}T}}{M_a \frac{P_a V}{\bar{R}T}}, && (3.263)\\
&= \frac{M_v P_v}{M_a P_a}, && (3.264)\\
&= \frac{\left(18.015 \ \frac{kg}{kmole}\right) P_v}{\left(28.97 \ \frac{kg}{kmole}\right) P_a}, && (3.265)\\
&= 0.622 \frac{P_v}{P_a}, && (3.266)\\
&= \boxed{0.622 \frac{P_v}{P - P_v}.} && (3.267)
\end{aligned}$$

- *dew point*: temperature at which the vapor condenses when it is cooled isobarically.

- *saturated air*: The vapor in the air-vapor mixture is at the saturation temperature and pressure.

- *relative humidity*: The ratio of the mole fraction of the vapor in the mixture to the mole fraction of vapor in a saturated mixture at the same temperature and *total* pressure:

$$\phi \equiv \frac{\frac{n_v}{n}}{\frac{n_g}{n}}, \tag{3.268}$$

$$= \frac{n_v}{n_g}, \tag{3.269}$$

$$= \frac{\frac{P_v V}{\overline{R}T}}{\frac{P_g V}{\overline{R}T}}, \tag{3.270}$$

$$= \boxed{\frac{P_v}{P_g}.} \tag{3.271}$$

Note, here the subscript g denotes saturated gas values. Combining, one can relate the relative humidity to the absolute humidity:

$$\phi = \frac{\omega P_a}{0.622 P_g}. \tag{3.272}$$

Example 3.6

(from Çengal and Boles, p. 670) A 5 $m \times 5\ m \times 3\ m$ room contains air at 25 $°C$ and 100 kPa at a relative humidity of 75%. Find the

- partial pressure of dry air,
- absolute humidity (i.e. humidity ratio),
- masses of dry air and water vapor in the room, and the
- dew point.

The relation between partial and total pressure is

$$P = P_a + P_v. \tag{3.273}$$

Now from the definition of relative humidity,

$$P_v = \phi P_g. \tag{3.274}$$

Here P_g is the saturation pressure at the same temperature, which is 25 $°C$. At 25 $°C$, the tables give

$$P_g|_{25\ ^\circ C} = 3.169\ kPa. \tag{3.275}$$

So

$$P_v = 0.75(3.169\ kPa) = 2.3675\ kPa. \tag{3.276}$$

So from the definition of partial pressure

$$P_a = P - P_v, \tag{3.277}$$

$$= 100\ kPa - 2.3675\ kPa, \tag{3.278}$$

$$= \boxed{97.62\ kPa.} \tag{3.279}$$

Now for the absolute humidity (or specific humidity), one has

$$\begin{aligned} \omega &= 0.622\frac{P_v}{P_a}, && (3.280)\\ &= 0.622\frac{2.3675\ kPa}{97.62\ kPa}, && (3.281)\\ &= \boxed{0.0152\ \frac{kg\ H_2O}{kg\ dry\ air}.} && (3.282) \end{aligned}$$

Now for the masses of air and water, one can use the partial pressures:

$$\begin{aligned} m_a &= \frac{P_a V}{\overline{R}T}M_a, && (3.283)\\ &= \frac{P_a V}{R_a T}, && (3.284)\\ &= \frac{(97.62\ kPa)\left(75\ m^3\right)}{\left(\frac{8.314\ \frac{kJ}{kmole\ K}}{28.97\ \frac{kg}{kmole}}\right)(298\ K)}, && (3.285)\\ &= \boxed{85.61\ kg.} && (3.286)\\ m_v &= \frac{P_v V}{\overline{R}T}M_v, && (3.287)\\ &= \frac{P_v V}{R_v T}, && (3.288)\\ &= \frac{(2.3675\ kPa)\left(75\ m^3\right)}{\left(\frac{8.314\ \frac{kJ}{kmole\ K}}{18.015\ \frac{kg}{kmole}}\right)(298\ K)}, && (3.289)\\ &= \boxed{1.3\ kg.} && (3.290) \end{aligned}$$

Also one could get m_v from

$$\begin{aligned} m_v &= \omega m_a, && (3.291)\\ &= (0.0152)(85.61\ kg), && (3.292)\\ &= 1.3\ kg. && (3.293) \end{aligned}$$

Now the dew point is the saturation temperature at the partial pressure of the water vapor. With $P_v = 2.3675\ kPa$, the saturation tables give

$$T_{dew\ point} = \boxed{20.08\ ^\circ C.} \quad (3.294)$$

3.4.1 First law

The first law can be applied to air-water mixtures.

Example 3.7

(BS, Ex. 13.5, pp. 536-537.) An air-water vapor mixture enters the cooling coils of an air conditioner unit. The inlet is at $P_1 = 105\ kPa$, $T_1 = 30\ ^\circ C$, $\phi_1 = 0.80$. The exit state is $P_2 = 100\ kPa$, $T_2 = 15\ ^\circ C$, $\phi_2 = 0.95$. Liquid water at $15\ ^\circ C$ also exits the system. Find the heat transfer per kilogram of dry air.

Mass conservation for air and water give

$$\dot{m}_{a1} = \dot{m}_{a2} \equiv \dot{m}_a, \tag{3.295}$$
$$\dot{m}_{v1} = \dot{m}_{v2} + \dot{m}_{l2}. \tag{3.296}$$

Note at state 2, the mass flow of water is in both liquid and vapor form.

The first law for the control volume give

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \dot{Q}_{cv} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1} - \dot{m}_a h_{a2} - \dot{m}_{v2} h_{v2} - \dot{m}_{l2} h_{l2}, \tag{3.297}$$
$$\dot{Q}_{cv} + \dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1} = \dot{m}_a h_{a2} + \dot{m}_{v2} h_{v2} + (\dot{m}_{v1} - \dot{m}_{v2}) h_{l2}, \tag{3.298}$$
$$\frac{\dot{Q}_{cv}}{\dot{m}_a} + h_{a1} + \frac{\dot{m}_{v1}}{\dot{m}_a} h_{v1} = h_{a2} + \frac{\dot{m}_{v2}}{\dot{m}_a} h_{v2} + \frac{\dot{m}_{v1} - \dot{m}_{v2}}{\dot{m}_a} h_{l2}, \tag{3.299}$$
$$\frac{\dot{Q}_{cv}}{\dot{m}_a} + h_{a1} + \omega_1 h_{v1} = h_{a2} + \omega_2 h_{v2} + (\omega_1 - \omega_2) h_{l2}, \tag{3.300}$$
$$\frac{\dot{Q}_{cv}}{\dot{m}_a} = h_{a2} - h_{a1} - \omega_1 h_{v1} + \omega_2 h_{v2} + (\omega_1 - \omega_2) h_{l2}, \tag{3.301}$$
$$= c_{pa}(T_2 - T_1) - \omega_1 h_{v1} + \omega_2 h_{v2} + (\omega_1 - \omega_2) h_{l2}. \tag{3.302}$$

Now at the inlet, one has from the definition of relative humidity

$$\phi_1 = \frac{P_{v1}}{P_{g1}}. \tag{3.303}$$

Here P_g is the saturated vapor pressure at the inlet temperature, $T_1 = 30\ ^\circ C$. This is $P_{g1} = 4.246\ kPa$. So one gets

$$P_{v1} = \phi_1 P_{g1}, \tag{3.304}$$
$$= (0.80)(4.246\ kPa), \tag{3.305}$$
$$= 3.397\ kPa. \tag{3.306}$$

Now the absolute humidity (humidity ratio) is

$$\omega_1 = 0.622 \frac{P_{v1}}{P_1 - P_{v1}}, \tag{3.307}$$
$$= 0.622 \frac{3.397\ kPa}{105\ kPa - 3.397\ kPa}, \tag{3.308}$$
$$= 0.0208. \tag{3.309}$$

At the exit temperature, the saturation pressure is $P_{g2} = 1.705\ kPa$. So

$$P_{v2} = \phi_2 P_{g2}, \tag{3.310}$$
$$= (0.95)(1.705\ kPa), \tag{3.311}$$
$$= 1.620\ kPa. \tag{3.312}$$

Now the absolute humidity (humidity ratio) is

$$\omega_2 = 0.622\frac{P_{v2}}{P_2 - P_{v2}}, \tag{3.313}$$

$$= 0.622\frac{1.620\ kPa}{100\ kPa - 1.620\ kPa}, \tag{3.314}$$

$$= 0.0102. \tag{3.315}$$

Then, substituting, one gets

$$\frac{\dot{Q}_{cv}}{\dot{m}_a} = \left(1.004\ \frac{kJ}{kg\ K}\right)(15\ ^\circ C - 30\ ^\circ C) - 0.0208\left(2556.3\ \frac{kJ}{kg}\right) + 0.0102\left(2528.9\ \frac{kJ}{kg}\right) + (0.0208 - 0.0102)\left(62.99\ \frac{kJ}{kg}\right), \tag{3.316}$$

$$= \boxed{-41.77\ \frac{kJ}{kg\ dry\ air}}. \tag{3.317}$$

3.4.2 Adiabatic saturation

In an adiabatic saturation process, an air-vapor mixture contacts a body of water in a well insulated duct. If the initial humidity of the mixture is less than 100%, some water will evaporate and join the mixture.

If the mixture leaving the duct is saturated, and the process is adiabatic, the exit temperature is the adiabatic saturation temperature. Assume the liquid water entering the system enters at the exit temperature of the mixture.

Mass conservation for air and water and the first law for the control volume give

$$\underbrace{\frac{dm_{cv}^{air}}{dt}}_{=0} = \dot{m}_{a1} - \dot{m}_{a2}, \qquad \text{air} \tag{3.318}$$

$$\underbrace{\frac{dm_{cv}^{water}}{dt}}_{=0} = \dot{m}_{v1} + \dot{m}_l - \dot{m}_{v2}, \qquad \text{water} \tag{3.319}$$

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \underbrace{\dot{Q}_{cv}}_{=0} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}_{a1}h_{a1} + \dot{m}_{v1}h_{v1} + \dot{m}_l h_l - \dot{m}_{a2}h_{a2} - \dot{m}_{v2}h_{v2}. \tag{3.320}$$

For steady state results, these reduce to

$$0 = \dot{m}_{a1} - \dot{m}_{a2}, \qquad \text{air} \tag{3.321}$$

$$0 = \dot{m}_{v1} + \dot{m}_l - \dot{m}_{v2}, \qquad \text{water} \tag{3.322}$$

$$0 = \dot{m}_{a1}h_{a1} + \dot{m}_{v1}h_{v1} + \dot{m}_l h_l - \dot{m}_{a2}h_{a2} - \dot{m}_{v2}h_{v2}. \tag{3.323}$$

Now mass conservation for air gives

$$\dot{m}_{a1} = \dot{m}_{a2} \equiv \dot{m}_a. \tag{3.324}$$

Mass conservation for water gives

$$\dot{m}_l = \dot{m}_{v2} - \dot{m}_{v1}. \tag{3.325}$$

Then energy conservation becomes

$$\begin{aligned}
0 &= \dot{m}_a h_{a1} + \dot{m}_{v1} h_{v1} + (\dot{m}_{v2} - \dot{m}_{v1}) h_l - \dot{m}_a h_{a2} - \dot{m}_{v2} h_{v2}, && (3.326)\\
0 &= h_{a1} + \frac{\dot{m}_{v1}}{\dot{m}_a} h_{v1} + \left(\frac{\dot{m}_{v2}}{\dot{m}_a} - \frac{\dot{m}_{v1}}{\dot{m}_a} \right) h_l - h_{a2} - \frac{\dot{m}_{v2}}{\dot{m}_a} h_{v2}, && (3.327)\\
0 &= h_{a1} + \omega_1 h_{v1} + (\omega_2 - \omega_1)\, h_l - h_{a2} - \omega_2 h_{v2}, && (3.328)\\
0 &= h_{a1} - h_{a2} + \omega_1 (h_{v1} - h_l) + \omega_2 (h_l - h_{v2}), && (3.329)\\
-\omega_1 (h_{v1} - h_l) &= h_{a1} - h_{a2} + \omega_2 (h_l - h_{v2}), && (3.330)\\
\omega_1 (h_{v1} - h_l) &= h_{a2} - h_{a1} + \omega_2 (h_{v2} - h_l), && (3.331)\\
\omega_1 (h_{v1} - h_l) &= c_{pa} (T_2 - T_1) + \omega_2 h_{fg2}. && (3.332)
\end{aligned}$$

Example 3.8

(BS, 13.7E, p. 540). The pressure of the mixture entering and leaving the adiabatic saturater is 14.7 $psia$, the entering temperature is 84 F, and the temperature leaving is 70 F, which is the adiabatic saturation temperature. Calculate the humidity ratio and the relative humidity of the air-water vapor mixture entering.

The exit state 2 is saturated, so

$$P_{v2} = P_{g2}. \tag{3.333}$$

The tables give $P_{v2} = P_{g2} = 0.363\ psia$. Thus one can calculate the absolute humidity by its definition:

$$\begin{aligned}
\omega_2 &= 0.622 \frac{P_{v2}}{P_2 - P_{v2}}, && (3.334)\\
&= 0.622 \frac{0.363\ psia}{(14.7\ psia) - (0.363\ psia)}, && (3.335)\\
&= 0.0157485\ \frac{lbm\ H_2O}{lbm\ dry\ air}. && (3.336)
\end{aligned}$$

The earlier derived result from the energy balance allows calculation then of ω_1:

$$\begin{aligned}
\omega_1 (h_{v1} - h_l) &= c_{pa} (T_2 - T_1) + \omega_2 h_{fg2}, && (3.337)\\
\omega_1 &= \frac{c_{pa} (T_2 - T_1) + \omega_2 h_{fg2}}{h_{v1} - h_l}, && (3.338)\\
&= \frac{0.240\ \frac{Btu}{lbm\ F} ((70\ F) - (84\ F)) + 0.0157485 \left(1054.0\ \frac{Btu}{lbm}\right)}{\left(1098.1\ \frac{Btu}{lbm}\right) - \left(38.1\ \frac{Btu}{lbm}\right)}, && (3.339)\\
&= \boxed{0.012895\ \frac{lbm\ H_2O}{lbm\ dry\ air}.} && (3.340)
\end{aligned}$$

Here h_{v1} was estimated as the saturated vapor value at $T = 84\ F$ by interpolating the tables. In the absence of more information regarding the initial vapor state, this estimate is good as any. The value of h_l is estimated as the saturated liquid value at $T = 70\ F$. Now

$$\omega_1 = 0.622\frac{P_{v1}}{P_1 - P_{v1}}, \tag{3.341}$$

$$P_{v1} = \frac{P_1\omega_1}{0.622 + \omega_1}, \tag{3.342}$$

$$= \frac{(14.7\ psia)(0.0124895)}{0.622 + 0.0124895}, \tag{3.343}$$

$$= 0.28936\ psia. \tag{3.344}$$

For the relative humidity

$$\phi_1 = \frac{P_{v1}}{P_{g1}}, \tag{3.345}$$

$$= \frac{0.28936\ psia}{0.584\ psia}, \tag{3.346}$$

$$= \boxed{0.495.} \tag{3.347}$$

3.4.3 Wet-bulb and dry-bulb temperatures

Humidity is often measured with a *psychrometer*, which has a *wet bulb* and *dry bulb* thermometer.

- The dry bulb measures the air temperature.
- The wet bulb measures the temperature of a water soaked thermometer.
- If the two temperatures are equal, the air is saturated. If they are different, some of the water on the web bulb evaporates, cooling the wet bulb thermometer.
- The evaporative cooling process is commonly modeled (with some error) as an adiabatic saturation process.
- These temperatures are also influenced by non-thermodynamic issues such as heat and mass transfer rates, which induce errors in the device.
- Capacitance-based electronic devices are often used as an alternative to the traditional psychrometer.

3.4.4 Psychrometric chart

This well-known chart summarizes much of what is important for binary mixtures of air and water, in which the properties depend on *three* variables, e.g. temperature, pressure, and composition of the mixture.

Chapter 4

Mathematical foundations of thermodynamics

Read BS, 12.2-12.4, 12.9, 14.1-14.4.
Read Abbott and van Ness, Chapter 3.
See Vincenti and Kruger, Chapter 3, for more background.

4.1 Exact differentials and state functions

In thermodynamics, one is faced with many systems of the form of the well-known Gibbs equation, Eq. (1.1):

$$\boxed{du = Tds - Pdv.} \tag{4.1}$$

This is known to be an exact differential with the consequence that internal energy u is a function of the state of the system and not the details of any process which led to the state. As a counter-example, the work,

$$\boxed{\delta w = Pdv,} \tag{4.2}$$

can be shown to be an inexact differential so that the work is indeed a function of the process involved. Here we use the notation δ to emphasize that this is an inexact differential.

Example 4.1

Show the work is not a state function. *If* work were a state function, one might expect it to have the form

$$w = w(P, v), \qquad \textit{provisional assumption, to be tested.} \tag{4.3}$$

In such a case, one would have the corresponding differential form

$$\delta w = \left.\frac{\partial w}{\partial v}\right|_P dv + \left.\frac{\partial w}{\partial P}\right|_v dP. \tag{4.4}$$

Now since $\delta w = Pdv$ from Newtonian mechanics, one deduces that

$$\left.\frac{\partial w}{\partial v}\right|_P = P, \tag{4.5}$$

$$\left.\frac{\partial w}{\partial P}\right|_v = 0. \tag{4.6}$$

Integrating Eq. (4.5), one finds

$$w = Pv + f(P), \tag{4.7}$$

where $f(P)$ is some function of P to be determined. Differentiating Eq. (4.7) with respect to P, one gets

$$\left.\frac{\partial w}{\partial P}\right|_v = v + \frac{df(P)}{dP}. \tag{4.8}$$

Now use Eq. (4.6) to eliminate $\partial w/\partial P|_v$ in Eq. (4.8) so as to obtain

$$0 = v + \frac{df(P)}{dP}, \tag{4.9}$$

$$\frac{df(P)}{dP} = -v. \tag{4.10}$$

Equation (4.10) cannot be: a function of P only cannot be a function of v. So, w cannot be a state property:

$$\boxed{w \neq w(P, v).} \tag{4.11}$$

Consider now the more general form

$$\psi_1 dx_1 + \psi_2 dx_2 + \cdots + \psi_N dx_N = \sum_{i=1}^{N} \psi_i dx_i. \tag{4.12}$$

Here ψ_i and x_i, $i = 1, \ldots, N$, may be thermodynamic variables. This form is known in mathematics as a *Pfaff differential form*. As formulated, one takes at this stage

- x_i: independent thermodynamic variables, and
- ψ_i: thermodynamic variables which are functions of x_i.

Now, if the differential in Eq. (4.12), when set to a differential dy, can be integrated to form the function

$$y = y(x_1, x_2, \ldots, x_N), \tag{4.13}$$

the differential is said to be *exact*. In such a case, one has

$$dy = \psi_1 dx_1 + \psi_2 dx_2 + \cdots + \psi_N dx_N = \sum_{i=1}^{N} \psi_i dx_i. \tag{4.14}$$

Now, if the algebraic definition of Eq. (4.13) holds, what amounts to the definition of the partial derivative gives the parallel result that

$$dy = \left.\frac{\partial y}{\partial x_1}\right|_{x_j, j\neq 1} dx_1 + \left.\frac{\partial y}{\partial x_2}\right|_{x_j, j\neq 2} dx_2 + \cdots + \left.\frac{\partial y}{\partial x_N}\right|_{x_j, j\neq N} dx_N. \tag{4.15}$$

Now, combining Eqs. (4.14) and (4.15) to eliminate dy, one gets

$$\psi_1 dx_1 + \psi_2 dx_2 + \cdots + \psi_N dx_N = \left.\frac{\partial y}{\partial x_1}\right|_{x_j, j\neq 1} dx_1 + \left.\frac{\partial y}{\partial x_2}\right|_{x_j, j\neq 2} dx_2 + \cdots + \left.\frac{\partial y}{\partial x_N}\right|_{x_j, j\neq N} dx_N. \tag{4.16}$$

Rearranging, one gets

$$0 = \left(\left.\frac{\partial y}{\partial x_1}\right|_{x_j, j\neq 1} - \psi_1\right) dx_1 + \left(\left.\frac{\partial y}{\partial x_2}\right|_{x_j, j\neq 2} - \psi_2\right) dx_2 + \cdots + \left(\left.\frac{\partial y}{\partial x_N}\right|_{x_j, j\neq N} - \psi_N\right) dx_N. \tag{4.17}$$

Since the variables x_i, $i = 1, \ldots, N$, are independent, dx_i, $i = 1, \ldots, N$, are all independent in Eq. (4.17), and in general non-zero. For equality, one must require that *each* of the coefficients be zero, so

$$\boxed{\psi_1 = \left.\frac{\partial y}{\partial x_1}\right|_{x_j, j\neq 1}, \quad \psi_2 = \left.\frac{\partial y}{\partial x_2}\right|_{x_j, j\neq 2}, \ldots, \quad \psi_N = \left.\frac{\partial y}{\partial x_N}\right|_{x_j, j\neq N}.} \tag{4.18}$$

So when dy is exact, one says that each of the ψ_i and x_i are *conjugate* to each other.

From here on out, for notational ease, the $j \neq 1, j \neq 2, \ldots, j \neq N$ will be ignored in the notation for the partial derivatives. It becomes especially confusing for higher order derivatives, and is fairly obvious for all derivatives.

If y and all its derivatives are continuous and differentiable, then one has for all $i = 1, \ldots, N$, and $k = 1, \ldots, N$ that

$$\frac{\partial^2 y}{\partial x_k \partial x_i} = \frac{\partial^2 y}{\partial x_i \partial x_k}. \tag{4.19}$$

Now from Eq. (4.18), one has

$$\psi_k = \left.\frac{\partial y}{\partial x_k}\right|_{x_j}, \qquad \psi_l = \left.\frac{\partial y}{\partial x_l}\right|_{x_j}. \tag{4.20}$$

Taking the partial of the first of Eq. (4.20) with respect to x_l and the second with respect to x_k, one gets

$$\left.\frac{\partial \psi_k}{\partial x_l}\right|_{x_j} = \frac{\partial^2 y}{\partial x_l \partial x_k}, \qquad \left.\frac{\partial \psi_l}{\partial x_k}\right|_{x_j} = \frac{\partial^2 y}{\partial x_k \partial x_l}. \tag{4.21}$$

Since by Eq. (4.19) the order of the mixed second partials does not matter, one deduces from Eq. (4.21) that

$$\boxed{\left.\frac{\partial \psi_k}{\partial x_l}\right|_{x_j} = \left.\frac{\partial \psi_l}{\partial x_k}\right|_{x_j}.} \tag{4.22}$$

This is a necessary and sufficient condition for the exact-ness of Eq. (4.12). It is a generalization of what can be found in most introductory calculus texts for functions of two variables.

For the Gibbs equation, (4.1), $du = -Pdv + Tds$, one has

$$y \to u, \quad x_1 \to v, \quad x_2 \to s, \quad \psi_1 \to -P \quad \psi_2 \to T. \tag{4.23}$$

and one expects the natural, or *canonical* form of

$$u = u(v, s). \tag{4.24}$$

Here, $-P$ is conjugate to v, and T is conjugate to s. Application of the general form of Eq. (4.22) to the Gibbs equation (4.1) gives then

$$\boxed{\left.\frac{\partial T}{\partial v}\right|_s = -\left.\frac{\partial P}{\partial s}\right|_v.} \tag{4.25}$$

Equation (4.25) is known as a *Maxwell relation*. Moreover, specialization of Eq. (4.20) to the Gibbs equation (4.1) gives

$$\boxed{-P = \left.\frac{\partial u}{\partial v}\right|_s,} \qquad \boxed{T = \left.\frac{\partial u}{\partial s}\right|_v.} \tag{4.26}$$

If the general differential $dy = \sum_{i=1}^{N} \psi_i dx_i$ is exact, one also can show

- The path integral $y_B - y_A = \int_A^B \sum_{i=1}^{N} \psi_i dx_i$ is independent of the path of the integral.
- The integral around a closed contour is zero:

$$\oint dy = \oint \sum_{i=1}^{N} \psi_i dx_i = 0. \tag{4.27}$$

- The function y can only be determined to within an additive constant. That is, there is no absolute value of y; physical significance is only ascribed to differences in y. In fact now, other means, extraneous to this analysis, can be used to provide absolute values of key thermodynamic variables. This will be important especially for flows with reaction.

Example 4.2

Show the heat transfer q is not a state function. Assume all processes are fully reversible. The first law gives

$$\begin{aligned} du &= \delta q - \delta w, && (4.28)\\ \delta q &= du + \delta w, && (4.29)\\ &= du + Pdv. && (4.30) \end{aligned}$$

Take now the non-canonical, although acceptable, form $u = u(T, v)$. Then one gets

$$du = \left.\frac{\partial u}{\partial v}\right|_T dv + \left.\frac{\partial u}{\partial T}\right|_v dT. \tag{4.31}$$

So

$$\begin{aligned} \delta q &= \left.\frac{\partial u}{\partial v}\right|_T dv + \left.\frac{\partial u}{\partial T}\right|_v dT + Pdv, && (4.32)\\ &= \underbrace{\left(\left.\frac{\partial u}{\partial v}\right|_T + P\right)}_{\equiv M} dv + \underbrace{\left.\frac{\partial u}{\partial T}\right|_v}_{\equiv N} dT. && (4.33)\\ &= M\ dv + N\ dT. && (4.34) \end{aligned}$$

Now by Eq. (4.22), for δq to be exact, one must have

$$\begin{aligned} \left.\frac{\partial M}{\partial T}\right|_v &= \left.\frac{\partial N}{\partial v}\right|_T, && (4.35)\\ & && (4.36) \end{aligned}$$

This reduces to

$$\frac{\partial^2 u}{\partial T \partial v} + \left.\frac{\partial P}{\partial T}\right|_v = \frac{\partial^2 u}{\partial v \partial T}. \tag{4.37}$$

This can only be true if $\left.\frac{\partial P}{\partial T}\right|_v = 0$. But this is not the case; consider an ideal gas for which $\left.\frac{\partial P}{\partial T}\right|_v = R/v$. So δq is not exact.

Example 4.3

Show conditions for ds to be exact in the Gibbs equation.

$$\begin{aligned} du &= Tds - Pdv, && (4.38)\\ ds &= \frac{du}{T} + \frac{P}{T}dv, && (4.39)\\ &= \frac{1}{T}\left(\left.\frac{\partial u}{\partial v}\right|_T dv + \left.\frac{\partial u}{\partial T}\right|_v dT\right) + \frac{P}{T}dv, && (4.40)\\ &= \underbrace{\left(\frac{1}{T}\left.\frac{\partial u}{\partial v}\right|_T + \frac{P}{T}\right)}_{\equiv M} dv + \underbrace{\frac{1}{T}\left.\frac{\partial u}{\partial T}\right|_v}_{\equiv N} dT. && (4.41) \end{aligned}$$

Again, invoking Eq. (4.22), one gets then

$$\frac{\partial}{\partial T}\left(\frac{1}{T}\left.\frac{\partial u}{\partial v}\right|_T + \frac{P}{T}\right)_v = \frac{\partial}{\partial v}\left(\frac{1}{T}\left.\frac{\partial u}{\partial T}\right|_v\right)_T, \tag{4.42}$$

$$\frac{1}{T}\frac{\partial^2 u}{\partial T \partial v} - \frac{1}{T^2}\left.\frac{\partial u}{\partial v}\right|_T + \frac{1}{T}\left.\frac{\partial P}{\partial T}\right|_v - \frac{P}{T^2} = \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T}, \tag{4.43}$$

$$-\frac{1}{T^2}\left.\frac{\partial u}{\partial v}\right|_T + \frac{1}{T}\left.\frac{\partial P}{\partial T}\right|_v - \frac{P}{T^2} = 0. \tag{4.44}$$

This is the condition for an exact ds. Experiment can show if it is true. For example, for an ideal gas, one finds from experiment that $u = u(T)$ and $Pv = RT$, so one gets

$$0 + \frac{1}{T}\frac{R}{v} - \frac{1}{T^2}\frac{RT}{v} = 0, \tag{4.45}$$

$$0 = 0. \tag{4.46}$$

So ds is exact for an ideal gas. In fact, the relation is verified for so many gases, ideal and non-ideal, that one simply asserts that ds is exact, rendering s to be path-independent and a state variable.

4.2 Two independent variables

Consider a general implicit function linking three variables, x, y, z:

$$f(x, y, z) = 0. \tag{4.47}$$

In $x - y - z$ space, this will represent a surface. If the function can be inverted, it will be possible to write the explicit forms

$$x = x(y, z), \qquad y = y(x, z), \qquad z = z(x, y). \tag{4.48}$$

Differentiating the first two of the Eqs. (4.48) gives

$$dx = \left.\frac{\partial x}{\partial y}\right|_z dy + \left.\frac{\partial x}{\partial z}\right|_y dz, \tag{4.49}$$

$$dy = \left.\frac{\partial y}{\partial x}\right|_z dx + \left.\frac{\partial y}{\partial z}\right|_x dz. \tag{4.50}$$

Now use Eq. (4.50) to eliminate dy in Eq. (4.49):

$$dx = \left.\frac{\partial x}{\partial y}\right|_z \underbrace{\left(\left.\frac{\partial y}{\partial x}\right|_z dx + \left.\frac{\partial y}{\partial z}\right|_x dz\right)}_{=dy} + \left.\frac{\partial x}{\partial z}\right|_y dz, \tag{4.51}$$

$$\left(1 - \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z\right) dx = \left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y\right) dz, \tag{4.52}$$

$$0dx + 0dz = \underbrace{\left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z - 1\right)}_{=0} dx + \underbrace{\left(\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y\right)}_{=0} dz. \tag{4.53}$$

Since x and z are independent, so are dx and dz, and the coefficients on each in Eq. (4.53) must be zero. Therefore from the coefficient on dx in Eq. (4.53)

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z - 1 = 0, \tag{4.54}$$

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial x}\right|_z = 1. \tag{4.55}$$

So

$$\boxed{\left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\frac{\partial y}{\partial x}\right|_z},} \tag{4.56}$$

and also from the coefficient on dz in Eq. (4.53)

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x + \left.\frac{\partial x}{\partial z}\right|_y = 0, \tag{4.57}$$

$$\left.\frac{\partial x}{\partial z}\right|_y = -\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x, . \tag{4.58}$$

So

$$\boxed{\left.\frac{\partial x}{\partial z}\right|_y \left.\frac{\partial y}{\partial x}\right|_z \left.\frac{\partial z}{\partial y}\right|_x = -1.} \tag{4.59}$$

If one now divides Eq. (4.49) by a fourth differential, dw, one gets

$$\frac{dx}{dw} = \left.\frac{\partial x}{\partial y}\right|_z \frac{dy}{dw} + \left.\frac{\partial x}{\partial z}\right|_y \frac{dz}{dw}. \tag{4.60}$$

Demanding that z be held constant in Eq. (4.60) gives

$$\left.\frac{\partial x}{\partial w}\right|_z = \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial w}\right|_z, \tag{4.61}$$

$$\frac{\left.\frac{\partial x}{\partial w}\right|_z}{\left.\frac{\partial y}{\partial w}\right|_z} = \left.\frac{\partial x}{\partial y}\right|_z, \tag{4.62}$$

$$\left.\frac{\partial x}{\partial w}\right|_z \left.\frac{\partial w}{\partial y}\right|_z = \left.\frac{\partial x}{\partial y}\right|_z. \tag{4.63}$$

If $x = x(y, w)$, one then gets

$$dx = \left.\frac{\partial x}{\partial y}\right|_w dy + \left.\frac{\partial x}{\partial w}\right|_y dw. \tag{4.64}$$

Divide now by dy while holding z constant so

$$\boxed{\left.\frac{\partial x}{\partial y}\right|_z = \left.\frac{\partial x}{\partial y}\right|_w + \left.\frac{\partial x}{\partial w}\right|_y \left.\frac{\partial w}{\partial y}\right|_z .} \tag{4.65}$$

These general operations can be applied to a wide variety of thermodynamic operations.

Example 4.4

Apply Eq. (4.65) to a standard $P - v - T$ system and let

$$\left.\frac{\partial x}{\partial y}\right|_z = \left.\frac{\partial T}{\partial v}\right|_s . \tag{4.66}$$

So $T = x$, $v = y$, and $s = z$. Let now $u = w$. So Eq. (4.65) becomes

$$\left.\frac{\partial T}{\partial v}\right|_s = \left.\frac{\partial T}{\partial v}\right|_u + \left.\frac{\partial T}{\partial u}\right|_v \left.\frac{\partial u}{\partial v}\right|_s . \tag{4.67}$$

Now by definition

$$c_v = \left.\frac{\partial u}{\partial T}\right|_v , \tag{4.68}$$

so

$$\left.\frac{\partial T}{\partial u}\right|_v = \frac{1}{c_v}. \tag{4.69}$$

Now by Eq. (4.26), one has $\left.\frac{\partial u}{\partial v}\right|_s = -P$, so one gets

$$\left.\frac{\partial T}{\partial v}\right|_s = \left.\frac{\partial T}{\partial v}\right|_u - \frac{P}{c_v}. \tag{4.70}$$

For an ideal gas, $u = u(T)$. Inverting, one gets $T = T(u)$, and so $\left.\frac{\partial T}{\partial v}\right|_u = 0$, thus

$$\left.\frac{\partial T}{\partial v}\right|_s = -\frac{P}{c_v}. \tag{4.71}$$

For an isentropic process in an ideal gas, one gets

$$\frac{dT}{dv} = -\frac{P}{c_v} = -\frac{RT}{c_v v}, \tag{4.72}$$

$$\frac{dT}{T} = -\frac{R}{c_v}\frac{dv}{v}, \tag{4.73}$$

$$= -(k-1)\frac{dv}{v}, \tag{4.74}$$

$$\ln\frac{T}{T_o} = (k-1)\ln\frac{v_o}{v}, \tag{4.75}$$

$$\frac{T}{T_o} = \left(\frac{v_o}{v}\right)^{k-1}. \tag{4.76}$$

4.3 Legendre transformations

The Gibbs equation (4.1), $du = -Pdv + Tds$, is the fundamental equation of classical thermodynamics. It is a canonical form which suggests the most natural set of variables in which to express internal energy u are s and v:

$$u = u(v, s). \tag{4.77}$$

However, v and s may not be convenient for a particular problem. There may be other combinations of variables whose canonical form gives a more convenient set of independent variables for a particular problem. An example is the enthalpy:

$$h \equiv u + Pv. \tag{4.78}$$

Differentiating the enthalpy gives

$$dh = du + Pdv + vdP. \tag{4.79}$$

Use now Eq. (4.79) to eliminate du in the Gibbs equation to give

$$\underbrace{dh - Pdv - vdP}_{=du} = -Pdv + Tds. \tag{4.80}$$

So

$$\boxed{dh = Tds + vdP.} \tag{4.81}$$

So the canonical variables for h are s and P. One then expects

$$h = h(s, P). \tag{4.82}$$

This exercise can be systematized with the Legendre transformation,[1] which defines a set of second order polynomial combinations of variables. Consider again the exact differential Eq. (4.14):

$$dy = \psi_1 dx_1 + \psi_2 dx_2 + \cdots + \psi_N dx_N. \tag{4.83}$$

[1]Two differentiable functions f and g are said to be Legendre transformations of each other if their first derivatives are inverse functions of each other: $Df = (Dg)^{-1}$. With some effort, not shown here, one can prove that the Legendre transformations of this section satisfy this general condition.

For N independent variables x_i and N conjugate variables ψ_i, by definition there are $2^N - 1$ Legendre transformed variables:

$$\begin{aligned}
\tau_1 &= \tau_1(\psi_1, x_2, x_3, \ldots, x_N) = y - \psi_1 x_1, && (4.84)\\
\tau_2 &= \tau_2(x_1, \psi_2, x_3, \ldots, x_N) = y - \psi_2 x_2, && (4.85)\\
&\vdots \\
\tau_N &= \tau_N(x_1, x_2, x_3, \ldots, \psi_N) = y - \psi_N x_N, && (4.86)\\
\tau_{1,2} &= \tau_{1,2}(\psi_1, \psi_2, x_3, \ldots, x_N) = y - \psi_1 x_1 - \psi_2 x_2, && (4.87)\\
\tau_{1,3} &= \tau_{1,3}(\psi_1, x_2, \psi_3, \ldots, x_N) = y - \psi_1 x_1 - \psi_3 x_3, && (4.88)\\
&\vdots \\
\tau_{1,\ldots,N} &= \tau_{1,\ldots,N}(\psi_1, \psi_2, \psi_3, \ldots, \psi_N) = y - \sum_{i=1}^{N} \psi_i x_i. && (4.89)
\end{aligned}$$

Each τ is a new dependent variable. *Each τ has the property that when it is known as a function of its N canonical variables, the remaining N variables from the original expression (the x_i and the conjugate ψ_i) can be recovered by differentiation of τ.* In general this is not true for arbitrary transformations.

Example 4.5

Let $y = y(x_1, x_2, x_3)$. This has the associated differential form

$$dy = \psi_1 dx_1 + \psi_2 dx_2 + \psi_3 dx_3. \tag{4.90}$$

Choose now a Legendre transformed variable $\tau_1 \equiv z(\psi_1, x_2, x_3)$:

$$z = y - \psi_1 x_1. \tag{4.91}$$

Then

$$dz = \left.\frac{\partial z}{\partial \psi_1}\right|_{x_2,x_3} d\psi_1 + \left.\frac{\partial z}{\partial x_2}\right|_{\psi_1,x_3} dx_2 + \left.\frac{\partial z}{\partial x_3}\right|_{\psi_1,x_2} dx_3. \tag{4.92}$$

Now differentiating Eq. (4.91), one also gets

$$dz = dy - \psi_1 dx_1 - x_1 d\psi_1. \tag{4.93}$$

Elimination of dy in Eq. (4.93) by using Eq. (4.90) gives

$$\begin{aligned}
dz &= \underbrace{\psi_1\ dx_1 + \psi_2\ dx_2 + \psi_3\ dx_3}_{=dy} - \psi_1\ dx_1 - x_1\ d\psi_1, && (4.94)\\
&= -x_1\ d\psi_1 + \psi_2\ dx_2 + \psi_3\ dx_3. && (4.95)
\end{aligned}$$

Thus from Eq. (4.92), one gets

$$x_1 = -\left.\frac{\partial z}{\partial \psi_1}\right|_{x_2,x_3}, \qquad \psi_2 = \left.\frac{\partial z}{\partial x_2}\right|_{\psi_1,x_3}, \qquad \psi_3 = \left.\frac{\partial z}{\partial x_3}\right|_{\psi_1,x_2}. \tag{4.96}$$

So the original expression had three independent variables x_1, x_2, x_3, and three conjugate variables ψ_1, ψ_2, ψ_3. Definition of the Legendre function z with canonical variables ψ_1, x_2, and x_3 allowed determination of the remaining variables x_1, ψ_2, and ψ_3 in terms of the canonical variables.

For the Gibbs equation, (4.1), $du = -Pdv + Tds$, one has $y = u$, two canonical variables, $x_1 = v$ and $x_2 = s$, and two conjugates, $\psi_1 = -P$ and $\psi_2 = T$. Thus $N = 2$, and one can expect $2^2 - 1 = 3$ Legendre transformations. They are

$$\tau_1 = y - \psi_1 x_1 = h = h(P,s) = u + Pv, \quad \text{enthalpy,} \tag{4.97}$$

$$\tau_2 = y - \psi_2 x_2 = a = a(v,T) = u - Ts, \quad \text{Helmholtz free energy,} \tag{4.98}$$

$$\tau_{1,2} = y - \psi_1 x_1 - \psi_2 x_2 = g = g(P,T) = u + Pv - Ts, \quad \text{Gibbs free energy.} \tag{4.99}$$

It has already been shown for the enthalpy that $dh = Tds + vdP$, so that the canonical variables are s and P. One then also has

$$dh = \left.\frac{\partial h}{\partial s}\right|_P ds + \left.\frac{\partial h}{\partial P}\right|_s dP, \tag{4.100}$$

from which one deduces that

$$\boxed{T = \left.\frac{\partial h}{\partial s}\right|_P}, \qquad \boxed{v = \left.\frac{\partial h}{\partial P}\right|_s}. \tag{4.101}$$

From Eq. (4.101), a second Maxwell relation can be deduced by differentiation of the first with respect to P and the second with respect to s:

$$\boxed{\left.\frac{\partial T}{\partial P}\right|_s = \left.\frac{\partial v}{\partial s}\right|_P}. \tag{4.102}$$

The relations for Helmholtz and Gibbs free energies each supply additional useful relations including two new Maxwell relations. First consider the Helmholtz free energy

$$a = u - Ts, \tag{4.103}$$

$$da = du - Tds - sdT, \tag{4.104}$$

$$= (-Pdv + Tds) - Tds - sdT, \tag{4.105}$$

$$= -Pdv - sdT. \tag{4.106}$$

So the canonical variables for a are v and T. The conjugate variables are $-P$ and $-s$. Thus

$$da = \left.\frac{\partial a}{\partial v}\right|_T dv + \left.\frac{\partial a}{\partial T}\right|_v dT. \tag{4.107}$$

So one gets

$$\boxed{-P = \left.\frac{\partial a}{\partial v}\right|_T}, \qquad \boxed{-s = \left.\frac{\partial a}{\partial T}\right|_v}. \tag{4.108}$$

and the consequent Maxwell relation

$$\boxed{\left.\frac{\partial P}{\partial T}\right|_v = \left.\frac{\partial s}{\partial v}\right|_T}. \tag{4.109}$$

For the Gibbs free energy

$$\begin{aligned} g &= \underbrace{u + Pv}_{=h} - Ts, && (4.110)\\ &= h - Ts, && (4.111)\\ dg &= dh - Tds - sdT, && (4.112)\\ &= \underbrace{(Tds + vdP)}_{=dh} - Tds - sdT, && (4.113)\\ &= vdP - sdT. && (4.114) \end{aligned}$$

So for Gibbs free energy, the canonical variables are P and T while the conjugate variables are v and $-s$. One then has $g = g(P,T)$, which gives

$$dg = \left.\frac{\partial g}{\partial P}\right|_T dP + \left.\frac{\partial g}{\partial T}\right|_P dT. \tag{4.115}$$

So one finds

$$\boxed{v = \left.\frac{\partial g}{\partial P}\right|_T}, \qquad \boxed{-s = \left.\frac{\partial g}{\partial T}\right|_P}. \tag{4.116}$$

The resulting Maxwell function is then

$$\boxed{\left.\frac{\partial v}{\partial T}\right|_P = -\left.\frac{\partial s}{\partial P}\right|_T}. \tag{4.117}$$

Example 4.6

Canonical Form

If

$$h(s,P) = c_P T_o \left(\frac{P}{P_o}\right)^{R/c_P} \exp\left(\frac{s}{c_P}\right) + (h_o - c_P T_o), \tag{4.118}$$

and c_P, T_o, R, P_o, and h_o are all constants, derive both thermal and caloric state equations $P(v,T)$ and $u(v,T)$.

Now for this material

$$\begin{aligned} \left.\frac{\partial h}{\partial s}\right|_P &= T_o \left(\frac{P}{P_o}\right)^{R/c_P} \exp\left(\frac{s}{c_P}\right), && (4.119)\\ \left.\frac{\partial h}{\partial P}\right|_s &= \frac{RT_o}{P_o}\left(\frac{P}{P_o}\right)^{R/c_P - 1} \exp\left(\frac{s}{c_P}\right). && (4.120) \end{aligned}$$

Now since

$$\left.\frac{\partial h}{\partial s}\right|_P = T, \tag{4.121}$$

$$\left.\frac{\partial h}{\partial P}\right|_s = v, \tag{4.122}$$

one has

$$T = T_o\left(\frac{P}{P_o}\right)^{R/c_P}\exp\left(\frac{s}{c_P}\right), \tag{4.123}$$

$$v = \frac{RT_o}{P_o}\left(\frac{P}{P_o}\right)^{R/c_P-1}\exp\left(\frac{s}{c_P}\right). \tag{4.124}$$

Dividing Eq. (4.123) by Eq. (4.124) gives

$$\frac{T}{v} = \frac{P}{R}, \tag{4.125}$$

$$Pv = RT, \tag{4.126}$$

which is the thermal equation of state. Substituting from Eq. (4.123) into the canonical equation for h, Eq. (4.118), one also finds for the caloric equation of state

$$h = c_P T + (h_o - c_P T_o), \tag{4.127}$$

$$h = c_P(T - T_o) + h_o, \tag{4.128}$$

which is useful in itself. Substituting in for T and T_o,

$$h = c_P\left(\frac{Pv}{R} - \frac{P_o v_o}{R}\right) + h_o. \tag{4.129}$$

Using, Eq. (4.78), $h \equiv u + Pv$, we get

$$u + Pv = c_P\left(\frac{Pv}{R} - \frac{P_o v_o}{R}\right) + u_o + P_o v_o. \tag{4.130}$$

So

$$u = \left(\frac{c_P}{R} - 1\right)Pv - \left(\frac{c_P}{R} - 1\right)P_o v_o + u_o, \tag{4.131}$$

$$u = \left(\frac{c_P}{R} - 1\right)(Pv - P_o v_o) + u_o, \tag{4.132}$$

$$u = \left(\frac{c_P}{R} - 1\right)(RT - RT_o) + u_o, \tag{4.133}$$

$$u = (c_P - R)(T - T_o) + u_o, \tag{4.134}$$

$$u = (c_P - (c_P - c_v))(T - T_o) + u_o, \tag{4.135}$$

$$u = c_v(T - T_o) + u_o. \tag{4.136}$$

So *one* canonical equation gives us all the information one needs. Often, it is difficult to do a single experiment to get the canonical form.

4.4 Heat capacity

Recall that

$$c_v = \left.\frac{\partial u}{\partial T}\right|_v, \tag{4.137}$$

$$c_P = \left.\frac{\partial h}{\partial T}\right|_P. \tag{4.138}$$

Then perform operations on the Gibbs equation

$$du = Tds - Pdv, \tag{4.139}$$

$$\left.\frac{\partial u}{\partial T}\right|_v = T\left.\frac{\partial s}{\partial T}\right|_v, \tag{4.140}$$

$$c_v = T\left.\frac{\partial s}{\partial T}\right|_v. \tag{4.141}$$

Likewise,

$$dh = Tds + vdP, \tag{4.142}$$

$$\left.\frac{\partial h}{\partial T}\right|_P = T\left.\frac{\partial s}{\partial T}\right|_P, \tag{4.143}$$

$$c_P = T\left.\frac{\partial s}{\partial T}\right|_P. \tag{4.144}$$

One finds further useful relations by operating on the Gibbs equation:

$$du = Tds - Pdv, \tag{4.145}$$

$$\left.\frac{\partial u}{\partial v}\right|_T = T\left.\frac{\partial s}{\partial v}\right|_T - P, \tag{4.146}$$

$$= T\left.\frac{\partial P}{\partial T}\right|_v - P. \tag{4.147}$$

So one can then say

$$u = u(T, v), \tag{4.148}$$

$$du = \left.\frac{\partial u}{\partial T}\right|_v dT + \left.\frac{\partial u}{\partial v}\right|_T dv, \tag{4.149}$$

$$= c_v dT + \left(T\left.\frac{\partial P}{\partial T}\right|_v - P\right) dv. \tag{4.150}$$

For an ideal gas, one has

$$\left.\frac{\partial u}{\partial v}\right|_T = T\left.\frac{\partial P}{\partial T}\right|_v - P = T\left(\frac{R}{v}\right) - \frac{RT}{v}, \tag{4.151}$$

$$= 0. \tag{4.152}$$

Consequently, u is not a function of v for an ideal gas, so $u = u(T)$ alone. Since Eq. (4.78), $h = u + Pv$, for an ideal gas reduces to $h = u + RT$

$$h = u(T) + RT = h(T). \tag{4.153}$$

Now return to general equations of state. With $s = s(T, v)$ or $s = s(T, P)$, one gets

$$ds = \left.\frac{\partial s}{\partial T}\right|_v dT + \left.\frac{\partial s}{\partial v}\right|_T dv, \tag{4.154}$$

$$ds = \left.\frac{\partial s}{\partial T}\right|_P dT + \left.\frac{\partial s}{\partial P}\right|_T dP. \tag{4.155}$$

Now using Eqs. (4.102, 4.117, 4.141, 4.144) one gets

$$ds = \frac{c_v}{T} dT + \left.\frac{\partial P}{\partial T}\right|_v dv, \tag{4.156}$$

$$ds = \frac{c_P}{T} dT - \left.\frac{\partial v}{\partial T}\right|_P dP. \tag{4.157}$$

Subtracting Eq. (4.157) from Eq. (4.156), one finds

$$0 = \frac{c_v - c_P}{T} dT + \left.\frac{\partial P}{\partial T}\right|_v dv + \left.\frac{\partial v}{\partial T}\right|_P dP, \tag{4.158}$$

$$(c_P - c_v) dT = T \left.\frac{\partial P}{\partial T}\right|_v dv + T \left.\frac{\partial v}{\partial T}\right|_P dP. \tag{4.159}$$

Now divide both sides by dT and hold *either* P or v constant. In either case, one gets

$$c_P - c_v = T \left.\frac{\partial P}{\partial T}\right|_v \left.\frac{\partial v}{\partial T}\right|_P. \tag{4.160}$$

Also, since $\partial P/\partial T|_v = -(\partial P/\partial v|_T)(\partial v/\partial T|_P)$, Eq. (4.160) can be rewritten as

$$c_P - c_v = -T \left(\left.\frac{\partial v}{\partial T}\right|_P \right)^2 \left.\frac{\partial P}{\partial v}\right|_T. \tag{4.161}$$

Now since $T > 0$, $(\partial v/\partial T|_P)^2 > 0$, and for all known materials $\partial P/\partial v|_T < 0$, we must have

$$c_P > c_v. \tag{4.162}$$

Example 4.7

For an ideal gas find $c_P - c_v$.

For the ideal gas, $Pv = RT$, one has

$$\left.\frac{\partial P}{\partial T}\right|_v = \frac{R}{v}, \qquad \left.\frac{\partial v}{\partial T}\right|_P = \frac{R}{P}. \tag{4.163}$$

So, from Eq. (4.160), we have

$$\begin{aligned} c_P - c_v &= T\frac{R}{v}\frac{R}{P}, && (4.164)\\ &= T\frac{R^2}{RT}, && (4.165)\\ &= R. && (4.166) \end{aligned}$$

This holds even if the ideal gas is calorically imperfect. That is

$$\boxed{c_P(T) - c_v(T) = R.} \tag{4.167}$$

For the ratio of specific heats for a general material, one can use Eqs. (4.141) and (4.144) to get

$$\begin{aligned} k = \frac{c_P}{c_v} &= \frac{T\left.\frac{\partial s}{\partial T}\right|_P}{T\left.\frac{\partial s}{\partial T}\right|_v}, \quad \text{then apply Eq. (4.56) to get} && (4.168)\\ &= \left.\frac{\partial s}{\partial T}\right|_P \left.\frac{\partial T}{\partial s}\right|_v, \quad \text{then apply Eq. (4.58) to get} && (4.169)\\ &= \left(-\left.\frac{\partial s}{\partial P}\right|_T \left.\frac{\partial P}{\partial T}\right|_s\right)\left(-\left.\frac{\partial T}{\partial v}\right|_s \left.\frac{\partial v}{\partial s}\right|_T\right), && (4.170)\\ &= \left(\left.\frac{\partial v}{\partial s}\right|_T \left.\frac{\partial s}{\partial P}\right|_T\right)\left(\left.\frac{\partial P}{\partial T}\right|_s \left.\frac{\partial T}{\partial v}\right|_s\right). && (4.171) \end{aligned}$$

So for general materials

$$\boxed{k = \left.\frac{\partial v}{\partial P}\right|_T \left.\frac{\partial P}{\partial v}\right|_s.} \tag{4.172}$$

The first term can be obtained from $P - v - T$ data. The second term is related to the isentropic sound speed of the material, which is also a measurable quantity.

Example 4.8

For a calorically perfect ideal gas with gas constant R and specific heat at constant volume c_v, find expressions for the thermodynamic variable s and thermodynamic potentials u, h, a, and g, as functions of T and P.

First get the entropy:

$$
\begin{aligned}
du &= Tds - Pdv, && (4.173)\\
Tds &= du + Pdv, && (4.174)\\
Tds &= c_v dT + Pdv, && (4.175)\\
ds &= c_v \frac{dT}{T} + \frac{P}{T}\, dv, && (4.176)\\
&= c_v \frac{dT}{T} + R\frac{dv}{v}, && (4.177)\\
\int ds &= \int c_v \frac{dT}{T} + \int R\frac{dv}{v}, && (4.178)\\
s - s_0 &= c_v \ln\frac{T}{T_0} + R\ln\frac{v}{v_0}, && (4.179)\\
\frac{s-s_0}{c_v} &= \ln\frac{T}{T_0} + \frac{R}{c_v}\ln\frac{RT/P}{RT_0/P_0}, && (4.180)\\
&= \ln\left(\frac{T}{T_0}\right) + \ln\left(\frac{T}{T_0}\frac{P_0}{P}\right)^{R/c_v}, && (4.181)\\
&= \ln\left(\frac{T}{T_0}\right)^{1+R/c_v} + \ln\left(\frac{P_0}{P}\right)^{R/c_v}, && (4.182)\\
&= \ln\left(\frac{T}{T_0}\right)^{1+(c_p-c_v)/c_v} + \ln\left(\frac{P_0}{P}\right)^{(c_p-c_v)/c_v}, && (4.183)\\
&= \ln\left(\frac{T}{T_0}\right)^{k} + \ln\left(\frac{P_0}{P}\right)^{k-1}. && (4.184)
\end{aligned}
$$

So

$$\boxed{s = s_0 + c_v \ln\left(\frac{T}{T_0}\right)^{k} + c_v \ln\left(\frac{P_0}{P}\right)^{k-1}.} \qquad (4.185)$$

Now, for the calorically perfect ideal gas, one has

$$\boxed{u = u_o + c_v(T - T_o).} \qquad (4.186)$$

For the enthalpy, one gets

$$
\begin{aligned}
h &= u + Pv, && (4.187)\\
&= u + RT, && (4.188)\\
&= u_o + c_v(T - T_o) + RT, && (4.189)\\
&= u_o + c_v(T - T_o) + RT + RT_o - RT_o, && (4.190)\\
&= \underbrace{u_o + RT_o}_{=h_o} + c_v(T - T_o) + R(T - T_o), && (4.191)\\
&= h_o + \underbrace{(c_v + R)}_{=c_p}(T - T_o). && (4.192)
\end{aligned}
$$

So

$$\boxed{h = h_o + c_p(T - T_o).} \qquad (4.193)$$

For the Helmholtz free energy, one gets

$$a = u - Ts. \tag{4.194}$$

Thus,

$$\boxed{a = u_o + c_v(T - T_o) - T\left(s_0 + c_v \ln\left(\frac{T}{T_0}\right)^k + c_v \ln\left(\frac{P_0}{P}\right)^{k-1}\right).} \tag{4.195}$$

For the Gibbs free energy, one gets

$$g = h - Ts. \tag{4.196}$$

Thus

$$\boxed{g = h_o + c_p(T - T_o) - T\left(s_0 + c_v \ln\left(\frac{T}{T_0}\right)^k + c_v \ln\left(\frac{P_0}{P}\right)^{k-1}\right).} \tag{4.197}$$

4.5 Van der Waals gas

A van der Waals gas is a common model for a non-ideal gas. It can capture some of the behavior of a gas as it approaches the vapor dome. Its form is

$$\boxed{P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2},} \tag{4.198}$$

where b accounts for the finite volume of the molecules, and a accounts for intermolecular forces.

Example 4.9

Find a general expression for $u(T, v)$ if

$$P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{4.199}$$

Proceed as before: First we have

$$du = \left.\frac{\partial u}{\partial T}\right|_v dT + \left.\frac{\partial u}{\partial v}\right|_T dv, \tag{4.200}$$

recalling that

$$\left.\frac{\partial u}{\partial T}\right|_v = c_v, \qquad \left.\frac{\partial u}{\partial v}\right|_T = T\left.\frac{\partial P}{\partial T}\right|_v - P. \tag{4.201}$$

Now for the van der Waals gas, we have

$$\left.\frac{\partial P}{\partial T}\right|_v = \frac{R}{v-b}, \tag{4.202}$$

$$T\left.\frac{\partial P}{\partial T}\right|_v - P = \frac{RT}{v-b} - P, \tag{4.203}$$

$$= \frac{RT}{v-b} - \left(\frac{RT}{v-b} - \frac{a}{v^2}\right) = \frac{a}{v^2}. \tag{4.204}$$

So we have

$$\left.\frac{\partial u}{\partial v}\right|_T = \frac{a}{v^2}, \tag{4.205}$$

$$u(T,v) = -\frac{a}{v} + f(T). \tag{4.206}$$

Here $f(T)$ is some as-of-yet arbitrary function of T. To evaluate $f(T)$, take the derivative with respect to T holding v constant:

$$\left.\frac{\partial u}{\partial T}\right|_v = \frac{df}{dT} = c_v. \tag{4.207}$$

Since f is a function of T at most, here c_v can be a function of T at most, so we allow $c_v = c_v(T)$. Integrating, we find $f(T)$ as

$$f(T) = C + \int_{T_o}^{T} c_v(\hat{T})d\hat{T}, \tag{4.208}$$

where C is an integration constant. Thus u is

$$u(T,v) = C + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} - \frac{a}{v}. \tag{4.209}$$

Taking $C = u_o + a/v_o$, we get

$$\boxed{u(T,v) = u_o + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} + a\left(\frac{1}{v_o} - \frac{1}{v}\right).} \tag{4.210}$$

We also find

$$h = u + Pv = u_o + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} + a\left(\frac{1}{v_o} - \frac{1}{v}\right) + Pv, \tag{4.211}$$

$$h(T,v) = u_o + \int_{T_o}^{T} c_v(\hat{T})d\hat{T} + a\left(\frac{1}{v_o} - \frac{1}{v}\right) + \frac{RTv}{v-b} - \frac{a}{v}. \tag{4.212}$$

Example 4.10

A van der Waals gas with

$$R = 200\ \frac{J}{kg\ K}, \tag{4.213}$$

$$a = 150\ \frac{Pa\ m^6}{kg^2}, \tag{4.214}$$

$$b = 0.001\ \frac{m^3}{kg}, \tag{4.215}$$

$$c_v = \left(350\ \frac{J}{kg\ K}\right) + \left(0.2\ \frac{J}{kg\ K^2}\right)(T - (300\ K)), \tag{4.216}$$

begins at $T_1 = 300\ K$, $P_1 = 1 \times 10^5\ Pa$. It is isothermally compressed to state 2 where $P_2 = 1 \times 10^6\ Pa$. It is then isochorically heated to state 3 where $T_3 = 1000\ K$. Find ${}_1w_3$, ${}_1q_3$, and $s_3 - s_1$. Assume the surroundings are at $1000\ K$.

Recall

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \tag{4.217}$$

so at state 1

$$\left(10^5\ Pa\right) = \frac{\left(200\ \frac{J}{kg\ K}\right)(300\ K)}{v_1 - \left(0.001\ \frac{m^3}{kg}\right)} - \frac{150\ \frac{Pa\ m^6}{kg^2}}{v_1^2}. \tag{4.218}$$

Expanding, one gets

$$-0.15 + \left(150\ \frac{kg}{m^3}\right) v_1 - \left(60100\ \frac{kg^2}{m^6}\right) v_1^2 + \left(100000\ \frac{kg^3}{m^9}\right) v_1^3 = 0. \tag{4.219}$$

This is a cubic equation which has three solutions:

$$v_1 = 0.598\ \frac{m^3}{kg}, \qquad \text{physical}, \tag{4.220}$$

$$v_1 = 0.00125 - 0.0097i\ \frac{m^3}{kg} \qquad \text{not physical}, \tag{4.221}$$

$$v_1 = 0.00125 + 0.0097i\ \frac{m^3}{kg} \qquad \text{not physical}. \tag{4.222}$$

Now at state 2, P_2 and T_2 are known, so v_2 can be determined:

$$\left(10^6\ Pa\right) = \frac{\left(200\ \frac{J}{kg\ K}\right)(300\ K)}{v_2 - \left(0.001\ \frac{m^3}{kg}\right)} - \frac{150\ \frac{Pa\ m^6}{kg^2}}{v_2^2}. \tag{4.223}$$

The physical solution is $v_2 = 0.0585\ m^3/kg$. Now at state 3 it is known that $v_3 = v_2$ and $T_3 = 1000\ K$. Determine P_3:

$$P_3 = \frac{\left(200\ \frac{J}{kg\ K}\right)(1000\ K)}{\left(0.0585\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)} - \frac{150\ \frac{Pa\ m^6}{kg^2}}{\left(0.0585\ \frac{m^3}{kg}\right)^2}, \tag{4.224}$$

$$= (3478261\ Pa) - (43831\ Pa), \tag{4.225}$$

$$= 3434430\ Pa. \tag{4.226}$$

Now ${}_1w_3 = {}_1w_2 + {}_2w_3 = \int_1^2 P dv + \int_2^3 P dv = \int_1^2 P dv$ since $2 \rightarrow 3$ is at constant volume. So

$$
\begin{aligned}
{}_1w_3 &= \int_{v_1}^{v_2} \left(\frac{RT}{v-b} - \frac{a}{v^2} \right) dv, && (4.227)\\
&= RT_1 \int_{v_1}^{v_2} \frac{dv}{v-b} - a \int_{v_1}^{v_2} \frac{dv}{v^2}, && (4.228)\\
&= RT_1 \ln\left(\frac{v_2 - b}{v_1 - b} \right) + a \left(\frac{1}{v_2} - \frac{1}{v_1} \right), && (4.229)\\
&= \left(200 \ \frac{J}{kg \ K} \right) (300 \ K) \ln \left(\frac{\left(0.0585 \ \frac{m^3}{kg} \right) - \left(0.001 \ \frac{m^3}{kg} \right)}{\left(0.598 \ \frac{m^3}{kg} \right) - \left(0.001 \ \frac{m^3}{kg} \right)} \right) \\
&\quad + \left(150 \ \frac{Pa \ m^6}{kg^2} \right) \left(\frac{1}{0.0585 \ \frac{m^3}{kg}} - \frac{1}{0.598 \ \frac{m^3}{kg}} \right), && (4.230)\\
&= \left(-140408 \ \frac{J}{kg} \right) + \left(2313 \ \frac{J}{kg} \right), && (4.231)\\
&= -138095 \ \frac{J}{kg}, && (4.232)\\
&= \boxed{-138.095 \ \frac{kJ}{kg}.} && (4.233)
\end{aligned}
$$

The gas is compressed, so the work is negative. Since u is a state property:

$$u_3 - u_1 = \int_{T_1}^{T_3} c_v(T) dT + a \left(\frac{1}{v_1} - \frac{1}{v_3} \right). \tag{4.234}$$

Now

$$
\begin{aligned}
c_v &= \left(350 \ \frac{J}{kg \ K} \right) + \left(0.2 \ \frac{J}{kg \ K^2} \right) (T - (300 \ K)), && (4.235)\\
&= \left(290 \ \frac{J}{kg \ K} \right) + \left(0.2 \ \frac{J}{kg \ K^2} \right) T. && (4.236)
\end{aligned}
$$

so

$$
\begin{aligned}
u_3 - u_1 &= \int_{T_1}^{T_3} \left(\left(290 \ \frac{J}{kg \ K} \right) + \left(0.2 \ \frac{J}{kg \ K^2} \right) T \right) dT + a \left(\frac{1}{v_1} - \frac{1}{v_3} \right), && (4.237)\\
&= \left(290 \ \frac{J}{kg \ K} \right) (T_3 - T_1) + \left(0.1 \ \frac{J}{kg \ K^2} \right) \left(T_3^2 - T_1^2 \right) + a \left(\frac{1}{v_1} - \frac{1}{v_3} \right), && (4.238)\\
&= \left(290 \ \frac{J}{kg \ K} \right) ((1000 \ K) - (300 \ K)) + \left(0.1 \ \frac{J}{kg \ K^2} \right) \left((1000 \ K)^2 - (300 \ K)^2 \right) \\
&\quad + \left(150 \ \frac{Pa \ m^6}{kg^2} \right) \left(\frac{1}{0.598 \ \frac{m^3}{kg}} - \frac{1}{0.0585 \ \frac{m^3}{kg}} \right), && (4.239)\\
&= \left(203000 \ \frac{J}{kg} \right) + \left(91000 \ \frac{J}{kg} \right) - \left(2313 \ \frac{J}{kg} \right), && (4.240)\\
&= 291687 \ \frac{J}{kg}, && (4.241)\\
&= 292 \ \frac{kJ}{kg}. && (4.242)
\end{aligned}
$$

Now from the first law

$$\begin{aligned} u_3 - u_1 &= {}_1q_3 - {}_1w_3, && (4.243)\\ {}_1q_3 &= u_3 - u_1 + {}_1w_3, && (4.244)\\ {}_1q_3 &= \left(292\ \frac{kJ}{kg}\right) - \left(138\ \frac{kJ}{kg}\right), && (4.245)\\ {}_1q_3 &= \boxed{154\ \frac{kJ}{kg}.} && (4.246) \end{aligned}$$

The heat transfer is positive as heat was added to the system.

Now find the entropy change. Manipulate the Gibbs equation:

$$\begin{aligned} Tds &= du + Pdv, && (4.247)\\ ds &= \frac{1}{T}du + \frac{P}{T}dv, && (4.248)\\ ds &= \frac{1}{T}\left(c_v(T)dT + \frac{a}{v^2}dv\right) + \frac{P}{T}dv, && (4.249)\\ ds &= \frac{1}{T}\left(c_v(T)dT + \frac{a}{v^2}dv\right) + \frac{1}{T}\left(\frac{RT}{v-b} - \frac{a}{v^2}\right)dv, && (4.250)\\ ds &= \frac{c_v(T)}{T}dT + \frac{R}{v-b}dv, && (4.251)\\ s_3 - s_1 &= \int_{T_1}^{T_3} \frac{c_v(T)}{T}dT + R\ln\frac{v_3-b}{v_1-b}, && (4.252)\\ &= \int_{300}^{1000} \left(\frac{\left(290\ \frac{J}{kg\ K}\right)}{T} + \left(0.2\ \frac{J}{kg\ K^2}\right)\right)dT + R\ln\frac{v_3-b}{v_1-b}, && (4.253)\\ &= \left(290\ \frac{J}{kg\ K}\right)\ln\left(\frac{1000\ K}{300\ K}\right) + \left(0.2\ \frac{J}{kg\ K^2}\right)((1000\ K) - (300\ K))\\ &\quad + \left(200\ \frac{J}{kg\ K}\right)\ln\frac{\left(0.0585\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)}{\left(0.598\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)}, && (4.254)\\ &= \left(349\ \frac{J}{kg\ K}\right) + \left(140\ \frac{J}{kg\ K}\right) - \left(468\ \frac{J}{kg\ K}\right), && (4.255)\\ &= 21\ \frac{J}{kg\ K}, && (4.256)\\ &= \boxed{0.021\ \frac{kJ}{kg\ K}.} && (4.257) \end{aligned}$$

Is the second law satisfied for each portion of the process?

First look at $1 \to 2$

$$\begin{aligned} u_2 - u_1 &= {}_1q_2 - {}_1w_2, && (4.258)\\ {}_1q_2 &= u_2 - u_1 + {}_1w_2, && (4.259)\\ {}_1q_2 &= \left(\int_{T_1}^{T_2} c_v(T)dT + a\left(\frac{1}{v_1} - \frac{1}{v_2}\right)\right) + \left(RT_1\ln\left(\frac{v_2-b}{v_1-b}\right) + a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)\right). && (4.260) \end{aligned}$$

Recalling that $T_1 = T_2$ and canceling the terms in a, one gets

$$
\begin{aligned}
{}_1q_2 &= RT_1 \ln\left(\frac{v_2 - b}{v_1 - b}\right), && (4.261)\\
&= \left(200\ \frac{J}{kg\ K}\right)(300\ K) \ln\left(\frac{\left(0.0585\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)}{\left(0.598\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)}\right), && (4.262)\\
&= -140408\ \frac{J}{kg}. && (4.263)
\end{aligned}
$$

Since the process is isothermal,

$$
\begin{aligned}
s_2 - s_1 &= R \ln\left(\frac{v_2 - b}{v_1 - b}\right) && (4.264)\\
&= \left(200\ \frac{J}{kg\ K}\right) \ln\left(\frac{\left(0.0585\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)}{\left(0.598\ \frac{m^3}{kg}\right) - \left(0.001\ \frac{m^3}{kg}\right)}\right), && (4.265)\\
&= -468.0\ \frac{J}{kg\ K}. && (4.266)
\end{aligned}
$$

Entropy *drops* because heat was transferred *out* of the system.

Check the second law. Note that in this portion of the process in which the heat is transferred out of the system, that the surroundings must have $T_{surr} \leq 300\ K$. For this portion of the process let us take $T_{surr} = 300\ K$.

$$
\begin{aligned}
s_2 - s_1 &\geq \frac{{}_1q_2}{T}? && (4.267)\\
-468.0\ \frac{J}{kg\ K} &\geq \frac{-140408\ \frac{J}{kg}}{300\ K}, && (4.268)\\
-468.0\ \frac{J}{kg\ K} &\geq -468.0\ \frac{J}{kg\ K} \qquad \text{ok.} && (4.269)
\end{aligned}
$$

Next look at $2 \rightarrow 3$

$$
\begin{aligned}
{}_2q_3 &= u_3 - u_2 + {}_2w_3, && (4.270)\\
{}_2q_3 &= \left(\int_{T_2}^{T_3} c_v(T)dT + a\left(\frac{1}{v_2} - \frac{1}{v_3}\right)\right) + \left(\int_{v_2}^{v_3} P dv\right), && (4.271)
\end{aligned}
$$

since isochoric

$$
\begin{aligned}
{}_2q_3 &= \int_{T_2}^{T_3} c_v(T)dT, && (4.272)\\
&= \int_{300\ K}^{1000\ K} \left(\left(290\ \frac{J}{kg\ K}\right) + \left(0.2\ \frac{J}{kg\ K^2}\right)T\right) dT, && (4.273)\\
&= 294000\ \frac{J}{kg}. && (4.274)
\end{aligned}
$$

Now look at the entropy change for the isochoric process:

$$s_3 - s_2 = \int_{T_2}^{T_3} \frac{c_v(T)}{T} dT, \tag{4.275}$$

$$= \int_{T_2}^{T_3} \left(\frac{\left(290 \ \frac{J}{kg \ K}\right)}{T} + \left(0.2 \ \frac{J}{kg \ K^2}\right) \right) dT, \tag{4.276}$$

$$= \left(290 \ \frac{J}{kg \ K}\right) \ln\left(\frac{1000 \ K}{300 \ K}\right) + \left(0.2 \ \frac{J}{kg \ K^2}\right) ((1000 \ K) - (300 \ K)), \tag{4.277}$$

$$= 489 \ \frac{J}{kg \ K}. \tag{4.278}$$

Entropy *rises* because heat transferred *into* system.

In order to transfer heat into the system we must have a different thermal reservoir. This one must have $T_{surr} \geq 1000 \ K$. Assume here that the heat transfer was from a reservoir held at $1000 \ K$ to assess the influence of the second law.

$$s_3 - s_2 \geq \frac{^2q_3}{T}? \tag{4.279}$$

$$489 \ \frac{J}{kg \ K} \geq \frac{294000 \ \frac{J}{kg}}{1000 \ K}, \tag{4.280}$$

$$489 \ \frac{J}{kg \ K} \geq 294 \ \frac{J}{kg \ K}, \qquad \text{ok.} \tag{4.281}$$

4.6 Redlich-Kwong gas

The Redlich-Kwong equation of state is

$$\boxed{P = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{1/2}}.} \tag{4.282}$$

It is modestly more accurate than the van der Waals equation in predicting material behavior.

Example 4.11

For the case in which $b = 0$, find an expression for $u(T, v)$ consistent with the Redlich-Kwong state equation.

Here the equation of state is now

$$P = \frac{RT}{v} - \frac{a}{v^2 T^{1/2}}. \tag{4.283}$$

Proceeding as before, we have

$$\left.\frac{\partial u}{\partial v}\right|_T = T\left.\frac{\partial P}{\partial T}\right|_v - P, \tag{4.284}$$

$$= T\left(\frac{R}{v} + \frac{a}{2v^2T^{3/2}}\right) - \left(\frac{RT}{v} - \frac{a}{v^2T^{1/2}}\right), \tag{4.285}$$

$$= \frac{3a}{2v^2T^{1/2}}. \tag{4.286}$$

Integrating, we find

$$u(T,v) = -\frac{3a}{2vT^{1/2}} + f(T). \tag{4.287}$$

Here $f(T)$ is a yet-to-be-specified function of temperature only. Now the specific heat is found by the temperature derivative of u:

$$c_v(T,v) = \left.\frac{\partial u}{\partial T}\right|_v = \frac{3a}{4vT^{3/2}} + \frac{df}{dT}. \tag{4.288}$$

Obviously, for this material, c_v is a function of both T and v.

Let us define $c_{vo}(T)$ via

$$\frac{df}{dT} \equiv c_{vo}(T). \tag{4.289}$$

Integrating, then one gets

$$f(T) = C + \int_{T_o}^{T} c_{vo}(\hat{T})\, d\hat{T}. \tag{4.290}$$

Let us take $C = u_o + 3a/2/v_o/T_o^{1/2}$. Thus we arrive at the following expressions for $c_v(T,v)$ and $u(T,v)$:

$$c_v(T,v) = c_{vo}(T) + \frac{3a}{4vT^{3/2}}, \tag{4.291}$$

$$\boxed{u(T,v) = u_o + \int_{T_o}^{T} c_{vo}(\hat{T})\, d\hat{T} + \frac{3a}{2}\left(\frac{1}{v_oT_o^{1/2}} - \frac{1}{vT^{1/2}}\right).} \tag{4.292}$$

4.7 Compressibility and generalized charts

A simple way to quantify the deviation from ideal gas behavior is to determine the so-called compressibility Z, where

$$Z \equiv \frac{Pv}{RT}. \tag{4.293}$$

For an ideal gas, $Z = 1$. For substances with a simple molecular structure, Z can be tabulated as functions of the so-called reduced pressure P_r and reduced temperature T_r. T_r and P_r are dimensionless variables found by scaling their dimensional counterparts by the specific material's temperature and pressure at the critical point, T_c and P_c:

$$T_r \equiv \frac{T}{T_c}, \qquad P_r \equiv \frac{P}{P_c}. \tag{4.294}$$

Often charts are available which give predictions of all reduced thermodynamic properties. These are most useful to capture the non-ideal gas behavior of materials for which tables are not available.

4.8 Mixtures with variable composition

Consider now mixtures of N species. The focus here will be on extensive properties and molar properties. Assume that each species has n_i moles, and the the total number of moles is $n = \sum_{i=1}^{N} n_i$. Now one might expect the extensive energy to be a function of the entropy, the volume *and* the number of moles of each species:

$$U = U(V, S, n_i). \tag{4.295}$$

The extensive version of the Gibbs law in which *all of the n_i are held constant* is

$$dU = -PdV + TdS. \tag{4.296}$$

Thus

$$\left.\frac{\partial U}{\partial V}\right|_{S,n_i} = -P, \qquad \left.\frac{\partial U}{\partial S}\right|_{V,n_i} = T. \tag{4.297}$$

In general, since $U = U(S, V, n_i)$, one should expect, for systems in which *the n_i are allowed to change* that

$$dU = \left.\frac{\partial U}{\partial V}\right|_{S,n_i} dV + \left.\frac{\partial U}{\partial S}\right|_{V,n_i} dS + \sum_{i=1}^{N} \left.\frac{\partial U}{\partial n_i}\right|_{S,V,n_j} dn_i. \tag{4.298}$$

Defining the new thermodynamics property, the *chemical potential* $\overline{\mu}_i$, as

$$\boxed{\overline{\mu}_i \equiv \left.\frac{\partial U}{\partial n_i}\right|_{S,V,n_j},} \tag{4.299}$$

one has the important *Gibbs equation for multicomponent systems*:

$$\boxed{dU = -PdV + TdS + \sum_{i=1}^{N} \overline{\mu}_i dn_i.} \tag{4.300}$$

Obviously, by its definition, $\overline{\mu}_i$ is on a per mole basis, so it is given the appropriate overline notation. In Eq. (4.300), the independent variables and their conjugates are

$$\begin{aligned} x_1 &= V, & \psi_1 &= -P, && (4.301)\\ x_2 &= S, & \psi_2 &= T, && (4.302)\\ x_3 &= n_1, & \psi_3 &= \overline{\mu}_1, && (4.303)\\ x_4 &= n_2, & \psi_4 &= \overline{\mu}_2, && (4.304)\\ &\vdots & &\vdots & \\ x_{N+2} &= n_N, & \psi_{N+2} &= \overline{\mu}_N. && (4.305) \end{aligned}$$

Equation (4.300) has $2^{N+1}-1$ Legendre functions. Three are in wide usage: the extensive analog to those earlier found. They are

$$\begin{aligned} H &= U + PV, && (4.306)\\ A &= U - TS, && (4.307)\\ G &= U + PV - TS. && (4.308) \end{aligned}$$

A set of non-traditional, but perfectly acceptable additional Legendre functions would be formed from $U - \overline{\mu}_1 n_1$. Another set would be formed from $U + PV - \overline{\mu}_2 n_2$. There are many more, but one in particular is sometimes noted in the literature: the so-called *grand potential*, Ω. The grand potential is defined as

$$\Omega \equiv U - TS - \sum_{i=1}^{N} \overline{\mu}_i n_i. \tag{4.309}$$

Differentiating each defined Legendre function, Eqs. (4.306-4.309), and combining with Eq. (4.300), one finds

$$\begin{aligned} dH &= TdS + VdP + \sum_{i=1}^{N} \overline{\mu}_i dn_i, && (4.310)\\ dA &= -SdT - PdV + \sum_{i=1}^{N} \overline{\mu}_i dn_i, && (4.311)\\ dG &= -SdT + VdP + \sum_{i=1}^{N} \overline{\mu}_i dn_i, && (4.312)\\ d\Omega &= -PdV - SdT - \sum_{i=1}^{N} n_i d\overline{\mu}_i. && (4.313) \end{aligned}$$

Thus, canonical variables for H are $H = H(S, P, n_i)$. One finds a similar set of relations as

before from each of the differential forms:

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,n_i} = \left.\frac{\partial H}{\partial S}\right|_{P,n_i}, \tag{4.314}$$

$$P = -\left.\frac{\partial U}{\partial V}\right|_{S,n_i} = -\left.\frac{\partial A}{\partial V}\right|_{T,n_i} = -\left.\frac{\partial \Omega}{\partial V}\right|_{T,\overline{\mu}_i}, \tag{4.315}$$

$$V = \left.\frac{\partial H}{\partial P}\right|_{S,n_i} = \left.\frac{\partial G}{\partial P}\right|_{T,n_i}, \tag{4.316}$$

$$S = -\left.\frac{\partial A}{\partial T}\right|_{V,n_i} = -\left.\frac{\partial G}{\partial T}\right|_{P,n_i} = -\left.\frac{\partial \Omega}{\partial T}\right|_{V,\overline{\mu}_i}, \tag{4.317}$$

$$n_i = -\left.\frac{\partial \Omega}{\partial \overline{\mu}_i}\right|_{V,T,\overline{\mu}_j}. \tag{4.318}$$

$$\overline{\mu}_i = \left.\frac{\partial U}{\partial n_i}\right|_{S,V,n_j} = \left.\frac{\partial H}{\partial n_i}\right|_{S,P,n_j} = \left.\frac{\partial A}{\partial n_i}\right|_{T,V,n_j} = \left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} \tag{4.319}$$

Each of these induces a corresponding Maxwell relation, obtained by cross differentiation. These are

$$\left.\frac{\partial T}{\partial V}\right|_{S,n_i} = -\left.\frac{\partial P}{\partial S}\right|_{V,n_i}, \tag{4.320}$$

$$\left.\frac{\partial T}{\partial P}\right|_{S,n_i} = \left.\frac{\partial V}{\partial S}\right|_{P,n_i}, \tag{4.321}$$

$$\left.\frac{\partial P}{\partial T}\right|_{V,n_i} = \left.\frac{\partial S}{\partial V}\right|_{T,n_i}, \tag{4.322}$$

$$\left.\frac{\partial V}{\partial T}\right|_{P,n_i} = -\left.\frac{\partial S}{\partial P}\right|_{T,n_i}, \tag{4.323}$$

$$\left.\frac{\partial \overline{\mu}_i}{\partial T}\right|_{P,n_j} = -\left.\frac{\partial S}{\partial n_i}\right|_{V,n_j}, \tag{4.324}$$

$$\left.\frac{\partial \overline{\mu}_i}{\partial P}\right|_{T,n_j} = \left.\frac{\partial V}{\partial n_i}\right|_{V,n_j}, \tag{4.325}$$

$$\left.\frac{\partial \overline{\mu}_l}{\partial n_k}\right|_{T,P,n_j} = \left.\frac{\partial \overline{\mu}_k}{\partial n_l}\right|_{T,P,n_j}, \tag{4.326}$$

$$\left.\frac{\partial S}{\partial V}\right|_{T,\overline{\mu}_i} = \left.\frac{\partial P}{\partial T}\right|_{V,\overline{\mu}_i}, \tag{4.327}$$

$$\left.\frac{\partial n_i}{\partial \overline{\mu}_k}\right|_{V,T,\overline{\mu}_j,j\neq k} = \left.\frac{\partial n_k}{\partial \overline{\mu}_i}\right|_{V,T,\overline{\mu}_j,j\neq i} \tag{4.328}$$

4.9 Partial molar properties

4.9.1 Homogeneous functions

In mathematics, a *homogeneous function* $f(x_1, \ldots, x_N)$ *of order* m is one such that

$$f(\lambda x_1, \ldots, \lambda x_N) = \lambda^m f(x_1, \ldots, x_N). \tag{4.329}$$

If $m = 1$, one has

$$f(\lambda x_1, \ldots, \lambda x_N) = \lambda f(x_1, \ldots, x_N). \tag{4.330}$$

Thermodynamic variables are examples of homogeneous functions.

4.9.2 Gibbs free energy

Consider an extensive property, such as the Gibbs free energy G. One has the canonical form

$$G = G(T, P, n_1, n_2, \ldots, n_N). \tag{4.331}$$

One would like to show that if each of the mole numbers n_i is increased by a common factor, say λ, with T and P constant, that G increases by the same factor λ:

$$\lambda G(T, P, n_1, n_2, \ldots, n_N) = G(T, P, \lambda n_1, \lambda n_2, \ldots, \lambda n_N). \tag{4.332}$$

Differentiate both sides of Eq. (4.332) with respect to λ, while holding P, T, and n_j constant, to get

$$G(T, P, n_1, n_2, \ldots, n_N) =$$

$$\left.\frac{\partial G}{\partial(\lambda n_1)}\right|_{n_j,P,T} \frac{d(\lambda n_1)}{d\lambda} + \left.\frac{\partial G}{\partial(\lambda n_2)}\right|_{n_j,P,T} \frac{d(\lambda n_2)}{d\lambda} + \cdots + \left.\frac{\partial G}{\partial(\lambda n_N)}\right|_{n_j,P,T} \frac{d(\lambda n_N)}{d\lambda}, \tag{4.333}$$

$$= \left.\frac{\partial G}{\partial(\lambda n_1)}\right|_{n_j,P,T} n_1 + \left.\frac{\partial G}{\partial(\lambda n_2)}\right|_{n_j,P,T} n_2 + \cdots + \left.\frac{\partial G}{\partial(\lambda n_N)}\right|_{n_j,P,T} n_N, \tag{4.334}$$

This must hold for all λ, including $\lambda = 1$, so one requires

$$G(T, P, n_1, n_2, \ldots, n_N) = \left.\frac{\partial G}{\partial n_1}\right|_{n_j,P,T} n_1 + \left.\frac{\partial G}{\partial n_2}\right|_{n_j,P,T} n_2 + \cdots + \left.\frac{\partial G}{\partial n_N}\right|_{n_j,P,T} n_N, \tag{4.335}$$

$$= \sum_{i=1}^{N} \left.\frac{\partial G}{\partial n_i}\right|_{n_j,P,T} n_i. \tag{4.336}$$

Recall now the definition *partial molar property*, the derivative of an extensive variable with respect to species n_i holding n_j, $i \neq j$, T, and P constant. Because the result has units per

mole, an overline superscript is utilized. The partial molar Gibbs free energy of species i, $\overline{g}_i$ is then

$$\overline{g}_i \equiv \left.\frac{\partial G}{\partial n_i}\right|_{n_j,P,T}, \tag{4.337}$$

so that

$$G = \sum_{i=1}^{N} \overline{g}_i n_i. \tag{4.338}$$

Using the definition of chemical potential, Eq. (4.319), one also notes then that

$$G(T, P, n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} \overline{\mu}_i n_i. \tag{4.339}$$

The temperature and pressure dependence of G must lie entirely within $\overline{\mu}_i(T, P, n_j)$, which one notes is also allowed to be a function of n_j as well. Consequently, one also sees that the Gibbs free energy per unit mole of species i is the chemical potential of that species:

$$\overline{g}_i = \overline{\mu}_i. \tag{4.340}$$

Using Eq. (4.338) to eliminate G in Eq. (4.308), one recovers an equation for the energy:

$$U = -PV + TS + \sum_{i=1}^{N} \overline{\mu}_i n_i. \tag{4.341}$$

4.9.3 Other properties

A similar result also holds for any other extensive property such as V, U, H, A, or S. One can also show that

$$V = \sum_{i=1}^{N} n_i \left.\frac{\partial V}{\partial n_i}\right|_{n_j,A,T}, \tag{4.342}$$

$$U = \sum_{i=1}^{N} n_i \left.\frac{\partial U}{\partial n_i}\right|_{n_j,V,S} \tag{4.343}$$

$$H = \sum_{i=1}^{N} n_i \left.\frac{\partial H}{\partial n_i}\right|_{n_j,P,S}, \tag{4.344}$$

$$A = \sum_{i=1}^{N} n_i \left.\frac{\partial A}{\partial n_i}\right|_{n_j,T,V}, \tag{4.345}$$

$$S = \sum_{i=1}^{N} n_i \left.\frac{\partial S}{\partial n_i}\right|_{n_j,U,T}. \tag{4.346}$$

Note that these expressions do not formally involve partial molar properties since P and T are not constant.

Take now the appropriate partial molar derivatives of G for an ideal mixture of ideal gases to get some useful relations:

$$\begin{aligned} G &= H - TS, && (4.347)\\ \left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} &= \left.\frac{\partial H}{\partial n_i}\right|_{T,P,n_j} - T\left.\frac{\partial S}{\partial n_i}\right|_{T,P,n_j}. && (4.348) \end{aligned}$$

Now from the definition of an ideal mixture $\overline{h}_i = \overline{h}_i(T,P)$, so one has

$$\begin{aligned} H &= \sum_{k=1}^{N} n_k \overline{h}_k(T,P), && (4.349)\\ \left.\frac{\partial H}{\partial n_i}\right|_{T,P,n_j} &= \frac{\partial}{\partial n_i}\left(\sum_{k=1}^{N} n_k \overline{h}_k(T,P)\right), && (4.350)\\ &= \sum_{k=1}^{N} \underbrace{\frac{\partial n_k}{\partial n_i}}_{=\delta_{ik}} \overline{h}_k(T,P), && (4.351)\\ &= \sum_{k=1}^{N} \delta_{ik} \overline{h}_k(T,P), && (4.352)\\ &= \overline{h}_i(T,P). && (4.353) \end{aligned}$$

Here, the Kronecker delta function δ_{ki} has been again used. Now for an ideal gas one further has $\overline{h}_i = \overline{h}_i(T)$. The analysis is more complicated for the entropy, in which

$$\begin{aligned} S &= \sum_{k=1}^{N} n_k \left(\overline{s}^o_{T,k} - \overline{R}\ln\left(\frac{P_k}{P_o}\right)\right), && (4.354)\\ &= \sum_{k=1}^{N} n_k \left(\overline{s}^o_{T,k} - \overline{R}\ln\left(\frac{y_k P}{P_o}\right)\right), && (4.355)\\ &= \sum_{k=1}^{N} n_k \left(\overline{s}^o_{T,k} - \overline{R}\ln\left(\frac{P}{P_o}\right) - \overline{R}\ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right), && (4.356)\\ &= \sum_{k=1}^{N} n_k \left(\overline{s}^o_{T,k} - \overline{R}\ln\left(\frac{P}{P_o}\right)\right) - \overline{R}\sum_{k=1}^{N} n_k \ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right), && (4.357) \end{aligned}$$

$$\left.\frac{\partial S}{\partial n_i}\right|_{T,P,n_j} = \frac{\partial}{\partial n_i}\sum_{k=1}^{N} n_k\left(\overline{s}^o_{T,k} - \overline{R}\ln\left(\frac{P}{P_o}\right)\right) - \overline{R}\left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j}\left(\sum_{k=1}^{N} n_k \ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right), \tag{4.358}$$

$$= \sum_{k=1}^{N} \underbrace{\frac{\partial n_k}{\partial n_i}}_{=\delta_{ik}}\left(\overline{s}^o_{T,k} - \overline{R}\ln\left(\frac{P}{P_o}\right)\right) - \overline{R}\left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j}\left(\sum_{k=1}^{N} n_k \ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right), \tag{4.359}$$

$$= \left(\overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{P}{P_o}\right)\right) - \overline{R}\left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j}\left(\sum_{k=1}^{N} n_k \ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right). \tag{4.360}$$

Evaluation of the final term on the right side requires closer examination, and in fact, after tedious but straightforward analysis, yields a simple result which can easily be verified by direct calculation:

$$\left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j}\left(\sum_{k=1}^{N} n_k \ln\left(\frac{n_k}{\sum_{q=1}^{N} n_q}\right)\right) = \ln\left(\frac{n_i}{\sum_{q=1}^{N} n_q}\right). \tag{4.361}$$

So the partial molar entropy is in fact

$$\left.\frac{\partial S}{\partial n_i}\right|_{T,P,n_j} = \overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{P}{P_o}\right) - \overline{R}\ln\left(\frac{n_i}{\sum_{q=1}^{N} n_q}\right), \tag{4.362}$$

$$= \overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{P}{P_o}\right) - \overline{R}\ln y_i, \tag{4.363}$$

$$= \overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{P_i}{P_o}\right), \tag{4.364}$$

$$= \overline{s}_i \tag{4.365}$$

Thus, one can in fact claim for the ideal mixture of ideal gases that

$$\boxed{\overline{g}_i = \overline{h}_i - T\overline{s}_i.} \tag{4.366}$$

4.9.4 Relation between mixture and partial molar properties

A simple analysis shows how the partial molar property for an individual species is related to the partial molar property for the mixture. Consider, for example, the Gibbs free energy. The mixture-averaged Gibbs free energy per unit mole is

$$\overline{g} = \frac{G}{n}. \tag{4.367}$$

Now take a partial molar derivative and analyze to get

$$\left.\frac{\partial \overline{g}}{\partial n_i}\right|_{T,P,n_j} = \frac{1}{n}\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} - \frac{G}{n^2}\left.\frac{\partial n}{\partial n_i}\right|_{T,P,n_j}, \tag{4.368}$$

$$= \frac{1}{n}\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} - \frac{G}{n^2}\left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j}\left(\sum_{k=1}^{N} n_k\right), \tag{4.369}$$

$$= \frac{1}{n}\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} - \frac{G}{n^2}\sum_{k=1}^{N}\left.\frac{\partial n_k}{\partial n_i}\right|_{T,P,n_j}, \tag{4.370}$$

$$= \frac{1}{n}\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} - \frac{G}{n^2}\sum_{k=1}^{N}\delta_{ik}, \tag{4.371}$$

$$= \frac{1}{n}\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j} - \frac{G}{n^2}, \tag{4.372}$$

$$= \frac{1}{n}\overline{g}_i - \frac{\overline{g}}{n}. \tag{4.373}$$

Multiplying by n and rearranging, one gets

$$\boxed{\overline{g}_i = \overline{g} + n\left.\frac{\partial \overline{g}}{\partial n_i}\right|_{T,P,n_j}}. \tag{4.374}$$

A similar result holds for other properties.

4.10 Irreversible entropy production in a closed system

Consider a multicomponent thermodynamic system *closed to mass exchanges with its surroundings* coming into equilibrium. Allow the system to be exchanging work and heat with its surroundings. Assume the temperature difference between the system and its surroundings is so small that both can be considered to be at temperature T. If δQ is introduced into the system, then the surroundings suffer a loss of entropy:

$$dS_{surr} = -\frac{\delta Q}{T}. \tag{4.375}$$

The system's entropy S can change via this heat transfer, as well as via other internal irreversible processes, such as internal chemical reaction. The second law of thermodynamics requires that the entropy change of the universe be positive semi-definite:

$$dS + dS_{surr} \geq 0. \tag{4.376}$$

Eliminating dS_{surr}, one requires for the system that

$$dS \geq \frac{\delta Q}{T}. \tag{4.377}$$

Consider temporarily the assumption that the work and heat transfer are both reversible. Thus, the irreversible entropy production must be associated with internal chemical reaction. Now the first law for the entire system gives

$$\begin{aligned} dU &= \delta Q - \delta W, && (4.378)\\ &= \delta Q - PdV, && (4.379)\\ \delta Q &= dU + PdV. && (4.380) \end{aligned}$$

Note because the system is closed, there can be no species entering or exiting, and so there is no change dU attributable to dn_i. While within the system the dn_i may not be 0, the *net* contribution to the change in total internal energy is zero. A non-zero dn_i within the system simply re-partitions a fixed amount of total energy from one species to another. Substituting Eq. (4.380) into Eq. (4.377) to eliminate δQ, one gets

$$\begin{aligned} dS &\geq \frac{1}{T}\underbrace{(dU + PdV)}_{=\delta Q}, && (4.381)\\ TdS - dU - PdV &\geq 0, && (4.382)\\ dU - TdS + PdV &\leq 0. && (4.383) \end{aligned}$$

Eq. (4.383) involves properties only and need not require assumptions of reversibility for processes in its derivation. In special cases, it reduces to simpler forms.

For processes which are isentropic and isochoric, the second law expression, Eq. (4.383), reduces to

$$dU|_{S,V} \leq 0. \tag{4.384}$$

For processes which are isoenergetic and isochoric, the second law expression, Eq. (4.383), reduces to

$$dS|_{U,V} \geq 0. \tag{4.385}$$

Now using Eq. (4.300) to eliminate dS in Eq. (4.385), one can express the second law as

$$\begin{aligned} \underbrace{\left(\frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i\right)}_{=dS}\Bigg|_{U,V} &\geq 0, && (4.386)\\ \underbrace{-\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i}_{\text{irreversible entropy production}} &\geq 0. && (4.387) \end{aligned}$$

The irreversible entropy production associated with the internal chemical reaction must be the left side of Eq. (4.387). Often the irreversible entropy production is defined as σ, with

the second law requiring $d\sigma \geq 0$. Equation (4.387) in terms of $d\sigma$ is

$$d\sigma = -\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i \geq 0. \tag{4.388}$$

Now, while most standard texts focusing on equilibrium thermodynamics go to great lengths to avoid the introduction of time, it really belongs in a discussion describing the approach to equilibrium. One can divide Eq. (4.387) by a *positive* time increment dt to get

$$-\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i\frac{dn_i}{dt} \geq 0. \tag{4.389}$$

Since $T \geq 0$, one can multiply Eq. (4.389) by $-T$ to get

$$\sum_{i=1}^{N}\overline{\mu}_i\frac{dn_i}{dt} \leq 0. \tag{4.390}$$

This will hold *if* a model for $\frac{dn_i}{dt}$ is employed which guarantees that the left side of Eq. (4.390) is negative semi-definite. One will expect then for dn_i/dt to be related to the chemical potentials $\overline{\mu}_i$.

Elimination of dU in Eq. (4.383) in favor of dH from $dH = dU + PdV + VdP$ gives

$$\underbrace{dH - PdV - VdP}_{=dU} - TdS + PdV \leq 0, \tag{4.391}$$

$$dH - VdP - TdS \leq 0. \tag{4.392}$$

Thus, one finds for isobaric, isentropic equilibration that

$$dH|_{P,S} \leq 0. \tag{4.393}$$

For the Helmholtz and Gibbs free energies, one analogously finds

$$dA|_{T,V} \leq 0, \tag{4.394}$$

$$dG|_{T,P} \leq 0. \tag{4.395}$$

The expression of the second law in terms of dG is especially useful as it may be easy in an experiment to control so that P and T are constant. This is especially true in an isobaric phase change, in which the temperature is guaranteed to be constant as well.

Now one has

$$G = \sum_{i=1}^{N} n_i\overline{g}_i, \tag{4.396}$$

$$= \sum_{i=1}^{N} n_i\overline{\mu}_i. \tag{4.397}$$

One also has from Eq. (4.312): $dG = -SdT + VdP + \sum_{i=1}^{N} \overline{\mu}_i dn_i$, holding T and P constant that

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i. \tag{4.398}$$

Here the dn_i are associated entirely with internal chemical reactions. Substituting Eq. (4.398) into Eq. (4.395), one gets the important version of the second law which holds that

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i \leq 0. \tag{4.399}$$

In terms of time rates of change, one can divide Eq. (4.399) by a positive time increment $dt > 0$ to get

$$\boxed{\left.\frac{\partial G}{\partial t}\right|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt} \leq 0.} \tag{4.400}$$

4.11 Equilibrium in a two-component system

A major task of *non-equilibrium thermodynamics* is to find a functional form for dn_i/dt which guarantees satisfaction of the second law, Eq. (4.400) and gives predictions which agree with experiment. This will be discussed in more detail in the following chapter on thermochemistry. At this point, some simple examples will be given in which a naïve but useful functional form for dn_i/dt is posed which leads at least to predictions of the correct equilibrium values. A much better model which gives the correct dynamics in the time domain of the system as it approaches equilibrium will be presented in the chapter on thermochemistry.

4.11.1 Phase equilibrium

Here, consider two examples describing systems in phase equilibrium.

Example 4.12

Consider an equilibrium two-phase mixture of liquid and vapor H_2O at $T = 100\ ^\circ C$, $x = 0.5$. Use the steam tables to check if equilibrium properties are satisfied.

In a two-phase gas liquid mixture one can expect the following reaction:

$$H_2O_{(l)} \leftrightharpoons H_2O_{(g)}. \tag{4.401}$$

That is one mole of liquid, in the forward phase change, evaporates to form one mole of gas. In the reverse phase change, one mole of gas condenses to form one mole of liquid.

Because T is fixed at 100 $^\circ C$ and the material is a two phase mixture, the pressure is also fixed at a constant. Here there are two phases at saturation; g for gas and l for liquid. Equation (4.399) reduces to

$$\overline{\mu}_l dn_l + \overline{\mu}_g dn_g \leq 0. \tag{4.402}$$

Now for the pure H_2O if a loss of moles from one phase must be compensated by the addition to another. So one must have

$$dn_l + dn_g = 0. \tag{4.403}$$

Hence

$$dn_g = -dn_l. \tag{4.404}$$

So Eq. (4.402), using Eq. (4.404) becomes

$$\begin{aligned} \overline{\mu}_l dn_l - \overline{\mu}_g dn_l &\leq 0, & (4.405)\\ dn_l(\overline{\mu}_l - \overline{\mu}_g) &\leq 0. & (4.406) \end{aligned}$$

At this stage of the analysis, most texts, grounded in equilibrium thermodynamics, assert that $\overline{\mu}_l = \overline{\mu}_g$, ignoring the fact that they could be different but dn_l could be zero. That approach will not be taken here. Instead divide Eq. (4.406) by a positive time increment, $dt \geq 0$ to write the second law as

$$\frac{dn_l}{dt}(\overline{\mu}_l - \overline{\mu}_g) \leq 0. \tag{4.407}$$

One convenient, albeit naïve, way to guarantee second law satisfaction is to let

$$\frac{dn_l}{dt} = -\kappa(\overline{\mu}_l - \overline{\mu}_g), \qquad \kappa \geq 0, \qquad \textit{convenient, but naïve model} \tag{4.408}$$

Here κ is some positive semi-definite scalar rate constant which dictates the time scale of approach to equilibrium. Note that Eq. (4.408) is just a hypothesized model. It has *no experimental verification*; in fact, other more complex models exist which both agree with experiment and satisfy the second law. For the purposes of the present argument, however, Eq. (4.408) will suffice. With this assumption, the second law reduces to

$$-\kappa(\overline{\mu}_l - \overline{\mu}_g)^2 \leq 0, \qquad \kappa \geq 0, \tag{4.409}$$

which is always true.

Eq. (4.408) has two important consequences:

- Differences in chemical potential drive changes in the number of moles.
- The number of moles of liquid, n_l, *increases* when the chemical potential of the liquid is less than that of the gas, $\overline{\mu}_l < \overline{\mu}_g$. That is to say, when the liquid has a lower chemical potential than the gas, the gas is driven towards the phase with the lower potential. Because such a phase change is isobaric and isothermal, the Gibbs free energy is the appropriate variable to consider, and one takes $\overline{\mu} = \overline{g}$. When this is so, the Gibbs free energy of the mixture, $G = n_l\overline{\mu}_l + n_g\overline{\mu}_g$ is being driven to a lower value. So when $dG = 0$, the system has a minimum G.
- The system is in equilibrium when the chemical potentials of liquid and gas are equal: $\overline{\mu}_l = \overline{\mu}_g$.

The chemical potentials, and hence the molar specific Gibbs free energies must be the same for each constituent of the binary mixture at the phase equilibrium. That is

$$\overline{g}_l = \overline{g}_g. \tag{4.410}$$

Now since both the liquid and gas have the same molecular mass, one also has the mass specific Gibbs free energies equal at phase equilibrium:

$$g_l = g_g. \tag{4.411}$$

This can be verified from the steam tables, using the definition $g = h - Ts$. From the tables

$$g_l = h_l - Ts_l = 419.02\ \frac{kJ}{kg} - ((100 + 273.15)\ K)\left(1.3068\ \frac{kJ}{kg\ K}\right) = -68.6\ \frac{kJ}{kg}, \tag{4.412}$$

$$g_g = h_g - Ts_g = 2676.05\ \frac{kJ}{kg} - ((100 + 273.15)\ K)\left(7.3548\ \frac{kJ}{kg\ K}\right) = -68.4\ \frac{kJ}{kg}. \tag{4.413}$$

The two values are essentially the same; the difference is likely due to table inaccuracies.

Example 4.13

This example is from BS, 16.20, p. 700. A container has liquid water at 20 $°C$, 100 kPa, in equilibrium with a mixture of water vapor and dry air, also at 20 $°C$, 100 kPa. Find the water vapor pressure and the saturated water vapor pressure.

Now at this temperature, the tables easily show that the pressure of a saturated vapor is $P_{sat} = \boxed{2.339\ kPa}$. From the previous example, it is known that for the water liquid and vapor in equilibrium, one has

$$g_{liq} = g_{vap}. \tag{4.414}$$

Now if both the liquid and the vapor were at the saturated state, they would be in phase equilibrium and that would be the end of the problem. But they have slight deviations from the saturated state. One can estimate these deviations with the standard formula

$$dg = -sdT + vdP. \tag{4.415}$$

The tables will be used to get values at 20 $°C$, for which one can take $dT = 0$. This allows the approximation of $dg \sim v\ dP$. So for the liquid,

$$g_{liq} - g_f = \int v\ dP \sim v_f(P - P_{sat}), \tag{4.416}$$

$$g_{liq} = g_f + v_f(P - P_{sat}). \tag{4.417}$$

For the vapor, approximated here as an ideal gas, one has

$$g_{vap} - g_g = \int v\ dP, \tag{4.418}$$

$$= RT \int \frac{dP}{P}, \tag{4.419}$$

$$= RT \ln \frac{P_{vap}}{P_{sat}}, \tag{4.420}$$

$$g_{vap} = g_g + RT \ln \frac{P_{vap}}{P_{sat}}. \tag{4.421}$$

Here, once again, one allows for deviations of the pressure of the vapor from the saturation pressure. Now at equilibrium, one enforces $g_{liq} = g_{vap}$, so one has

$$\underbrace{g_f + v_f(P - P_{sat})}_{=g_{liq}} = \underbrace{g_g + RT \ln \frac{P_{vap}}{P_{sat}}}_{=g_{vap}}. \tag{4.422}$$

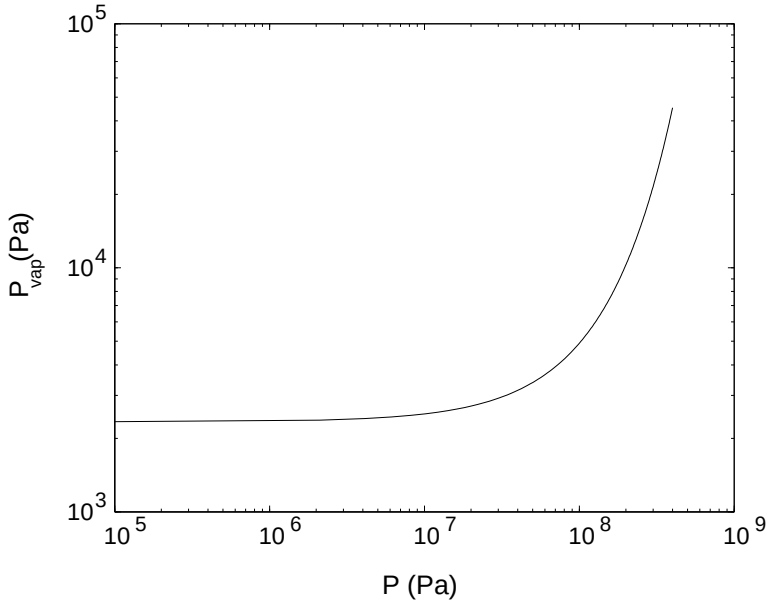

Figure 4.1: Pressure of water vapor as a function of total pressure for example problem.

Now $g_f = g_g$, so one gets

$$v_f(P - P_{sat}) = RT \ln \frac{P_{vap}}{P_{sat}}. \tag{4.423}$$

Solving for P_{vap}, one gets

$$\begin{aligned} P_{vap} &= P_{sat} \exp\left(\frac{v_f(P - P_{sat})}{RT}\right), & (4.424)\\ &= (2.339\ kPa) \exp\left(\frac{\left(0.001002\ \frac{m^3}{kg}\right)(100\ kPa - 2.339\ kPa)}{\left(0.4615\ \frac{kJ}{kg\ K}\right)(293.15\ K)}\right), & (4.425)\\ &= \boxed{2.3407\ kPa.} & (4.426) \end{aligned}$$

The pressure is very near the saturation pressure. This justifies assumptions that for such mixtures, one can take the pressure of the water vapor to be that at saturation if the mixture is in equilibrium. If the pressure is higher, the pressure of the vapor becomes higher as well. Figure 4.1 shows how the pressure of the equilibrium vapor pressure varies with total pressure. Clearly, a very high total pressure, on the order of 1 GPa is needed to induce the vapor pressure to deviate significantly from the saturation value.

4.11.2 Chemical equilibrium: introduction

Here consider two examples which identify the equilibrium state of a chemically reactive system.

4.11.2.1 Isothermal, isochoric system

The simplest system to consider is isothermal and isochoric. The isochoric assumption implies there is no work in coming to equilibrium.

Example 4.14

At high temperatures, collisions between diatomic nitrogen molecules induce the production of monatomic nitrogen molecules. The chemical reaction can be described by the model

$$N_2 + N_2 \leftrightharpoons 2N + N_2. \tag{4.427}$$

Here one of the N_2 molecules behaves as an inert third body. An N_2 molecule has to collide with *something*, to induce the reaction. Some authors leave out the third body and write instead $N_2 \leftrightharpoons 2N$, but this does not reflect the true physics as well. The inert third body is especially important when the time scales of reaction are considered. It plays no role in equilibrium chemistry.

Consider 1 $kmole$ of N_2 and 0 $kmole$ of N at a pressure of 100 kPa and a temperature of 6000 K. Using the ideal gas tables, find the equilibrium concentrations of N and N_2 if the equilibration process is *isothermal* and *isochoric*.

The ideal gas law can give the volume.

$$\begin{aligned} P_1 &= \frac{n_{N_2}\overline{R}T}{V}, & (4.428)\\ V &= \frac{n_{N_2}\overline{R}T}{P_1}, & (4.429)\\ &= \frac{(1\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{100\ kPa}, & (4.430)\\ &= 498.84\ m^3. & (4.431) \end{aligned}$$

Initially, the mixture is all N_2, so its partial pressure is the total pressure, and the initial partial pressure of N is 0.

Now every time an N_2 molecule reacts and thus undergo a negative change, 2 N molecules are created and thus undergo a positive change, so

$$-dn_{N_2} = \frac{1}{2}dn_N. \tag{4.432}$$

This can be parameterized by a reaction progress variable ζ, also called the *degree of reaction*, defined such that

$$\begin{aligned} d\zeta &= -dn_{N_2}, & (4.433)\\ d\zeta &= \frac{1}{2}dn_N. & (4.434) \end{aligned}$$

As an aside, one can integrate this, taking $\zeta = 0$ at the initial state to get

$$\begin{aligned} \zeta &= n_{N_2}|_{t=0} - n_{N_2}, & (4.435)\\ \zeta &= \frac{1}{2}n_N. & (4.436) \end{aligned}$$

Thus

$$\begin{aligned} n_{N_2} &= n_{N_2}|_{t=0} - \zeta, & (4.437)\\ n_N &= 2\zeta. & (4.438) \end{aligned}$$

One can also eliminate ζ to get n_N in terms of n_{N_2}:

$$n_N = 2\left(n_{N_2}|_{t=0} - n_{N_2}\right). \tag{4.439}$$

Now for the reaction, one must have, for second law satisfaction, that

$$\begin{aligned}
\overline{\mu}_{N_2} dn_{N_2} + \overline{\mu}_N dn_N &\leq 0, && (4.440)\\
\overline{\mu}_{N_2}(-d\zeta) + \overline{\mu}_N (2d\zeta) &\leq 0, && (4.441)\\
\left(-\overline{\mu}_{N_2} + 2\overline{\mu}_N\right) d\zeta &\leq 0 && (4.442)\\
\left(-\overline{\mu}_{N_2} + 2\overline{\mu}_N\right) \frac{d\zeta}{dt} &\leq 0. && (4.443)
\end{aligned}$$

In order to satisfy the second law, one can usefully, but naïvely, hypothesize that the *non-equilibrium* reaction kinetics are given by

$$\frac{d\zeta}{dt} = -k(-\overline{\mu}_{N_2} + 2\overline{\mu}_N), \qquad k \geq 0, \qquad \textit{convenient, but naïve model} \tag{4.444}$$

Note there are other ways to guarantee second law satisfaction. In fact, a more complicated model is well known to fit data well, and will be studied later. For the present purposes, this naïve model will suffice. With this assumption, the second law reduces to

$$-k(-\overline{\mu}_{N_2} + 2\overline{\mu}_N)^2 \leq 0, \qquad k \geq 0, \tag{4.445}$$

which is always true. Obviously, the reaction ceases when $d\zeta/dt = 0$, which holds only when

$$2\overline{\mu}_N = \overline{\mu}_{N_2}. \tag{4.446}$$

Away from equilibrium, for the reaction to go forward, one must expect $d\zeta/dt > 0$, and then one must have

$$\begin{aligned}
-\overline{\mu}_{N_2} + 2\overline{\mu}_N &\leq 0, && (4.447)\\
2\overline{\mu}_N &\leq \overline{\mu}_{N_2}. && (4.448)
\end{aligned}$$

The chemical potentials are the molar specific Gibbs free energies; thus, for the reaction to go forward, one must have

$$2\overline{g}_N \leq \overline{g}_{N_2}. \tag{4.449}$$

Substituting using the definitions of Gibbs free energy, one gets

$$\begin{aligned}
2\left(\overline{h}_N - T\,\overline{s}_N\right) &\leq \overline{h}_{N_2} - T\,\overline{s}_{N_2}, && (4.450)\\
2\left(\overline{h}_N - T\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{y_N P}{P_o}\right)\right)\right) &\leq \overline{h}_{N_2} - T\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{y_{N_2} P}{P_o}\right)\right), && (4.451)\\
2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) - \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) &\leq -2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) + \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), && (4.452)\\
-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) &\geq 2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) - \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), && (4.453)\\
-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) &\geq \overline{R}T\ln\left(\frac{y_N^2 P^2}{P_o^2}\frac{P_o}{P y_{N_2}}\right), && (4.454)\\
-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) &\geq \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right). && (4.455)
\end{aligned}$$

At the initial state, one has $y_N = 0$, so the right hand side approaches $-\infty$, and the inequality holds. At equilibrium, one has equality.

$$-2\left(\overline{h}_N - T\ \overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\ \overline{s}^o_{T,N_2}\right) \quad = \quad \overline{R}T \ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right). \tag{4.456}$$

Taking numerical values from Table A.9:

$$\begin{aligned}
&-2\left(5.9727\times 10^5\ \frac{kJ}{kmole} - (6000\ K)\left(216.926\ \frac{kJ}{kmole\ K}\right)\right) + \\
&\quad\left(2.05848\times 10^5\ \frac{kJ}{kmole} - (6000\ K)\left(292.984\ \frac{kJ}{kmole\ K}\right)\right) \\
&\qquad = \left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)\ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right), \\
&\underbrace{-2.87635}_{\equiv \ln K_P} = \ln\left(\frac{y_N^2}{y_{N_2}}\frac{P}{P_o}\right), \qquad (4.457)\\
&\underbrace{0.0563399}_{\equiv K_P} = \frac{y_N^2}{y_{N_2}}\frac{P}{P_o}, \qquad (4.458)\\
&\qquad = \frac{\left(\frac{n_N}{n_N+n_{N_2}}\right)^2}{\left(\frac{n_{N_2}}{n_N+n_{N_2}}\right)}(n_N+n_{N_2})\frac{\overline{R}T}{P_oV}, \qquad (4.459)\\
&\qquad = \frac{n_N^2}{n_{N_2}}\frac{\overline{R}T}{P_oV}, \qquad (4.460)\\
&\qquad = \frac{\left(2\left(n_{N_2}|_{t=0} - n_{N_2}\right)\right)^2}{n_{N_2}}\frac{\overline{R}T}{P_oV}, \qquad (4.461)\\
&\qquad = \frac{\left(2\left(1\ kmole - n_{N_2}\right)\right)^2}{n_{N_2}}\frac{(8.314)(6000)}{(100)(498.84)}. \qquad (4.462)
\end{aligned}$$

This is a quadratic equation for n_{N_2}. It has two roots

$$n_{N_2} = 0.888154\ kmole \qquad \text{physical;} \qquad n_{N_2} = 1.12593\ kmole, \qquad \text{non-physical} \tag{4.463}$$

The second root generates more N_2 than at the start, and also yields non-physically negative $n_N = -0.25186\ kmole$. So at equilibrium, the physical root is

$$n_N = 2(1 - n_{N_2}) = 2(1 - 0.888154) = 0.223693\ kmole. \tag{4.464}$$

The diatomic species is preferred.

Note in the preceding analysis, the term K_P was introduced. This is the so-called equilibrium "constant" which is really a function of temperature. It will be described in more detail later, but one notes that it is commonly tabulated for some reactions. Its tabular value can be derived from the more fundamental quantities shown in this example. BS's Table A.11 gives for this reaction at 6000 K the value of $\ln K_P = -2.876$. Note that K_P is fundamentally defined in terms of thermodynamic properties for a system which may or may not be at chemical equilibrium. Only at chemical equilibrium, can it can further be related to mole fraction and pressure ratios.

The pressure at equilibrium is

$$\begin{aligned} P_2 &= \frac{(n_{N_2} + n_N)\overline{R}T}{V}, && (4.465)\\ &= \frac{(0.888154\ kmole + 0.223693\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{498.84}, && (4.466)\\ &= 111.185\ kPa. && (4.467) \end{aligned}$$

The pressure has increased because there are more molecules with the volume and temperature being equal.

The molar concentrations $\overline{\rho}_i$ at equilibrium, are

$$\begin{aligned} \overline{\rho}_N &= \frac{0.223693\ kmole}{498.84\ m^3} = 4.484 \times 10^{-4}\ \frac{kmole}{m^3} = \boxed{4.484 \times 10^{-7}\ \frac{mole}{cm^3},} && (4.468)\\ \overline{\rho}_{N_2} &= \frac{0.888154\ kmole}{498.84\ m^3} = 1.78044 \times 10^{-3}\ \frac{kmole}{m^3} = \boxed{1.78044 \times 10^{-6}\ \frac{mole}{cm^3}.} && (4.469) \end{aligned}$$

Now consider the heat transfer. One knows for the isochoric process that ${}_1Q_2 = U_2 - U_1$. The initial energy is given by

$$\begin{aligned} U_1 &= n_{N_2}\overline{u}_{N_2}, && (4.470)\\ &= n_{N_2}(\overline{h}_{N_2} - \overline{R}T), && (4.471)\\ &= (1\ kmole)\left(2.05848 \times 10^5\ \frac{kJ}{kmole} - \left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)\right), && (4.472)\\ &= 1.555964 \times 10^5\ kJ. && (4.473) \end{aligned}$$

The energy at the final state is

$$\begin{aligned} U_2 &= n_{N_2}\overline{u}_{N_2} + n_N\overline{u}_N, && (4.474)\\ &= n_{N_2}(\overline{h}_{N_2} - \overline{R}T) + n_N(\overline{h}_N - \overline{R}T), && (4.475)\\ &= (0.888154\ kmole)\left(2.05848 \times 10^5\ \frac{kJ}{kmole} - \left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)\right) && (4.476)\\ &\quad + (0.223693\ kmole)\left(5.9727 \times 10^5\ \frac{kJ}{kmole} - \left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)\right), && (4.477)\\ &= 2.60966 \times 10^5\ kJ. && (4.478) \end{aligned}$$

So

$$\begin{aligned} {}_1Q_2 &= U_2 - U_1, && (4.479)\\ &= 2.60966 \times 10^5\ kJ - 1.555964 \times 10^5\ kJ, && (4.480)\\ &= 1.05002 \times 10^5\ kJ. && (4.481) \end{aligned}$$

Heat needed to be added to keep the system at the constant temperature. This is because the nitrogen dissociation process is *endothermic*.

One can check for second law satisfaction in two ways. Fundamentally, one can demand that Eq. (4.377), $dS \geq \delta Q/T$, be satisfied for the process, giving

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}. \qquad (4.482)$$

For this isothermal process, this reduces to

$$\begin{aligned}
S_2 - S_1 &\geq \frac{{}_1Q_2}{T}, && (4.483)\\
(n_{N_2}\overline{s}_{N_2} + n_N\overline{s}_N)|_2 & \\
-\,(n_{N_2}\overline{s}_{N_2} + n_N\overline{s}_N)|_1 &\geq \frac{{}_1Q_2}{T}, && (4.484)\\
\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{y_{N_2}P}{P_o}\right)\right) + n_N\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{y_NP}{P_o}\right)\right)\right)\Big|_2 & \\
-\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{y_{N_2}P}{P_o}\right)\right) + n_N\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{y_NP}{P_o}\right)\right)\right)\Big|_1 &\geq \frac{{}_1Q_2}{T}, && (4.485)\\
\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{P_{N_2}}{P_o}\right)\right) + n_N\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{P_N}{P_o}\right)\right)\right)\Big|_2 & \\
-\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{P_{N_2}}{P_o}\right)\right) + n_N\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{P_N}{P_o}\right)\right)\right)\Big|_1 &\geq \frac{{}_1Q_2}{T}, && (4.486)\\
\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{n_{N_2}\overline{R}T}{P_oV}\right)\right) + n_N\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{n_N\overline{R}T}{P_oV}\right)\right)\right)\Big|_2 & \\
-\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{n_{N_2}\overline{R}T}{P_oV}\right)\right) + \underbrace{n_N}_{=0}\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{n_N\overline{R}T}{P_oV}\right)\right)\right)\Big|_1 &\geq \frac{{}_1Q_2}{T}. && (4.487)
\end{aligned}$$

Now at the initial state $n_N = 0$ *kmole*, and $\overline{R}T/P_o/V$ has a constant value of

$$\frac{\overline{R}T}{P_oV} = \frac{\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{(100\ kPa)(498.84\ m^3)} = 1\ \frac{1}{kmole}, \tag{4.488}$$

so Eq. (4.487) reduces to

$$\begin{aligned}
\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{n_{N_2}}{1\ kmole}\right)\right) + n_N\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{n_N}{1\ kmole}\right)\right)\right)\Big|_2 & \\
-\left(n_{N_2}\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{n_{N_2}}{1\ kmole}\right)\right)\right)\Big|_1 &\geq \frac{{}_1Q_2}{T}, && (4.489)\\
\left((0.888143)\left(292.984 - 8.314\ln(0.88143)\right) + (0.223714)\left(216.926 - 8.314\ln(0.223714)\right)\right)\Big|_2 & \\
-\left((1)\left(292.984 - 8.314\ln(1)\right)\right)\Big|_1 &\geq \frac{105002}{6000}, \\
19.4181\ \frac{kJ}{K} \geq 17.5004\ \frac{kJ}{K}. && (4.490)
\end{aligned}$$

Indeed, the second law is satisfied. Moreover the irreversible entropy production of the chemical reaction is $19.4181 - 17.5004 = +1.91772\ kJ/K$.

For the isochoric, isothermal process, it is also appropriate to use Eq. (4.394), $dA|_{T,V} \leq 0$, to check for second law satisfaction. This turns out to give an identical result. Since by Eq. (4.307), $A = U - TS$, $A_2 - A_1 = (U_2 - T_2S_2) - (U_1 - T_1S_1)$. Since the process is isothermal, $A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$. For $A_2 - A_1 \leq 0$, one must demand $U_2 - U_1 - T(S_2 - S_1) \leq 0$, or $U_2 - U_1 \leq T(S_2 - S_1)$, or $S_2 - S_1 \geq (U_2 - U_1)/T$. Since ${}_1Q_2 = U_2 - U_1$ for this isochoric process, one then recovers $S_2 - S_1 \geq {}_1Q_2/T$.

4.11.2.2 Isothermal, isobaric system

Allowing for isobaric rather than isochoric equilibration introduces small variation in the analysis.

Example 4.15

Consider the same reaction

$$N_2 + N_2 \leftrightharpoons 2N + N_2. \tag{4.491}$$

for an *isobaric* and *isothermal* process. That is, consider 1 *kmole* of N_2 and 0 *kmole* of N at a pressure of 100 kPa and a temperature of 6000 K. Using the ideal gas tables, find the equilibrium concentrations of N and N_2 if the equilibration process is isothermal and isobaric.

The initial volume is the same as from the previous example:

$$V_1 = 498.84\ m^3. \tag{4.492}$$

Note the volume will change in this isobaric process. Initially, the mixture is all N_2, so its partial pressure is the total pressure, and the initial partial pressure of N is 0.

A few other key results are identical to the previous example:

$$n_N = 2\left(n_{N_2}|_{t=0} - n_{N_2}\right), \tag{4.493}$$

and

$$2\overline{g}_N \leq \overline{g}_{N_2}. \tag{4.494}$$

Substituting using the definitions of Gibbs free energy, one gets

$$2\left(\overline{h}_N - T\,\overline{s}_N\right) \leq \overline{h}_{N_2} - T\,\overline{s}_{N_2}, \tag{4.495}$$

$$2\left(\overline{h}_N - T\left(\overline{s}^o_{T,N} - \overline{R}\ln\left(\frac{y_N P}{P_o}\right)\right)\right) \leq \overline{h}_{N_2} - T\left(\overline{s}^o_{T,N_2} - \overline{R}\ln\left(\frac{y_{N_2} P}{P_o}\right)\right), \tag{4.496}$$

$$2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) - \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \leq -2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) + \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), \tag{4.497}$$

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \geq 2\overline{R}T\ln\left(\frac{y_N P}{P_o}\right) - \overline{R}T\ln\left(\frac{y_{N_2} P}{P_o}\right), \tag{4.498}$$

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \geq \overline{R}T\ln\left(\frac{y_N^2 P^2}{P_o^2}\frac{P_o}{P y_{N_2}}\right). \tag{4.499}$$

In this case $P_o = P$, so one gets

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) \geq \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\right). \tag{4.500}$$

At the initial state, one has $y_N = 0$, so the right hand side approaches $-\infty$, and the inequality holds. At equilibrium, one has equality.

$$-2\left(\overline{h}_N - T\,\overline{s}^o_{T,N}\right) + \left(\overline{h}_{N_2} - T\,\overline{s}^o_{T,N_2}\right) = \overline{R}T\ln\left(\frac{y_N^2}{y_{N_2}}\right). \tag{4.501}$$

Taking numerical values from Table A.9:

$$-2\left(5.9727\times10^5\ \frac{kJ}{kmole}-(6000\ K)\left(216.926\ \frac{kJ}{kg\ K}\right)\right)+\left(2.05848\times10^5\ \frac{kJ}{kmole}-(6000\ K)\left(292.984\ \frac{kJ}{kg\ K}\right)\right)$$

$$= \left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)\ln\left(\frac{y_N^2}{y_{N_2}}\right), \tag{4.502}$$

$$\underbrace{-2.87635}_{\equiv \ln K_P} = \ln\left(\frac{y_N^2}{y_{N_2}}\right), \tag{4.503}$$

$$\underbrace{0.0563399}_{\equiv K_P} = \frac{y_N^2}{y_{N_2}}, \tag{4.504}$$

$$= \frac{\left(\frac{n_N}{n_N+n_{N_2}}\right)^2}{\left(\frac{n_{N_2}}{n_N+n_{N_2}}\right)}, \tag{4.505}$$

$$= \frac{n_N^2}{n_{N_2}(n_N+n_{N_2})}, \tag{4.506}$$

$$= \frac{\left(2\left(n_{N_2}|_{t=0}-n_{N_2}\right)\right)^2}{n_{N_2}(2\left(n_{N_2}|_{t=0}-n_{N_2}\right)+n_{N_2})}, \tag{4.507}$$

$$= \frac{\left(2\left(1\ kmole-n_{N_2}\right)\right)^2}{n_{N_2}(2\left(1\ kmole-n_{N_2}\right)+n_{N_2})}. \tag{4.508}$$

This is a quadratic equation for n_{N_2}. It has two roots

$$n_{N_2} = 0.882147\ kmole \qquad \text{physical;} \qquad n_{N_2} = 1.11785\ kmole, \qquad \text{non-physical} \tag{4.509}$$

The second root generates more N_2 than at the start, and also yields non-physically negative $n_N = -0.235706\ kmole$. So at equilibrium, the physical root is

$$n_N = 2(1-n_{N_2}) = 2(1-0.882147) = 0.235706\ kmole. \tag{4.510}$$

Again, the diatomic species is preferred. As the temperature is raised, one could show that the monatomic species would come to dominate.

The volume at equilibrium is

$$V_2 = \frac{(n_{N_2}+n_N)\overline{R}T}{P}, \tag{4.511}$$

$$= \frac{(0.882147\ kmole+0.235706\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{100\ kPa}, \tag{4.512}$$

$$= 557.630\ m^3. \tag{4.513}$$

The volume has increased because there are more molecules with the pressure and temperature being equal.

The molar concentrations $\overline{\rho}_i$ at equilibrium, are

$$\overline{\rho}_N = \frac{0.235706\ kmole}{557.636\ m^3} = 4.227\times10^{-4}\ \frac{kmole}{m^3} = \boxed{4.227\times10^{-7}\ \frac{mole}{cm^3}}, \tag{4.514}$$

$$\overline{\rho}_{N_2} = \frac{0.882147\ kmole}{557.636\ m^3} = 1.58196\times10^{-3}\ \frac{kmole}{m^3} = \boxed{1.58196\times10^{-6}\ \frac{mole}{cm^3}}. \tag{4.515}$$

The molar concentrations are a little smaller than for the isochoric case, mainly because the volume is larger at equilibrium.

Now consider the heat transfer. One knows for the isobaric process that $Q = H_2 - H_1$. The initial enthalpy is given by

$$H_1 = n_{N_2}\overline{h}_{N_2} = (1\ kmole)\left(2.05848 \times 10^5\ \frac{kJ}{kmole}\right) = 2.05848 \times 10^5\ kJ. \tag{4.515}$$

The enthalpy at the final state is

$$\begin{aligned} H_2 &= n_{N_2}\overline{h}_{N_2} + n_N\overline{h}_N, && (4.516)\\ &= (0.882147\ kmole)\left(2.05848 \times 10^5\ \frac{kJ}{kmole}\right) + (0.235706\ kmole)\left(5.9727 \times 10^5\ \frac{kJ}{kmole}\right), && (4.517)\\ &= 3.22368 \times 10^5\ kJ. && (4.518) \end{aligned}$$

So

$${}_1Q_2 = H_2 - H_1 = 3.22389 \times 10^5\ kJ - 2.05848 \times 10^5\ kJ = 1.16520 \times 10^5\ kJ. \tag{4.519}$$

Heat needed to be added to keep the system at the constant temperature. This is because the nitrogen dissociation process is *endothermic*. Relative to the isochoric process, *more* heat had to be added to maintain the temperature. This to counter the cooling effect of the expansion.

Lastly, it is a straightforward exercise to show that the second law is satisfied for this process.

4.11.3 Equilibrium condition

The results of both of the previous examples, in which a functional form of a progress variable's time variation, $d\zeta/dt$, was postulated in order to satisfy the second law gave a condition for equilibrium. This can be generalized so as to require at equilibrium that

$$\boxed{\underbrace{\sum_{i=1}^{N} \overline{\mu}_i \nu_i}_{\equiv -\overline{\alpha}} = 0.} \tag{4.520}$$

Here ν_i represents the *net* number of moles of species i generated in the forward reaction. This negation of the term on the left side of Eq (4.520) is sometimes defined as the *chemical affinity*, $\overline{\alpha}$:

$$\overline{\alpha} \equiv -\sum_{i=1}^{N} \overline{\mu}_i \nu_i. \tag{4.521}$$

So in the phase equilibrium example, Eq. (4.520) becomes

$$\overline{\mu}_l(-1) + \overline{\mu}_g(1) = 0. \tag{4.522}$$

In the nitrogen chemistry example, Eq. (4.520) becomes

$$\overline{\mu}_{N_2}(-1) + \overline{\mu}_N(2) = 0. \tag{4.523}$$

This will be discussed in detail in the following chapter.

Chapter 5

Thermochemistry of a single reaction

Read BS, Chapters 13, 14
See Powers, Chapter 4
See Abbott and Van Ness, Chapter 7
See Kondepudi and Prigogine, Chapters 4, 5, 7, 9
See Turns, Chapter 2
See Kuo, Chapters 1, 2

This chapter will further develop notions associated with the thermodynamics of chemical reactions. The focus will be on single chemical reactions.

5.1 Molecular mass

The molecular mass of a molecule is a straightforward notion from chemistry. One simply sums the product of the number of atoms and each atom's atomic mass to form the molecular mass. If one defines L as the number of elements present in species i, ϕ_{li} as the number of moles of atomic element l in species i, and $\mathcal{M}_l$ as the atomic mass of element l, the molecular mass M_i of species i

$$\boxed{M_i = \sum_{l=1}^{L} \mathcal{M}_l \phi_{li},} \qquad i = 1, \ldots, N. \tag{5.1}$$

In vector form, one would say

$$\mathbf{M}^T = \mathcal{M}^T \cdot \boldsymbol{\phi}, \qquad \text{or} \qquad \mathbf{M} = \boldsymbol{\phi}^T \cdot \mathcal{M}. \tag{5.2}$$

Here $\mathbf{M}$ is the vector of length N containing the molecular masses, $\mathcal{M}$ is the vector of length L containing the elemental masses, and $\boldsymbol{\phi}$ is the matrix of dimension $L \times N$ containing the number of moles of each element in each species. Generally, $\boldsymbol{\phi}$ is full rank. If $N > L$, $\boldsymbol{\phi}$ has rank L. If $N < L$, $\boldsymbol{\phi}$ has rank N. In any problem involving an actual chemical reaction, one will find $N \geq L$, and in most cases $N > L$. In isolated problems not involving a reaction,

one may have $N < L$. In any case, $\mathbf{M}$ lies in the column space of $\boldsymbol{\phi}^T$, which is the row space of $\boldsymbol{\phi}$.

Example 5.1

Find the molecular mass of H_2O. Here, one has two elements H and O, so $L = 2$, and one species, so $N = 1$; thus, in this isolated problem, $N < L$. Take $i = 1$ for species H_2O. Take $l = 1$ for element H. Take $l = 2$ for element O. From the periodic table, one gets $\mathcal{M}_1 = 1\ kg/kmole$ for H, $\mathcal{M}_2 = 16\ kg/kmole$ for O. For element 1, there are 2 atoms, so $\phi_{11} = 2$. For element 2, there is 1 atom so $\phi_{21} = 1$. So the molecular mass of species 1, H_2O is

$$\begin{aligned} M_1 &= \begin{pmatrix} \mathcal{M}_1 & \mathcal{M}_2 \end{pmatrix} \cdot \begin{pmatrix} \phi_{11} \\ \phi_{21} \end{pmatrix}, && (5.3) \\ &= \mathcal{M}_1\phi_{11} + \mathcal{M}_2\phi_{21}, && (5.4) \\ &= \left(1\ \frac{kg}{kmole}\right)(2) + \left(16\ \frac{kg}{kmole}\right)(1), && (5.5) \\ &= \boxed{18\ \frac{kg}{kmole}.} && (5.6) \end{aligned}$$

Example 5.2

Find the molecular masses of the two species C_8H_{18} and CO_2. Here, for practice, the vector matrix notation is exercised. In a certain sense this is overkill, but it is useful to be able to understand a general notation.

One has $N = 2$ species, and takes $i = 1$ for C_8H_{18} and $i = 2$ for CO_2. One also has $L = 3$ elements and takes $l = 1$ for C, $l = 2$ for H, and $l = 3$ for O. Now for each element, one has $\mathcal{M}_1 = 12\ kg/kmole$, $\mathcal{M}_2 = 1\ kg/kmole$, $\mathcal{M}_3 = 16\ kg/kmole$. The molecular masses are then given by

$$\begin{aligned} \begin{pmatrix} M_1 & M_2 \end{pmatrix} &= \begin{pmatrix} \mathcal{M}_1 & \mathcal{M}_2 & \mathcal{M}_3 \end{pmatrix} \cdot \begin{pmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \\ \phi_{31} & \phi_{32} \end{pmatrix}, && (5.7) \\ &= \begin{pmatrix} 12 & 1 & 16 \end{pmatrix} \cdot \begin{pmatrix} 8 & 1 \\ 18 & 0 \\ 0 & 2 \end{pmatrix}, && (5.8) \\ &= \boxed{\begin{pmatrix} 114 & 44 \end{pmatrix}.} && (5.9) \end{aligned}$$

That is for C_8H_{18}, one has molecular mass $M_1 = 114\ kg/kmole$. For CO_2, one has molecular mass $M_2 = 44\ kg/kmole$.

5.2 Stoichiometry

5.2.1 General development

Stoichiometry represents a mass balance on each element in a chemical reaction. For example, in the simple global reaction

$$2H_2 + O_2 \leftrightharpoons 2H_2O, \tag{5.10}$$

one has 4 H atoms in both the reactant and product sides and 2 O atoms in both the reactant and product sides. In this section stoichiometry will be systematized.

Consider now a general reaction with N species. This reaction can be represented by

$$\sum_{i=1}^{N} \nu_i' \chi_i \leftrightharpoons \sum_{i=1}^{N} \nu_i'' \chi_i. \tag{5.11}$$

Here χ_i is the i^{th} chemical species, ν_i' is the *forward stoichiometric coefficient* of the i^{th} reaction, and ν_i'' is the *reverse stoichiometric coefficient* of the i^{th} reaction. Both ν_i' and ν_i'' are to be interpreted as pure dimensionless numbers.

In Equation (5.10), one has $N = 3$ species. One might take $\chi_1 = H_2$, $\chi_2 = O_2$, and $\chi_3 = H_2O$. The reaction is written in more general form as

$$(2)\chi_1 + (1)\chi_2 + (0)\chi_3 \leftrightharpoons (0)\chi_1 + (0)\chi_2 + (2)\chi_3, \tag{5.12}$$

$$(2)H_2 + (1)O_2 + (0)H_2O \leftrightharpoons (0)H_2 + (0)O_2 + (2)H_2O. \tag{5.13}$$

Here, one has

$$\nu_1' = 2, \qquad \nu_1'' = 0, \tag{5.14}$$

$$\nu_2' = 1, \qquad \nu_2'' = 0, \tag{5.15}$$

$$\nu_3' = 0, \qquad \nu_3'' = 2. \tag{5.16}$$

It is common and useful to define another pure dimensionless number, the *net stoichiometric coefficients* for species i, ν_i. Here ν_i represents the net production of number if the reaction goes forward. It is given by

$$\nu_i = \nu_i'' - \nu_i'. \tag{5.17}$$

For the reaction $2H_2 + O_2 \leftrightharpoons 2H_2O$, one has

$$\nu_1 = \nu_1'' - \nu_1' = 0 - 2 = -2, \tag{5.18}$$

$$\nu_2 = \nu_2'' - \nu_2' = 0 - 1 = -1, \tag{5.19}$$

$$\nu_3 = \nu_3'' - \nu_3' = 2 - 0 = 2. \tag{5.20}$$

With these definitions, it is possible to summarize a chemical reaction as

$$\sum_{i=1}^{N} \nu_i \chi_i = 0. \tag{5.21}$$

In vector notation, one would say

$$\boxed{\boldsymbol{\nu}^T \cdot \boldsymbol{\chi} = 0.} \tag{5.22}$$

For the reaction of this section, one might write the non-traditional form

$$-2H_2 - O_2 + 2H_2O = 0. \tag{5.23}$$

It remains to enforce a stoichiometric balance. This is achieved if, for each element, $l = 1, \ldots, L$, one has the following equality:

$$\sum_{i=1}^{N} \phi_{li}\nu_i = 0, \qquad l = 1, \ldots, L. \tag{5.24}$$

That is to say, for each element, the sum of the product of the net species production and the number of elements in the species must be zero. In vector notation, this becomes

$$\boxed{\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}.} \tag{5.25}$$

One may recall from linear algebra that this demands that $\boldsymbol{\nu}$ lie in the *right null space* of $\boldsymbol{\phi}$.

Example 5.3

Show stoichiometric balance is achieved for $-2H_2 - O_2 + 2H_2O = 0$.

Here again, the number of elements $L = 2$, and one can take $l = 1$ for H and $l = 2$ for O. Also the number of species $N = 3$, and one takes $i = 1$ for H_2, $i = 2$ for O_2, and $i = 3$ for H_2O. Then for element 1, H, in species 1, H_2, one has

$$\phi_{11} = 2, H \text{ in } H_2. \tag{5.26}$$

Similarly, one gets

$$\begin{aligned}
\phi_{12} &= 0, \qquad H \text{ in } O_2, && (5.27)\\
\phi_{13} &= 2, \qquad H \text{ in } H_2O, && (5.28)\\
\phi_{21} &= 0, \qquad O \text{ in } H_2, && (5.29)\\
\phi_{22} &= 2, \qquad O \text{ in } O_2, && (5.30)\\
\phi_{23} &= 1, \qquad O \text{ in } H_2O. && (5.31)
\end{aligned}$$

In matrix form then, $\sum_{i=1}^{N} \phi_{li}\nu_i = 0$ gives

$$\begin{pmatrix} 2 & 0 & 2 \\ 0 & 2 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{5.32}$$

This is two equations in three unknowns. Thus, it is formally under-constrained. Certainly the trivial solution $\nu_1 = \nu_2 = \nu_3 = 0$ will satisfy, but one seeks non-trivial solutions. Assume ν_3 has a known value $\nu_3 = \xi$. Then, the system reduces to

$$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \begin{pmatrix} -2\xi \\ -\xi \end{pmatrix}. \tag{5.33}$$

The inversion here is easy, and one finds $\nu_1 = -\xi$, $\nu_2 = -\frac{1}{2}\xi$. Or in vector form,

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} -\xi \\ -\frac{1}{2}\xi \\ \xi \end{pmatrix}, \tag{5.34}$$

$$= \xi \begin{pmatrix} -1 \\ -\frac{1}{2} \\ 1 \end{pmatrix}, \qquad \xi \in \mathbb{R}^1. \tag{5.35}$$

Again, this amounts to saying the solution vector $(\nu_1, \nu_2, \nu_3)^T$ lies in the right null space of the coefficient matrix ϕ_{li}.

Here ξ is any real scalar. If one takes $\xi = 2$, one gets

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} -2 \\ -1 \\ 2 \end{pmatrix}, \tag{5.36}$$

This simply corresponds to

$$-2H_2 - O_2 + 2H_2O = 0. \tag{5.37}$$

If one takes $\xi = -4$, one still achieves stoichiometric balance, with

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} 4 \\ 2 \\ -4 \end{pmatrix}, \tag{5.38}$$

which corresponds to the equally valid

$$4H_2 + 2O_2 - 4H_2O = 0. \tag{5.39}$$

In summary, *the stoichiometric coefficients are non-unique but partially constrained by mass conservation.* Which set is chosen is to some extent arbitrary, and often based on traditional conventions from chemistry. But others are equally valid.

There is a small issue with units here, which will be seen to be difficult to reconcile. In practice, it will have little to no importance. In the previous example, one might be tempted to ascribe units of *kmoles* to ν_i. Later, it will be seen that in classical reaction kinetics, ν_i is best interpreted as a pure dimensionless number, consistent with the definition of this section. So in the context of the previous example, one would then take ξ to be dimensionless as well, which is perfectly acceptable for the example. In later problems, it will be more useful to give ξ the units of *kmoles*. Note that multiplication of ξ by any scalar, *e.g.* $kmole/(6.02 \times 10^{26})$, still yields an acceptable result.

Example 5.4

Balance an equation for hypothesized ethane combustion

$$\nu_1' C_2H_6 + \nu_2' O_2 \leftrightharpoons \nu_3'' CO_2 + \nu_4'' H_2O. \tag{5.40}$$

One could also say in terms of the net stoichiometric coefficients

$$\nu_1 C_2H_6 + \nu_2 O_2 + \nu_3 CO_2 + \nu_4 H_2O = 0. \tag{5.41}$$

Here one takes $\chi_1 = C_2H_6$, $\chi_2 = O_2$, $\chi_3 = CO_2$, and $\chi_4 = H_2O$. So there are $N = 4$ species. There are also $L = 3$ elements: $l = 1 : C$, $l = 2 : H$, $l = 3 : O$. One then has

$$\begin{aligned}
\phi_{11} &= 2, \quad && C \text{ in } C_2H_6, && (5.42)\\
\phi_{12} &= 0, \quad && C \text{ in } O_2, && (5.43)\\
\phi_{13} &= 1, \quad && C \text{ in } CO_2, && (5.44)\\
\phi_{14} &= 0, \quad && C \text{ in } H_2O, && (5.45)\\
\phi_{21} &= 6, \quad && H \text{ in } C_2H_6, && (5.46)\\
\phi_{22} &= 0, \quad && H \text{ in } O_2, && (5.47)\\
\phi_{23} &= 0, \quad && H \text{ in } CO_2, && (5.48)\\
\phi_{24} &= 2, \quad && H \text{ in } H_2O, && (5.49)\\
\phi_{31} &= 0, \quad && O \text{ in } C_2H_6, && (5.50)\\
\phi_{32} &= 2, \quad && O \text{ in } O_2, && (5.51)\\
\phi_{33} &= 2, \quad && O \text{ in } CO_2, && (5.52)\\
\phi_{34} &= 1, \quad && O \text{ in } H_2O. && (5.53)
\end{aligned}$$

So the stoichiometry equation, $\sum_{i=1}^{N} \phi_{li}\nu_i = 0$, is given by

$$\begin{pmatrix} 2 & 0 & 1 & 0 \\ 6 & 0 & 0 & 2 \\ 0 & 2 & 2 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.54}$$

Here, there are three equations in four unknowns, so the system is under-constrained. There are many ways to address this problem. Here, choose the robust way of casting the system into *row echelon form*. This is easily achieved by Gaussian elimination. Row echelon form seeks to have lots of zeros in the lower left part of the matrix. The lower left corner has a zero already, so that is useful. Now, multiply the top equation by 3 and subtract the result from the second to get

$$\begin{pmatrix} 2 & 0 & 1 & 0 \\ 0 & 0 & -3 & 2 \\ 0 & 2 & 2 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.55}$$

Next switch the last two equations to get

$$\begin{pmatrix} 2 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 \\ 0 & 0 & -3 & 2 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.56}$$

Now divide the first by 2, the second by 2 and the third by -3 to get unity in the diagonal:

$$\begin{pmatrix} 1 & 0 & \frac{1}{2} & 0 \\ 0 & 1 & 1 & \frac{1}{2} \\ 0 & 0 & 1 & -\frac{2}{3} \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.57}$$

So-called *bound variables* have non-zero coefficients on the diagonal, so one can take the bound variables to be ν_1, ν_2, and ν_3. The remaining variables are *free variables*. Here one takes the free variable to be ν_4. So, set $\nu_4 = \xi$, and rewrite the system as

$$\begin{pmatrix} 1 & 0 & \frac{1}{2} \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} 0 \\ -\frac{1}{2}\xi \\ \frac{2}{3}\xi \end{pmatrix}. \tag{5.58}$$

Solving, one finds

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} -\frac{1}{3}\xi \\ -\frac{7}{6}\xi \\ \frac{2}{3}\xi \\ \xi \end{pmatrix} = \xi \begin{pmatrix} -\frac{1}{3} \\ -\frac{7}{6} \\ \frac{2}{3} \\ 1 \end{pmatrix}, \qquad \xi \in \mathbb{R}^1. \tag{5.59}$$

Again, one finds a non-unique solution in the right null space of $\boldsymbol{\phi}$. If one chooses $\xi = 6$, then one gets

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \end{pmatrix} = \begin{pmatrix} -2 \\ -7 \\ 4 \\ 6 \end{pmatrix}, \tag{5.60}$$

which corresponds to the stoichiometrically balanced reaction

$$\boxed{2C_2H_6 + 7O_2 \leftrightharpoons 4CO_2 + 6H_2O.} \tag{5.61}$$

In this example, ξ is dimensionless.

Example 5.5

Consider stoichiometric balance for a propane oxidation reaction which may produce carbon monoxide and hydroxyl in addition to carbon dioxide and water.

The hypothesized reaction takes the form

$$\nu_1' C_3H_8 + \nu_2' O_2 \leftrightharpoons \nu_3'' CO_2 + \nu_4'' CO + \nu_5'' H_2O + \nu_6'' OH. \tag{5.62}$$

In terms of net stoichiometric coefficients, this becomes

$$\nu_1 C_3H_8 + \nu_2 O_2 + \nu_3 CO_2 + \nu_4 CO + \nu_5 H_2O + \nu_6 OH = 0. \tag{5.63}$$

There are $N = 6$ species and $L = 3$ elements. One then has

$$\begin{aligned}
\phi_{11} &= 3, \quad C \text{ in } C_3H_8, && (5.64)\\
\phi_{12} &= 0, \quad C \text{ in } O_2, && (5.65)\\
\phi_{13} &= 1, \quad C \text{ in } CO_2, && (5.66)\\
\phi_{14} &= 1, \quad C \text{ in } CO, && (5.67)\\
\phi_{15} &= 0, \quad C \text{ in } H_2O, && (5.68)\\
\phi_{16} &= 0, \quad C \text{ in } OH, && (5.69)\\
\phi_{21} &= 8, \quad H \text{ in } C_3H_8, && (5.70)\\
\phi_{22} &= 0, \quad H \text{ in } O_2, && (5.71)\\
\phi_{23} &= 0, \quad H \text{ in } CO_2, && (5.72)\\
\phi_{24} &= 0, \quad H \text{ in } CO, && (5.73)\\
\phi_{25} &= 2, \quad H \text{ in } H_2O, && (5.74)\\
\phi_{26} &= 1, \quad H \text{ in } OH, && (5.75)\\
\phi_{31} &= 0, \quad O \text{ in } C_3H_8, && (5.76)\\
\phi_{32} &= 2, \quad O \text{ in } O_2, && (5.77)\\
\phi_{33} &= 2, \quad O \text{ in } CO_2, && (5.78)\\
\phi_{34} &= 1, \quad O \text{ in } CO, && (5.79)\\
\phi_{35} &= 1, \quad O \text{ in } H_2O, && (5.80)\\
\phi_{36} &= 1, \quad O \text{ in } OH. && (5.81)
\end{aligned}$$

The equation $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = 0$, then becomes

$$\begin{pmatrix} 3 & 0 & 1 & 1 & 0 & 0 \\ 8 & 0 & 0 & 0 & 2 & 1 \\ 0 & 2 & 2 & 1 & 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.82}$$

Multiplying the first equation by $-8/3$ and adding it to the second gives

$$\begin{pmatrix} 3 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & -\frac{8}{3} & -\frac{8}{3} & 2 & 1 \\ 0 & 2 & 2 & 1 & 1 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.83}$$

Trading the second and third rows gives

$$\begin{pmatrix} 3 & 0 & 1 & 1 & 0 & 0 \\ 0 & 2 & 2 & 1 & 1 & 1 \\ 0 & 0 & -\frac{8}{3} & -\frac{8}{3} & 2 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.84}$$

Dividing the first row by 3, the second by 2 and the third by $-8/3$ gives

$$\begin{pmatrix} 1 & 0 & \frac{1}{3} & \frac{1}{3} & 0 & 0 \\ 0 & 1 & 1 & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 1 & 1 & -\frac{3}{4} & -\frac{3}{8} \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.85}$$

Take bound variables to be ν_1, ν_2, and ν_3 and free variables to be ν_4, ν_5, and ν_6. So set $\nu_4 = \xi_1$, $\nu_5 = \xi_2$, and $\nu_6 = \xi_3$, and get

$$\begin{pmatrix} 1 & 0 & \frac{1}{3} \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} -\frac{\xi_1}{3} \\ -\frac{\xi_1}{2} - \frac{\xi_2}{2} - \frac{\xi_3}{2} \\ -\xi_1 + \frac{3}{4}\xi_2 + \frac{3}{8}\xi_3 \end{pmatrix}. \tag{5.86}$$

Solving, one finds

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{8}(-2\xi_2 - \xi_3) \\ \frac{1}{8}(4\xi_1 - 10\xi_2 - 7\xi_3) \\ \frac{1}{8}(-8\xi_1 + 6\xi_2 + 3\xi_3) \end{pmatrix}. \tag{5.87}$$

For all the coefficients, one then has

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \begin{pmatrix} \frac{1}{8}(-2\xi_2 - \xi_3) \\ \frac{1}{8}(4\xi_1 - 10\xi_2 - 7\xi_3) \\ \frac{1}{8}(-8\xi_1 + 6\xi_2 + 3\xi_3) \\ \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = \frac{\xi_1}{8}\begin{pmatrix} 0 \\ 4 \\ -8 \\ 8 \\ 0 \\ 0 \end{pmatrix} + \frac{\xi_2}{8}\begin{pmatrix} -2 \\ -10 \\ 6 \\ 0 \\ 8 \\ 0 \end{pmatrix} + \frac{\xi_3}{8}\begin{pmatrix} -1 \\ -7 \\ 3 \\ 0 \\ 0 \\ 8 \end{pmatrix}. \tag{5.88}$$

Here, one finds *three* independent vectors in the right null space. To simplify the notation, take $\hat{\xi}_1 = \xi_1/8$, $\hat{\xi}_2 = \xi_2/8$, and $\hat{\xi}_3 = \xi_3/8$. Then,

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \\ \nu_6 \end{pmatrix} = \hat{\xi}_1\begin{pmatrix} 0 \\ 4 \\ -8 \\ 8 \\ 0 \\ 0 \end{pmatrix} + \hat{\xi}_2\begin{pmatrix} -2 \\ -10 \\ 6 \\ 0 \\ 8 \\ 0 \end{pmatrix} + \hat{\xi}_3\begin{pmatrix} -1 \\ -7 \\ 3 \\ 0 \\ 0 \\ 8 \end{pmatrix}. \tag{5.89}$$

The most general reaction that can achieve a stoichiometric balance is given by

$$(-2\hat{\xi}_2 - \hat{\xi}_3)C_3H_8 + (4\hat{\xi}_1 - 10\hat{\xi}_2 - 7\hat{\xi}_3)O_2 + (-8\hat{\xi}_1 + 6\hat{\xi}_2 + 3\hat{\xi}_3)CO_2 + 8\hat{\xi}_1\ CO + 8\hat{\xi}_2\ H_2O + 8\hat{\xi}_3\ OH = 0. \tag{5.90}$$

Rearranging, one gets

$$(2\hat{\xi}_2 + \hat{\xi}_3)C_3H_8 + (-4\hat{\xi}_1 + 10\hat{\xi}_2 + 7\hat{\xi}_3)O_2 \leftrightharpoons (-8\hat{\xi}_1 + 6\hat{\xi}_2 + 3\hat{\xi}_3)CO_2 + 8\hat{\xi}_1\ CO + 8\hat{\xi}_2\ H_2O + 8\hat{\xi}_3\ OH. \tag{5.91}$$

This will be balanced for all $\hat{\xi}_1$, $\hat{\xi}_2$, and $\hat{\xi}_3$. The values that are actually achieved in practice depend on the thermodynamics of the problem. Stoichiometry only provides some limitations.

A slightly more familiar form is found by taking $\hat{\xi}_2 = 1/2$ and rearranging, giving

$$\boxed{(1 + \hat{\xi}_3)\ C_3H_8 + (5 - 4\hat{\xi}_1 + 7\hat{\xi}_3)\ O_2 \leftrightharpoons (3 - 8\hat{\xi}_1 + 3\hat{\xi}_3)\ CO_2 + 4\ H_2O + 8\hat{\xi}_1\ CO + 8\hat{\xi}_3\ OH.} \tag{5.92}$$

One notes that often the production of CO and OH will be small. If there is no production of CO or OH, $\hat{\xi}_1 = \hat{\xi}_3 = 0$ and one recovers the familiar balance of

$$C_3H_8 + 5\ O_2 \leftrightharpoons 3\ CO_2 + 4\ H_2O. \tag{5.93}$$

One also notes that stoichiometry alone admits unusual solutions. For instance, if $\hat{\xi}_1 = 100$, $\hat{\xi}_2 = 1/2$, and $\hat{\xi}_3 = 1$, one has

$$2\ C_3H_8 + 794\ CO_2 \leftrightharpoons 388\ O_2 + 4\ H_2O + 800\ CO + 8\ OH. \tag{5.94}$$

This reaction is certainly admitted by stoichiometry but is not observed in nature. To determine precisely which of the infinitely many possible final states are realized requires a consideration of the equilibrium condition $\sum_{i=1}^{N} \nu_i \overline{\mu}_i = 0$.

Looked at in another way, we can think of three independent classes of reactions admitted by the stoichiometry, one for each of the linearly independent null space vectors. Taking first $\hat{\xi}_1 = 1/4$, $\hat{\xi}_2 = 0$, $\hat{\xi}_3 = 0$, one gets, after rearrangement

$$2CO + O_2 \leftrightharpoons 2CO_2, \tag{5.95}$$

as one class of reaction admitted by stoichiometry. Taking next $\hat{\xi}_1 = 0$, $\hat{\xi}_2 = 1/2$, $\hat{\xi}_3 = 0$, one gets

$$C_3H_8 + 5O_2 \leftrightharpoons 3CO_2 + 4H_2O, \tag{5.96}$$

as the second class admitted by stoichiometry. The third class is given by taking $\hat{\xi}_1 = 0$, $\hat{\xi}_2 = 0$, $\hat{\xi}_3 = 1$, and is

$$C_3H_8 + 7O_2 \leftrightharpoons 3CO_2 + 8OH. \tag{5.97}$$

In this example, both ξ and $\hat{\xi}$ are dimensionless.

In general, one can expect to find the stoichiometric coefficients for N species composed of L elements to be of the following form:

$$\boxed{\nu_i = \sum_{k=1}^{N-L} \mathcal{D}_{ik} \xi_k, \qquad i = 1, \ldots, N.} \tag{5.98}$$

Here $\mathcal{D}_{ik}$ is a dimensionless component of a full rank matrix of dimension $N \times (N - L)$ and rank $N - L$, and ξ_k is a dimensionless component of a vector of parameters of length $N - L$. The matrix whose components are $\mathcal{D}_{ik}$ are constructed by populating its columns with vectors which lie in the right null space of ϕ_{li}. Note that multiplication of ξ_k by any constant gives another set of ν_i, and mass conservation for each element is still satisfied.

For later use, we associate ν_i with the number of moles n_i, and consider a differential change in the number of moles dn_i from Eq. (5.98) and arrive at

$$\boxed{dn_i = \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N.} \tag{5.99}$$

5.2.2 Fuel-air mixtures

In combustion with air, one often models air as a simple mixture of diatomic oxygen and inert diatomic nitrogen:

$$(O_2 + 3.76N_2). \tag{5.100}$$

The *air-fuel ratio*, $\mathcal{A}$ and its reciprocal, the *fuel-air ratio*, $\mathcal{F}$, can be defined on a mass and mole basis.

$$\boxed{\mathcal{A}_{mass} = \frac{m_{air}}{m_{fuel}}, \qquad \mathcal{A}_{mole} = \frac{n_{air}}{n_{fuel}}.} \tag{5.101}$$

Via the molecular masses, one has

$$\mathcal{A}_{mass} = \frac{m_{air}}{m_{fuel}} = \frac{n_{air} M_{air}}{n_{fuel} M_{fuel}} = \mathcal{A}_{mole} \frac{M_{air}}{M_{fuel}}. \tag{5.102}$$

If there is not enough air to burn all the fuel, the mixture is said to be *rich*. If there is excess air, the mixture is said to be *lean*. If there is just enough, the mixture is said to be *stoichiometric*. The *equivalence ratio*, Φ, is defined as the actual fuel-air ratio scaled by the stoichiometric fuel-air ratio:

$$\boxed{\Phi \equiv \frac{\mathcal{F}_{actual}}{\mathcal{F}_{stoichiometric}} = \frac{\mathcal{A}_{stoichiometric}}{\mathcal{A}_{actual}}.} \tag{5.103}$$

The ratio Φ is the same whether $\mathcal{F}$'s are taken on a mass or mole basis, because the ratio of molecular masses cancel.

Example 5.6

Calculate the stoichiometry of the combustion of methane with air with an equivalence ratio of $\Phi = 0.5$. If the pressure is 0.1 MPa, find the dew point of the products.

First calculate the coefficients for stoichiometric combustion:

$$\nu_1' CH_4 + \nu_2' (O_2 + 3.76 N_2) \leftharpoons \nu_3'' CO_2 + \nu_4'' H_2O + \nu_5'' N_2, \tag{5.104}$$

or

$$\nu_1 CH_4 + \nu_2 O_2 + \nu_3 CO_2 + \nu_4 H_2O + (\nu_5 + 3.76\nu_2) N_2 = 0. \tag{5.105}$$

Here one has $N = 5$ species and $L = 4$ elements. Adopting a slightly more intuitive procedure for variety, one writes a conservation equation for each element to get

$$\begin{aligned} \nu_1 + \nu_3 &= 0, \qquad C, && (5.106)\\ 4\nu_1 + 2\nu_4 &= 0, \qquad H, && (5.107)\\ 2\nu_2 + 2\nu_3 + \nu_4 &= 0, \qquad O, && (5.108)\\ 3.76\nu_2 + \nu_5 &= 0, \qquad N. && (5.109) \end{aligned}$$

In matrix form this becomes

$$\begin{pmatrix} 1 & 0 & 1 & 0 & 0 \\ 4 & 0 & 0 & 2 & 0 \\ 0 & 2 & 2 & 1 & 0 \\ 0 & 3.76 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{5.110}$$

Now, one might expect to have one free variable, since one has five unknowns in four equations. While casting the equation in row echelon form is guaranteed to yield a proper solution, one can often use intuition to get a solution more rapidly. One certainly expects that CH_4 will need to be present for the reaction to take place. One might also expect to find an answer if there is one mole of CH_4. So take $\nu_1 = -1$. Realize that one could also get a physically valid answer by assuming ν_1 to be equal to *any* scalar. With $\nu_1 = -1$, one gets

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 2 & 2 & 1 & 0 \\ 3.76 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 1 \\ 4 \\ 0 \\ 0 \end{pmatrix}. \tag{5.111}$$

One easily finds the unique inverse does exist, and that the solution is

$$\begin{pmatrix} \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} -2 \\ 1 \\ 2 \\ 7.52 \end{pmatrix}. \tag{5.112}$$

If there had been more than one free variable, the four by four matrix would have been singular, and no unique inverse would have existed.

In any case, the reaction under stoichiometric conditions is

$$-CH_4 - 2O_2 + CO_2 + 2H_2O + (7.52 + (3.76)(-2))N_2 = 0, \tag{5.113}$$

$$CH_4 + 2(O_2 + 3.76N_2) \leftrightharpoons CO_2 + 2H_2O + 7.52N_2. \tag{5.114}$$

For the stoichiometric reaction, the fuel-air ratio on a mole basis is

$$\mathcal{F}_{stoichiometric} = \frac{1}{2 + 2(3.76)} = 0.1050. \tag{5.115}$$

Now $\Phi = 0.5$, so

$$\mathcal{F}_{actual} = \Phi \mathcal{F}_{stoichiometric}, \tag{5.116}$$

$$= (0.5)(0.1050), \tag{5.117}$$

$$= 0.0525. \tag{5.118}$$

By inspection, one can write the *actual* reaction equation as

$$\boxed{CH_4 + 4(O_2 + 3.76N_2) \leftrightharpoons CO_2 + 2H_2O + 2O_2 + 15.04N_2.} \tag{5.119}$$

Check:

$$\mathcal{F}_{actual} = \frac{1}{4 + 4(3.76)} = 0.0525. \tag{5.120}$$

For the dew point of the products, one needs the partial pressure of H_2O. The mole fraction of H_2O is

$$y_{H_2O} = \frac{2}{1 + 2 + 2 + 15.04} = 0.0499 \tag{5.121}$$

So the partial pressure of H_2O is

$$P_{H_2O} = y_{H_2O} P = 0.0499(100\ kPa) = 4.99\ kPa. \tag{5.122}$$

From the steam tables, the saturation temperature at this pressure is $T_{sat} = T_{dew\ point} = \boxed{32.88\ ^\circ C}$. If the products cool to this temperature in an exhaust device, the water could condense in the apparatus.

5.3 First law analysis of reacting systems

One can easily use the first law to learn much about chemically reacting systems.

5.3.1 Enthalpy of formation

The enthalpy of formation is the enthalpy that is required to form a molecule from combining its constituents at $P = 0.1\ MPa$ and $T = 298\ K$. Consider the reaction (taken here to be irreversible)

$$C + O_2 \rightarrow CO_2. \tag{5.123}$$

In order to maintain the process at constant temperature, it is found that heat transfer to the volume is necessary. For the steady constant pressure process, one has

$$\begin{aligned} U_2 - U_1 &= {}_1Q_2 - {}_1W_2, && (5.124)\\ &= {}_1Q_2 - \int_1^2 P dV, && (5.125)\\ &= {}_1Q_2 - P(V_2 - V_1), && (5.126)\\ {}_1Q_2 &= U_2 - U_1 + P(V_2 - V_1), && (5.127)\\ &= H_2 - H_1, && (5.128)\\ {}_1Q_2 &= H_{products} - H_{reactants}. && (5.129) \end{aligned}$$

So

$$\boxed{{}_1Q_2 = \sum_{products} n_i \overline{h}_i - \sum_{reactants} n_i \overline{h}_i.} \tag{5.130}$$

In this reaction, one measures that ${}_1Q_2 = -393522\ kJ$ for the reaction of 1 $kmole$ of C and O_2. That is the reaction liberates such energy to the environment. So measuring the heat transfer can give a measure of the enthalpy difference between reactants and products. Assign a value of enthalpy zero to elements in their standard state at the reference state. Thus, C and O_2 both have enthalpies of 0 $kJ/kmole$ at $T = 298\ K$, $P = 0.1\ MPa$. This enthalpy is designated, for species i,

$$\overline{h}^o_{f,i} = \overline{h}^o_{298,i}, \tag{5.131}$$

and is called the *enthalpy of formation*. So the energy balance for the products and reactants, here both at the standard state, becomes

$$\begin{aligned} {}_1Q_2 &= n_{CO_2}\overline{h}^o_{f,CO_2} - n_C\overline{h}^o_{f,C} - n_{O_2}\overline{h}^o_{f,O_2}, && (5.132)\\ -393522\ kJ &= (1\ kmole)\overline{h}^o_{f,CO_2} - (1\ kmole)\left(0\ \frac{kJ}{kmole}\right) - (1\ kmole)\left(0\ \frac{kJ}{kmole}\right). && (5.133) \end{aligned}$$

Thus, the enthalpy of formation of CO_2 is $\overline{h}^o_{f,CO_2} = -393522\ kJ/kmole$, since the reaction involved creation of 1 $kmole$ of CO_2.

Often values of enthalpy are tabulated in the forms of enthalpy differences $\Delta\overline{h}_i$. These are defined such that

$$\begin{aligned} \overline{h}_i &= \overline{h}^o_{f,i} + \underbrace{(\overline{h}_i - \overline{h}^o_{f,i})}_{=\Delta\overline{h}_i}, & (5.134)\\ &= \overline{h}^o_{f,i} + \Delta\overline{h}_i. & (5.135) \end{aligned}$$

Lastly, one notes for an ideal gas that the enthalpy is a function of temperature only, and so does not depend on the reference pressure; hence

$$\overline{h}_i = \overline{h}^o_i, \qquad \Delta\overline{h}_i = \Delta\overline{h}^o_i, \qquad \text{if ideal gas.} \tag{5.136}$$

Example 5.7

(BS, Ex. 15.6 pp. 629-630). Consider the heat of reaction of the following irreversible reaction in a steady state, steady flow process confined to the standard state of $P = 0.1\ MPa$, $T = 298\ K$:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(\ell). \tag{5.137}$$

The first law holds that

$$Q_{cv} = \sum_{products} n_i\overline{h}_i - \sum_{reactants} n_i\overline{h}_i. \tag{5.138}$$

All components are at their reference states. Table A.10 gives properties, and one finds

$$\begin{aligned} Q_{cv} &= n_{CO_2}\overline{h}_{CO_2} + n_{H_2O}\overline{h}_{H_2O} - n_{CH_4}\overline{h}_{CH_4} - n_{O_2}\overline{h}_{O_2}, & (5.139)\\ &= (1\ kmole)\left(-393522\ \frac{kJ}{kmole}\right) + (2\ kmole)\left(-285830\ \frac{kJ}{kmole}\right)\\ &\quad -(1\ kmole)\left(-74873\ \frac{kJ}{kmole}\right) - (2\ kmole)\left(0\ \frac{kJ}{kmole}\right), & (5.140)\\ &= \boxed{-890309\ kJ.} & (5.141) \end{aligned}$$

A more detailed analysis is required in the likely case in which the system is not at the reference state.

Example 5.8

(adopted from Moran and Shapiro, p. 619) A mixture of 1 $kmole$ of gaseous methane and 2 $kmole$ of oxygen initially at 298 K and 101.325 kPa burns completely in a closed, rigid, container. Heat transfer occurs until the final temperature is 900 K. Find the heat transfer and the final pressure.

The combustion is stoichiometric. Assume that no small concentration species are generated. The global reaction is given by

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \tag{5.142}$$

The first law analysis for the closed system is slightly different:

$$U_2 - U_1 = {}_1Q_2 - {}_1W_2. \tag{5.143}$$

Since the process is isochoric, ${}_1W_2 = 0$. So

$$\begin{aligned}
{}_1Q_2 &= U_2 - U_1, && (5.144)\\
&= n_{CO_2}\overline{u}_{CO_2} + n_{H_2O}\overline{u}_{H_2O} - n_{CH_4}\overline{u}_{CH_4} - n_{O_2}\overline{u}_{O_2}, && (5.145)\\
&= n_{CO_2}(\overline{h}_{CO_2} - \overline{R}T_2) + n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{CH_4}(\overline{h}_{CH_4} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1), && (5.146)\\
&= \overline{h}_{CO_2} + 2\overline{h}_{H_2O} - \overline{h}_{CH_4} - 2\overline{h}_{O_2} - 3\overline{R}(T_2 - T_1), && (5.147)\\
&= (\overline{h}^o_{CO_2,f} + \Delta\overline{h}_{CO_2}) + 2(\overline{h}^o_{H_2O,f} + \Delta\overline{h}_{H_2O}) - (\overline{h}^o_{CH_4,f} + \Delta\overline{h}_{CH_4}) - 2(\overline{h}^o_{O_2,f} + \Delta\overline{h}_{O_2})\\
&\quad -3\overline{R}(T_2 - T_1), && (5.148)\\
&= (-393522 + 28030) + 2(-241826 + 21937) - (-74873 + 0) - 2(0 + 0)\\
&\quad -3(8.314)(900 - 298), && (5.149)\\
&= \boxed{-745412\ kJ.} && (5.150)
\end{aligned}$$

For the pressures, one has

$$\begin{aligned}
P_1V_1 &= (n_{CH_4} + n_{O_2})\overline{R}T_1, && (5.151)\\
V_1 &= \frac{(n_{CH_4} + n_{O_2})\overline{R}T_1}{P_1}, && (5.152)\\
&= \frac{(1\ kmole + 2\ kmole)\left(8.314\ \frac{kJ}{kg\ K}\right)(298\ K)}{101.325\ kPa}, && (5.153)\\
&= 73.36\ m^3. && (5.154)
\end{aligned}$$

Now $V_2 = V_1$, so

$$\begin{aligned}
P_2 &= \frac{(n_{CO_2} + n_{H_2O})\overline{R}T_2}{V_2}, && (5.155)\\
&= \frac{(1\ kmole + 2\ kmole)\left(8.314\ \frac{kJ}{kg\ K}\right)(900\ K)}{73.36\ m^3}, && (5.156)\\
&= \boxed{306.0\ kPa.} && (5.157)
\end{aligned}$$

The pressure increased in the reaction. This is entirely attributable to the temperature rise, as the number of moles remained constant here.

5.3.2 Enthalpy and internal energy of combustion

The *enthalpy of combustion* is the difference between the enthalpy of products and reactants when complete combustion occurs at a given pressure and temperature. It is also known

as the *heating value* or the *heat of reaction*. The *internal energy of combustion* is related and is the difference between the internal energy of products and reactants when complete combustion occurs at a given volume and temperature.

The term *higher heating value* refers to the energy of combustion when liquid water is in the products. *Lower heating value* refers to the energy of combustion when water vapor is in the product.

5.3.3 Adiabatic flame temperature in isochoric stoichiometric systems

The *adiabatic flame temperature* refers to the temperature which is achieved when a fuel and oxidizer are combined with no loss of work or heat energy. Thus, it must occur in a closed, insulated, fixed volume. It is generally the highest temperature that one can expect to achieve in a combustion process. It generally requires an iterative solution. Of all mixtures, stoichiometric mixtures will yield the highest adiabatic flame temperatures because there is no need to heat the excess fuel or oxidizer.

Here four examples will be presented to illustrate the following points.

- The adiabatic flame temperature can be well over 5000 K for seemingly ordinary mixtures.
- Dilution of the mixture with an inert diluent lowers the adiabatic flame temperature. The same effect would happen in rich and lean mixtures.
- Preheating the mixture, such as one might find in the compression stroke of an engine, increases the adiabatic flame temperature.
- Consideration of the presence of minor species lowers the adiabatic flame temperature.

5.3.3.1 Undiluted, cold mixture

Example 5.9

A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 $kmole$ of H_2 and 1 $kmole$ of O_2 at 100 kPa and 298 K. Find the adiabatic flame temperature and final pressure assuming the irreversible reaction

$$2H_2 + O_2 \rightarrow 2H_2O. \tag{5.158}$$

The volume is given by

$$V = \frac{(n_{H_2} + n_{O_2})\overline{R}T_1}{P_1}, \tag{5.159}$$

$$= \frac{(2\ kmole + 1\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(298\ K)}{100\ kPa}, \tag{5.160}$$

$$= 74.33\ m^3. \tag{5.161}$$

The first law gives

$$\begin{aligned}
U_2 - U_1 &= {}_1Q_2 - {}_1W_2, && (5.162)\\
U_2 - U_1 &= 0, && (5.163)\\
n_{H_2O}\overline{u}_{H_2O} - n_{H_2}\overline{u}_{H_2} - n_{O_2}\overline{u}_{O_2} &= 0, && (5.164)\\
n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{H_2}(\overline{h}_{H_2} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1) &= 0, && (5.165)\\
2\overline{h}_{H_2O} - 2\underbrace{\overline{h}_{H_2}}_{=0} - \underbrace{\overline{h}_{O_2}}_{=0} + \overline{R}(-2T_2 + 3T_1) &= 0, && (5.166)\\
2\overline{h}_{H_2O} + (8.314)\left((-2)\,T_2 + (3)\,(298)\right) &= 0, && (5.167)\\
\overline{h}_{H_2O} - 8.314T_2 + 3716.4 &= 0, && (5.168)\\
\overline{h}^{o}_{f,H_2O} + \Delta\overline{h}_{H_2O} - 8.314T_2 + 3716.4 &= 0, && (5.169)\\
-241826 + \Delta\overline{h}_{H_2O} - 8.314T_2 + 3716.4 &= 0, && (5.170)\\
-238110 + \Delta\overline{h}_{H_2O} - 8.314T_2 &= 0. && (5.171)
\end{aligned}$$

At this point, one begins an iteration process, guessing a value of T_2 and an associated $\Delta\overline{h}_{H_2O}$. When T_2 is guessed at 5600 K, the left side becomes -6507.04. When T_2 is guessed at 6000 K, the left side becomes 14301.4. Interpolate then to arrive at

$$\boxed{T_2 = 5725\ K.} \tag{5.172}$$

This is an extremely high temperature. At such temperatures, in fact, one can expect other species to co-exist in the equilibrium state in large quantities. These may include H, OH, O, HO_2, and H_2O_2, among others.

The final pressure is given by

$$\begin{aligned}
P_2 &= \frac{n_{H_2O}\overline{R}T_2}{V}, && (5.173)\\
&= \frac{(2\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(5725\ K)}{74.33\ m^3}, && (5.174)\\
&= \boxed{1280.71\ kPa.} && (5.175)
\end{aligned}$$

The final concentration of H_2O is

$$\overline{\rho}_{H_2O} = \frac{2\ kmole}{74.33\ m^3} = 2.69 \times 10^{-2}\ \frac{kmole}{m^3}. \tag{5.176}$$

5.3.3.2 Dilute, cold mixture

Example 5.10

Consider a variant on the previous example in which the mixture is diluted with an inert, taken here to be N_2. A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 *kmole* of H_2, 1 *kmole* of O_2, and 8 *kmole* of N_2 at 100 kPa and 298 K. Find the adiabatic flame temperature and the final pressure, assuming the irreversible reaction

$$2H_2 + O_2 + 8N_2 \rightarrow 2H_2O + 8N_2. \tag{5.177}$$

The volume is given by

$$V = \frac{(n_{H_2} + n_{O_2} + n_{N_2})\overline{R}T_1}{P_1}, \tag{5.178}$$

$$= \frac{(2\ kmole + 1\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(298\ K)}{100\ kPa}, \tag{5.179}$$

$$= 272.533\ m^3. \tag{5.180}$$

The first law gives

$$\begin{aligned}
U_2 - U_1 &= {}_1Q_2 - {}_1W_2, \\
U_2 - U_1 &= 0, \\
n_{H_2O}\overline{u}_{H_2O} - n_{H_2}\overline{u}_{H_2} - n_{O_2}\overline{u}_{O_2} + n_{N_2}(\overline{u}_{N_2 2} - \overline{u}_{N_2 1}) &= 0, \\
n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{H_2}(\overline{h}_{H_2} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1) + n_{N_2}((\overline{h}_{N_{2_2}} - \overline{R}T_2) - (\overline{h}_{N_{2_1}} - \overline{R}T_1)) &= 0, \\
2\overline{h}_{H_2O} - 2\underbrace{\overline{h}_{H_2}}_{=0} - \underbrace{\overline{h}_{O_2}}_{=0} + \overline{R}(-10T_2 + 11T_1) + 8(\underbrace{\overline{h}_{N_{2_2}}}_{=\Delta\overline{h}_{N_2}} - \underbrace{\overline{h}_{N_{2_1}}}_{=0}) &= 0, \\
2\overline{h}_{H_2O} + (8.314)\left(-10T_2 + (11)(298)\right) + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
2\overline{h}_{H_2O} - 83.14T_2 + 27253.3 + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
2\overline{h}^{o}_{f,H_2O} + 2\Delta\overline{h}_{H_2O} - 83.14T_2 + 27253.3 + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
2(-241826) + 2\Delta\overline{h}_{H_2O} - 83.14T_2 + 27253.3 + 8\Delta\overline{h}_{N_{2_2}} &= 0, \\
-456399 + 2\Delta\overline{h}_{H_2O} - 83.14T_2 + 8\Delta\overline{h}_{N_{2_2}} &= 0.
\end{aligned}$$

At this point, one begins an iteration process, guessing a value of T_2 and an associated $\Delta\overline{h}_{H_2O}$. When T_2 is guessed at 2000 K, the left side becomes -28006.7. When T_2 is guessed at 2200 K, the left side becomes 33895.3. Interpolate then to arrive at

$$\boxed{T_2 = 2090.5\ K.} \tag{5.181}$$

The inert diluent significantly lowers the adiabatic flame temperature. This is because the N_2 serves as a heat sink for the energy of reaction. If the mixture were at non-stoichiometric conditions, the excess species would also serve as a heat sink, and the adiabatic flame temperature would be lower than that of the stoichiometric mixture.

The final pressure is given by

$$P_2 = \frac{(n_{H_2O} + n_{N_2})\overline{R}T_2}{V}, \tag{5.182}$$

$$= \frac{(2\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(2090.5\ K)}{272.533\ m^3}, \tag{5.183}$$

$$= \boxed{637.74\ kPa.} \tag{5.184}$$

The final concentrations of H_2O and N_2 are

$$\overline{\rho}_{H_2O} = \frac{2\ kmole}{272.533\ m^3} = 7.34 \times 10^{-3}\ \frac{kmole}{m^3}, \tag{5.185}$$

$$\overline{\rho}_{N_2} = \frac{8\ kmole}{272.533\ m^3} = 2.94 \times 10^{-2}\ \frac{kmole}{m^3}. \tag{5.186}$$

5.3.3.3 Dilute, preheated mixture

Example 5.11

Consider a variant on the previous example in which the diluted mixture is preheated to 1000 K. One can achieve this via an isentropic compression of the cold mixture, such as might occur in an engine. To simplify the analysis here, the temperature of the mixture will be increased, while the pressure will be maintained. A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 $kmole$ of H_2, 1 $kmole$ of O_2, and 8 $kmole$ of N_2 at 100 kPa and 1000 K. Find the adiabatic flame temperature and the final pressure, assuming the irreversible reaction

$$2H_2 + O_2 + 8N_2 \rightarrow 2H_2O + 8N_2. \tag{5.187}$$

The volume is given by

$$\begin{aligned} V &= \frac{(n_{H_2} + n_{O_2} + n_{N_2})\overline{R}T_1}{P_1}, & (5.188)\\ &= \frac{(2\ kmole + 1\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(1000\ K)}{100\ kPa}, & (5.189)\\ &= 914.54\ m^3. & (5.190) \end{aligned}$$

The first law gives

$$\begin{aligned} U_2 - U_1 &= {}_1Q_2 - {}_1W_2,\\ U_2 - U_1 &= 0,\\ n_{H_2O}\overline{u}_{H_2O} - n_{H_2}\overline{u}_{H_2} - n_{O_2}\overline{u}_{O_2} + n_{N_2}(\overline{u}_{N_2 2} - \overline{u}_{N_2 1}) &= 0,\\ n_{H_2O}(\overline{h}_{H_2O} - \overline{R}T_2) - n_{H_2}(\overline{h}_{H_2} - \overline{R}T_1) - n_{O_2}(\overline{h}_{O_2} - \overline{R}T_1) + n_{N_2}((\overline{h}_{N_2 2} - \overline{R}T_2) - (\overline{h}_{N_2 1} - \overline{R}T_1)) &= 0,\\ 2\overline{h}_{H_2O} - 2\overline{h}_{H_2} - \overline{h}_{O_2} + \overline{R}(-10T_2 + 11T_1) + 8(\overline{h}_{N_2 2} - \overline{h}_{N_2 1}) &= 0,\\ 2(-241826 + \Delta\overline{h}_{H_2O}) - 2(20663) - 22703 + (8.314)\left(-10T_2 + (11)(1000)\right) + 8\Delta\overline{h}_{N_2 2} - 8(21463) &= 0,\\ 2\Delta\overline{h}_{H_2O} - 83.14T_2 - 627931 + 8\Delta\overline{h}_{N_2 2} &= 0. \end{aligned}$$

At this point, one begins an iteration process, guessing a value of T_2 and an associated $\Delta\overline{h}_{H_2O}$. When T_2 is guessed at 2600 K, the left side becomes -11351. When T_2 is guessed at 2800 K, the left side becomes 52787. Interpolate then to arrive at

$$\boxed{T_2 = 2635.4\ K.} \tag{5.191}$$

The preheating raised the adiabatic flame temperature. Note that the preheating was by $(1000\ K) - (298\ K) = 702\ K$. The new adiabatic flame temperature is only $(2635.4\ K) - (2090.5\ K) = 544.9\ K$ greater.

The final pressure is given by

$$\begin{aligned} P_2 &= \frac{(n_{H_2O} + n_{N_2})\overline{R}T_2}{V}, & (5.192)\\ &= \frac{(2\ kmole + 8\ kmole)\left(8.314\ \frac{kJ}{kmole\ K}\right)(2635.4\ K)}{914.54\ m^3}, & (5.193)\\ &= \boxed{239.58\ kPa.} & (5.194) \end{aligned}$$

The final concentrations of H_2O and N_2 are

$$\begin{aligned} \overline{\rho}_{H_2O} &= \frac{2\ kmole}{914.54\ m^3} = 2.19 \times 10^{-3}\ \frac{kmole}{m^3}, & (5.195)\\ \overline{\rho}_{N_2} &= \frac{8\ kmole}{914.54\ m^3} = 8.75 \times 10^{-3}\ \frac{kmole}{m^3}. & (5.196) \end{aligned}$$

5.3.3.4 Dilute, preheated mixture with minor species

Example 5.12

Consider a variant on the previous example. Here allow for minor species to be present at equilibrium. A closed, fixed, adiabatic volume contains a stoichiometric mixture of 2 $kmole$ of H_2, 1 $kmole$ of O_2, and 8 $kmole$ of N_2 at 100 kPa and 1000 K. Find the adiabatic flame temperature and the final pressure, assuming reversible reactions. Here, the details of the analysis are postponed, but the result is given which is the consequence of a calculation involving detailed reactions rates. One can also solve an optimization problem to minimize the Gibbs free energy of a wide variety of products to get the same answer. In this case, the equilibrium temperature and pressure are found to be

$$T = 2484.8\ K, \qquad P = 227.89\ kPa. \tag{5.197}$$

Equilibrium species concentrations are found to be

$$\text{minor product} \quad \overline{\rho}_{H_2} = 1.3 \times 10^{-4}\ \frac{kmole}{m^3}, \tag{5.198}$$

$$\text{minor product} \quad \overline{\rho}_{H} = 1.9 \times 10^{-5}\ \frac{kmole}{m^3}, \tag{5.199}$$

$$\text{minor product} \quad \overline{\rho}_{O} = 5.7 \times 10^{-6}\ \frac{kmole}{m^3}, \tag{5.200}$$

$$\text{minor product} \quad \overline{\rho}_{O_2} = 3.6 \times 10^{-5}\ \frac{kmole}{m^3}, \tag{5.201}$$

$$\text{minor product} \quad \overline{\rho}_{OH} = 5.9 \times 10^{-5}\ \frac{kmole}{m^3}, \tag{5.202}$$

$$\textbf{major product} \quad \overline{\rho}_{H_2O} = 2.0 \times 10^{-3}\ \frac{kmole}{m^3}, \tag{5.203}$$

$$\text{trace product} \quad \overline{\rho}_{HO_2} = 1.1 \times 10^{-8}\ \frac{kmole}{m^3}, \tag{5.204}$$

$$\text{trace product} \quad \overline{\rho}_{H_2O_2} = 1.2 \times 10^{-9}\ \frac{kmole}{m^3}, \tag{5.205}$$

$$\text{trace product} \quad \overline{\rho}_N = 1.7 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{5.206}$$

$$\text{trace product} \quad \overline{\rho}_{NH} = 3.7 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{5.207}$$

$$\text{trace product} \quad \overline{\rho}_{NH_2} = 1.5 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{5.208}$$

$$\text{trace product} \quad \overline{\rho}_{NH_3} = 3.1 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{5.209}$$

$$\text{trace product} \quad \overline{\rho}_{NNH} = 1.0 \times 10^{-10} \ \frac{kmole}{m^3}, \tag{5.210}$$

$$\text{minor product} \quad \overline{\rho}_{NO} = 3.1 \times 10^{-6} \ \frac{kmole}{m^3}, \tag{5.211}$$

$$\text{trace product} \quad \overline{\rho}_{NO_2} = 5.3 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{5.212}$$

$$\text{trace product} \quad \overline{\rho}_{N_2O} = 2.6 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{5.213}$$

$$\text{trace product} \quad \overline{\rho}_{HNO} = 1.7 \times 10^{-9} \ \frac{kmole}{m^3}, \tag{5.214}$$

$$\textbf{major product} \quad \overline{\rho}_{N_2} = 8.7 \times 10^{-3} \ \frac{kmole}{m^3}. \tag{5.215}$$

Note that the concentrations of the major products went down when the minor species were considered. The adiabatic flame temperature also went down by a significant amount: $2635 - 2484.8 = 150.2 \ K$. Some thermal energy was necessary to break the bonds which induce the presence of minor species.

5.4 Chemical equilibrium

Often reactions are not simply unidirectional, as alluded to in the previous example. The reverse reaction, especially at high temperature, can be important.

Consider the four species reaction

$$\nu_1' \chi_1 + \nu_2' \chi_2 \leftrightharpoons \nu_3'' \chi_3 + \nu_4'' \chi_4. \tag{5.216}$$

In terms of the net stoichiometric coefficients, this becomes

$$\nu_1 \chi_1 + \nu_2 \chi_2 + \nu_3 \chi_3 + \nu_4 \chi_4 = 0. \tag{5.217}$$

One can define a variable ζ, the *reaction progress*. Take the dimension of ζ to be *kmoles*. When $t = 0$, one takes $\zeta = 0$. Now as the reaction goes forward, one takes $d\zeta > 0$. And a forward reaction will decrease the number of moles of χ_1 and χ_2 while increasing the number of moles of χ_3 and χ_4. This will occur in ratios dictated by the stoichiometric coefficients of the problem:

$$dn_1 = -\nu_1' d\zeta, \tag{5.218}$$
$$dn_2 = -\nu_2' d\zeta, \tag{5.219}$$
$$dn_3 = +\nu_3'' d\zeta, \tag{5.220}$$
$$dn_4 = +\nu_4'' d\zeta. \tag{5.221}$$

Note that if n_i is taken to have units of *kmoles*, ν_i', and ν_i'' are taken as dimensionless, then ζ must have units of *kmoles*. In terms of the net stoichiometric coefficients, one has

$$dn_1 = \nu_1 d\zeta, \tag{5.222}$$
$$dn_2 = \nu_2 d\zeta, \tag{5.223}$$
$$dn_3 = \nu_3 d\zeta, \tag{5.224}$$
$$dn_4 = \nu_4 d\zeta. \tag{5.225}$$

Again, for argument's sake, assume that at $t = 0$, one has

$$n_1\big|_{t=0} = n_{1o}, \tag{5.226}$$
$$n_2\big|_{t=0} = n_{2o}, \tag{5.227}$$
$$n_3\big|_{t=0} = n_{3o}, \tag{5.228}$$
$$n_4\big|_{t=0} = n_{4o}. \tag{5.229}$$

Then after integrating, one finds

$$n_1 = \nu_1 \zeta + n_{1o}, \tag{5.230}$$
$$n_2 = \nu_2 \zeta + n_{2o}, \tag{5.231}$$
$$n_3 = \nu_3 \zeta + n_{3o}, \tag{5.232}$$
$$n_4 = \nu_4 \zeta + n_{4o}. \tag{5.233}$$

One can also eliminate the parameter ζ in a variety of fashions and parameterize the reaction one of the species mole numbers. Choosing, for example, n_1 as a parameter, one gets

$$\zeta = \frac{n_1 - n_{1o}}{\nu_1}. \tag{5.234}$$

Eliminating ζ then one finds all other mole numbers in terms of n_1:

$$n_2 = \nu_2 \frac{n_1 - n_{1o}}{\nu_1} + n_{2o}, \tag{5.235}$$
$$n_3 = \nu_3 \frac{n_1 - n_{1o}}{\nu_1} + n_{3o}, \tag{5.236}$$
$$n_4 = \nu_4 \frac{n_1 - n_{1o}}{\nu_1} + n_{4o}. \tag{5.237}$$

Written another way, one has

$$\frac{n_1 - n_{1o}}{\nu_1} = \frac{n_2 - n_{2o}}{\nu_2} = \frac{n_3 - n_{3o}}{\nu_3} = \frac{n_4 - n_{4o}}{\nu_4} = \zeta. \tag{5.238}$$

For an N-species reaction, $\sum_{i=1}^{N} \nu_i \chi_i = 0$, one can generalize to say

$$\begin{aligned} dn_i &= \nu_i d\zeta, & (5.239)\\ n_i &= \nu_i \zeta + n_{io}, & (5.240)\\ \frac{n_i - n_{io}}{\nu_i} &= \zeta. & (5.241) \end{aligned}$$

Note that

$$\boxed{\frac{dn_i}{d\zeta} = \nu_i.} \tag{5.242}$$

Now, from the previous chapter, one manifestation of the second law is Eq. (4.399):

$$dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i \leq 0. \tag{5.243}$$

Now, one can eliminate dn_i in Eq. (5.243) by use of Eq. (5.239) to get

$$\begin{aligned} dG|_{T,P} &= \sum_{i=1}^{N} \overline{\mu}_i \nu_i d\zeta \leq 0, & (5.244)\\ \left.\frac{\partial G}{\partial \zeta}\right|_{T,P} &= \sum_{i=1}^{N} \overline{\mu}_i \nu_i \leq 0, & (5.245)\\ &= -\overline{\alpha} \leq 0. & (5.246) \end{aligned}$$

Then for the reaction to go forward, one must require that the affinity be positive:

$$\overline{\alpha} \geq 0. \tag{5.247}$$

One also knows from the previous chapter that the irreversible entropy production takes the form of Eq. (4.387):

$$\begin{aligned} -\frac{1}{T} \sum_{i=1}^{N} \overline{\mu}_i dn_i &\geq 0, & (5.248)\\ -\frac{1}{T} d\zeta \sum_{i=1}^{N} \overline{\mu}_i \nu_i &\geq 0, & (5.249)\\ -\frac{1}{T} \frac{d\zeta}{dt} \sum_{i=1}^{N} \overline{\mu}_i \nu_i &\geq 0. & (5.250) \end{aligned}$$

In terms of the chemical affinity, $\overline{\alpha} = -\sum_{i=1}^{N} \overline{\mu}_i \nu_i$, Eq. (5.250) can be written as

$$\frac{1}{T}\frac{d\zeta}{dt}\,\overline{\alpha} \geq 0. \tag{5.251}$$

Now one straightforward, albeit naïve, way to guarantee positive semi-definiteness of the irreversible entropy production and thus satisfaction of the second law is to construct the chemical kinetic rate equation so that

$$\frac{d\zeta}{dt} = -k\sum_{i=1}^{N}\overline{\mu}_i\nu_i = k\overline{\alpha}, \qquad k \geq 0, \qquad \textit{provisional, naïve assumption} \tag{5.252}$$

This provisional assumption of convenience will be supplanted later by a form which agrees well with experiment. Here k is a positive semi-definite scalar. In general, it is a function of temperature, $k = k(T)$, so that reactions proceed rapidly at high temperature and slowly at low temperature. Then certainly the reaction progress variable ζ will cease to change when the equilibrium condition

$$\boxed{\sum_{i=1}^{N}\overline{\mu}_i\nu_i = 0,} \tag{5.253}$$

is met. This is equivalent to requiring

$$\overline{\alpha} = 0. \tag{5.254}$$

Now, while Eq. (5.253) is the most compact form of the equilibrium condition, it is not the most commonly used form. One can perform the following analysis to obtain the form in most common usage. Start by equating the chemical potential with the Gibbs free energy per unit mole for each species i: $\overline{\mu}_i = \overline{g}_i$. Then employ the definition of Gibbs free energy for an ideal gas, and carry out a set of operations:

$$\sum_{i=1}^{N}\overline{g}_i\nu_i = 0, \qquad \text{at equilibrium,} \tag{5.255}$$

$$\sum_{i=1}^{N}(\overline{h}_i - T\overline{s}_i)\nu_i = 0, \qquad \text{at equilibrium.} \tag{5.256}$$

For the ideal gas, one can substitute for $\overline{h}_i(T)$ and $\overline{s}_i(T,P)$ and write the equilibrium condition as

$$\sum_{i=1}^{N}\left(\underbrace{\overline{h}^o_{298,i} + \underbrace{\int_{298}^{T}\overline{c}_{Pi}(\hat{T})\,d\hat{T}}_{=\Delta\overline{h}^o_{T,i}}}_{=\overline{h}^o_{T,i}=\overline{h}_{T,i}} - T\left(\underbrace{\overline{s}^o_{298,i} + \int_{298}^{T}\frac{\overline{c}_{Pi}(\hat{T})}{\hat{T}}d\hat{T}}_{=\overline{s}^o_{T,i}} - \overline{R}\ln\left(\frac{y_iP}{P_o}\right)\right)}_{=\overline{s}_{T,i}}\right)\nu_i = 0. \tag{5.257}$$

Now writing the equilibrium condition in terms of the enthalpies and entropies referred to the standard pressure, one gets

$$\sum_{i=1}^{N}\left(\overline{h}^o_{T,i} - T\left(\overline{s}^o_{T,i} - \overline{R}\ln\left(\frac{y_i P}{P_o}\right)\right)\right)\nu_i = 0, \tag{5.258}$$

$$\sum_{i=1}^{N}\underbrace{\left(\overline{h}^o_{T,i} - T\overline{s}^o_{T,i}\right)}_{=\overline{g}^o_{T,i}=\overline{\mu}^o_{T,i}}\nu_i = -\sum_{i=1}^{N}\overline{R}T\nu_i\ln\left(\frac{y_i P}{P_o}\right), \tag{5.259}$$

$$-\underbrace{\sum_{i=1}^{N}\overline{g}^o_{T,i}\nu_i}_{\equiv\Delta G^o} = \overline{R}T\sum_{i=1}^{N}\ln\left(\frac{y_i P}{P_o}\right)^{\nu_i}, \tag{5.260}$$

$$-\frac{\Delta G^o}{\overline{R}T} = \sum_{i=1}^{N}\ln\left(\frac{y_i P}{P_o}\right)^{\nu_i}, \tag{5.261}$$

$$= \ln\left(\prod_{i=1}^{N}\left(\frac{y_i P}{P_o}\right)^{\nu_i}\right), \tag{5.262}$$

$$\underbrace{\exp\left(-\frac{\Delta G^o}{\overline{R}T}\right)}_{\equiv K_P} = \prod_{i=1}^{N}\left(\frac{y_i P}{P_o}\right)^{\nu_i}, \tag{5.263}$$

$$K_P = \prod_{i=1}^{N}\left(\frac{y_i P}{P_o}\right)^{\nu_i}, \tag{5.264}$$

$$K_P = \left(\frac{P}{P_o}\right)^{\sum_{i=1}^{N}\nu_i}\prod_{i=1}^{n} y_i^{\nu_i}. \tag{5.265}$$

So

$$\boxed{K_P = \prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{\nu_i},} \text{ at equilibrium.} \tag{5.266}$$

Here K_P is what is known as the pressure-based *equilibrium constant*. It is dimensionless. Despite its name, it is not a constant. It is defined in terms of thermodynamic properties, and for the ideal gas is a function of T only:

$$\boxed{K_P \equiv \exp\left(-\frac{\Delta G^o}{\overline{R}T}\right),} \qquad \text{generally valid.} \tag{5.267}$$

Only at equilibrium does the property K_P also equal the product of the partial pressures as in Eq. (5.266). The subscript P for pressure comes about because it is also related to

the product of the ratio of the partial pressure to the reference pressure raised to the net stoichiometric coefficients. Also, the net change in Gibbs free energy of the reaction at the reference pressure, ΔG^o, which is a function of T only, has been defined as

$$\boxed{\Delta G^o \equiv \sum_{i=1}^{N} \overline{g}^o_{T,i} \nu_i.} \tag{5.268}$$

The term ΔG^o has units of $kJ/kmole$; it traditionally does not get an overbar. If $\Delta G^o > 0$, one has $0 < K_P < 1$, and reactants are favored over products. If $\Delta G^o < 0$, one gets $K_P > 1$, and products are favored over reactants. One can also deduce that higher pressures P push the equilibrium in such a fashion that fewer moles are present, all else being equal. One can also define ΔG^o in terms of the chemical affinity, referred to the reference pressure, as

$$\Delta G^o = -\overline{\alpha}^o. \tag{5.269}$$

One can also define another convenient thermodynamic property, which for an ideal gas is a function of T alone, the equilibrium constant K_c:

$$\boxed{K_c \equiv \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_i} \exp\left(-\frac{\Delta G^o}{\overline{R}T}\right),} \qquad \text{generally valid.} \tag{5.270}$$

This property is dimensional, and the units depend on the stoichiometry of the reaction. The units of K_c will be $(kmole/m^3)^{\sum_{i=1}^{N} \nu_i}$.

The equilibrium condition, Eq. (5.266), is often written in terms of molar concentrations and K_c. This can be achieved by the operations, valid only at an equilibrium state:

$$K_P = \prod_{i=1}^{N} \left(\frac{\overline{\rho}_i \overline{R}T}{P_o}\right)^{\nu_i}, \tag{5.271}$$

$$\exp\left(\frac{-\Delta G^o}{\overline{R}T}\right) = \left(\frac{\overline{R}T}{P_o}\right)^{\sum_{i=1}^{N} \nu_i} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i}, \tag{5.272}$$

$$\underbrace{\left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_i} \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right)}_{\equiv K_c} = \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i}. \tag{5.273}$$

So

$$\boxed{K_c = \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i},} \qquad \text{at equilibrium.} \tag{5.274}$$

One must be careful to distinguish between the general definition of K_c as given in Eq. (5.270), and the fact that at equilibrium it is driven to also have the value of product of molar species concentrations, raised to the appropriate stoichiometric power, as given in Eq. (5.274).

5.5 Chemical kinetics of a single isothermal reaction

In the same fashion in ordinary mechanics that an understanding of statics enables an understanding of dynamics, an understanding of chemical equilibrium is necessary to understand to more challenging topic of chemical kinetics. Chemical kinetics describes the time-evolution of systems which may have an initial state far from equilibrium; it typically describes the path of such systems to an equilibrium state. Here gas phase kinetics of ideal gas mixtures that obey Dalton's law will be studied. Important topics such as catalysis and solid or liquid reactions will not be considered.

Further, this section will be restricted to strictly *isothermal* systems. This simplifies the analysis greatly. It is straightforward to extend the analysis of this system to non-isothermal systems. One must then make further appeal to the energy equation to get an equation for temperature evolution.

The general form for evolution of species is taken to be

$$\frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) = \frac{\dot{\omega}_i}{\rho}. \tag{5.275}$$

Multiplying both sides of Eq. (5.275) by molecular mass M_i and using the definition of mass fraction c_i then gives the alternate form

$$\boxed{\frac{dc_i}{dt} = \frac{\dot{\omega}_i M_i}{\rho}.} \tag{5.276}$$

5.5.1 Isochoric systems

Consider the evolution of species concentration in a system which is isothermal, isochoric and spatially homogeneous. The system is undergoing a single chemical reaction involving N species of the familiar form

$$\sum_{i=1}^{N} \nu_i \chi_i = 0. \tag{5.277}$$

Because the density is constant for the isochoric system, Eq. (5.275) reduces to

$$\frac{d\overline{\rho}_i}{dt} = \dot{\omega}_i. \tag{5.278}$$

Then, experiment, as well as a more fundamental molecular collision theory, shows that the evolution of species concentration i is given by

$$\boxed{\frac{d\overline{\rho}_i}{dt} = \overbrace{\nu_i \underbrace{aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{\equiv k(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k{}^{\nu'_k}\right)}_{\text{forward reaction}} \left(1 - \frac{1}{K_c} \underbrace{\prod_{k=1}^{N} \overline{\rho}_k{}^{\nu_k}}_{\text{reverse reaction}}\right)}^{\equiv r}}^{\equiv \dot{\omega}_i}, \qquad \text{isochoric system.} \quad (5.279)$$

This relation actually holds for isochoric, non-isothermal systems as well, which will not be considered in any detail here. Here some new variables are defined as follows:

- a: a kinetic rate constant called the *collision frequency factor*. Its units will depend on the actual reaction and could involve various combinations of length, time, and temperature. It is constructed so that $d\overline{\rho}_i/dt$ has units of $kmole/m^3/s$; this requires it to have units of $(kmole/m^3)^{(1-\sum_{k=1}^{N}\nu'_k)}/s/K^\beta$.

- β: a dimensionless parameter whose value is set by experiments, sometimes combined with guiding theory, to account for weak temperature dependency of reaction rates.

- $\overline{E}$: the *activation energy*. It has units of $kJ/kmole$, though others are often used, and is fit by both experiment and fundamental theory to account for the strong temperature dependency of reaction.

Note that in Eq. (5.279) that molar concentrations are raised to the ν'_k and ν_k powers. As it does not make sense to raise a physical quantity to a power with units, one traditionally interprets the values of ν_k, ν'_k, as well as ν''_k to be dimensionless pure numbers. They are also interpreted in a standard fashion: the smallest integer values that actually correspond to the underlying molecular collision which has been modeled. While stoichiometric balance can be achieved by a variety of ν_k values, the kinetic rates are linked to one particular set which is defined by the community.

Equation (5.279) is written in such a way that the species concentration production rate *increases* when

- The net number of moles generated in the reaction, measured by ν_i increases,

- The temperature increases; here, the sensitivity may be very high, as one observes in nature,

- The species concentrations of species involved in the forward reaction increase; this embodies the principle that the *collision-based* reaction rates are enhanced when there are more molecules to collide,

- The species concentrations of species involved in the reverse reaction decrease.

Here, three intermediate variables which are in common usage have been defined. First one takes the reaction rate to be

$$\boxed{r \equiv \underbrace{aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{\equiv k(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k{}^{\nu'_k}\right)}_{\text{forward reaction}} \left(1 - \underbrace{\frac{1}{K_c}\prod_{k=1}^{N} \overline{\rho}_k{}^{\nu_k}}_{\text{reverse reaction}}\right)}, \tag{5.280}$$

or

$$\boxed{r = \underbrace{aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{\equiv k(T),\ \text{Arrhenius rate}} \underbrace{\left(\underbrace{\prod_{k=1}^{N} \overline{\rho}_k{}^{\nu'_k}}_{\text{forward reaction}} - \underbrace{\frac{1}{K_c}\prod_{k=1}^{N} \overline{\rho}_k{}^{\nu''_k}}_{\text{reverse reaction}}\right)}_{\text{law of mass action}}}. \tag{5.281}$$

The reaction rate r has units of $kmole/m^3/s$.

The temperature-dependency of the reaction rate is embodied in $k(T)$ is defined by what is known as an *Arrhenius rate law*:

$$\boxed{k(T) \equiv aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right).} \tag{5.282}$$

This equation was advocated by van't Hoff in 1884; in 1889 Arrhenius gave a physical justification. The units of $k(T)$ actually depend on the reaction. This is a weakness of the theory, and precludes a clean non-dimensionalization. The units must be $(kmole/m^3)^{(1-\sum_{k=1}^{N}\nu'_k)}/s$.

In terms of reaction progress, one can also take

$$r = \frac{1}{V}\frac{d\zeta}{dt}. \tag{5.283}$$

The factor of $1/V$ is necessary because r has units of molar concentration per time and ζ has units of $kmoles$. The over-riding importance of the temperature sensitivity is illustrated as part of the next example. The remainder of the expression involving the products of the species concentrations is the defining characteristic of systems which obey the *law of mass action*. Though the history is complex, most attribute the law of mass action to Waage and Guldberg in 1864.[1]

Last, the overall molar production rate of species i, is often written as $\dot{\omega}_i$, defined as

$$\boxed{\dot{\omega}_i \equiv \nu_i r.} \tag{5.284}$$

[1]P. Waage and C. M. Guldberg, 1864, "Studies Concerning Affinity, *Forhandlinger: Videnskabs-Selskabet i Christiania*, 35. English translation: *Journal of Chemical Education*, 63(12): 1044-1047.

As ν_i is considered to be dimensionless, the units of $\dot{\omega}_i$ must be $kmole/m^3/s$.

Example 5.13

Study the nitrogen dissociation problem considered in an earlier example, see p. 140, in which at $t = 0\ s$, $1\ kmole$ of N_2 exists at $P = 100\ kPa$ and $T = 6000\ K$. Take as before the reaction to be *isothermal* and *isochoric*. Consider again the elementary nitrogen dissociation reaction

$$N_2 + N_2 \leftrightharpoons 2N + N_2, \tag{5.285}$$

which has kinetic rate parameters of

$$\begin{aligned} a &= 7.0 \times 10^{21}\ \frac{cm^3\ K^{1.6}}{mole\ s}, && (5.286)\\ \beta &= -1.6, && (5.287)\\ \overline{E} &= 224928.4\ \frac{cal}{mole}. && (5.288) \end{aligned}$$

In SI units, this becomes

$$\begin{aligned} a &= \left(7.0 \times 10^{21}\ \frac{cm^3\ K^{1.6}}{mole\ s}\right)\left(\frac{1\ m}{100\ cm}\right)^3\left(\frac{1000\ mole}{kmole}\right) = 7.0 \times 10^{18}\ \frac{m^3\ K^{1.6}}{kmole\ s}, && (5.289)\\ \overline{E} &= \left(224928.4\ \frac{cal}{mole}\right)\left(4.186\ \frac{J}{cal}\right)\left(\frac{kJ}{1000\ J}\right)\left(\frac{1000\ mole}{kmole}\right) = 941550\ \frac{kJ}{kmole}. && (5.290) \end{aligned}$$

At the initial state, the material is all N_2, so $P_{N_2} = P = 100\ kPa$. The ideal gas law then gives at $t = 0$

$$\begin{aligned} P|_{t=0} &= P_{N_2}|_{t=0} = \overline{\rho}_{N_2}\big|_{t=0}\,\overline{R}T, && (5.291)\\ \overline{\rho}_{N_2}\big|_{t=0} &= \frac{P|_{t=0}}{\overline{R}T}, && (5.292)\\ &= \frac{100\ kPa}{\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}, && (5.293)\\ &= 2.00465 \times 10^{-3}\ \frac{kmole}{m^3}. && (5.294) \end{aligned}$$

Thus, the volume, constant for all time in the isochoric process, is

$$V = \frac{n_{N_2}|_{t=0}}{\overline{\rho}_{N_2}\big|_{t=0}} = \frac{1\ kmole}{2.00465 \times 10^{-3}\ \frac{kmole}{m^3}} = 4.9884 \times 10^2\ m^3. \tag{5.295}$$

Now the stoichiometry of the reaction is such that

$$\begin{aligned} -dn_{N_2} &= \frac{1}{2}dn_N, && (5.296)\\ -(n_{N_2} - \underbrace{n_{N_2}|_{t=0}}_{=1\ kmole}) &= \frac{1}{2}(n_N - \underbrace{n_N|_{t=0}}_{=0}), && (5.297)\\ n_N &= 2(1\ kmole - n_{N_2}), && (5.298)\\ \frac{n_N}{V} &= 2\left(\frac{1\ kmole}{V} - \frac{n_{N_2}}{V}\right), && (5.299)\\ \overline{\rho}_N &= 2\left(\frac{1\ kmole}{4.9884 \times 10^2\ m^3} - \overline{\rho}_{N_2}\right), && (5.300)\\ &= 2\left(2.00465 \times 10^{-3}\ \frac{kmole}{m^3} - \overline{\rho}_{N_2}\right). && (5.301) \end{aligned}$$

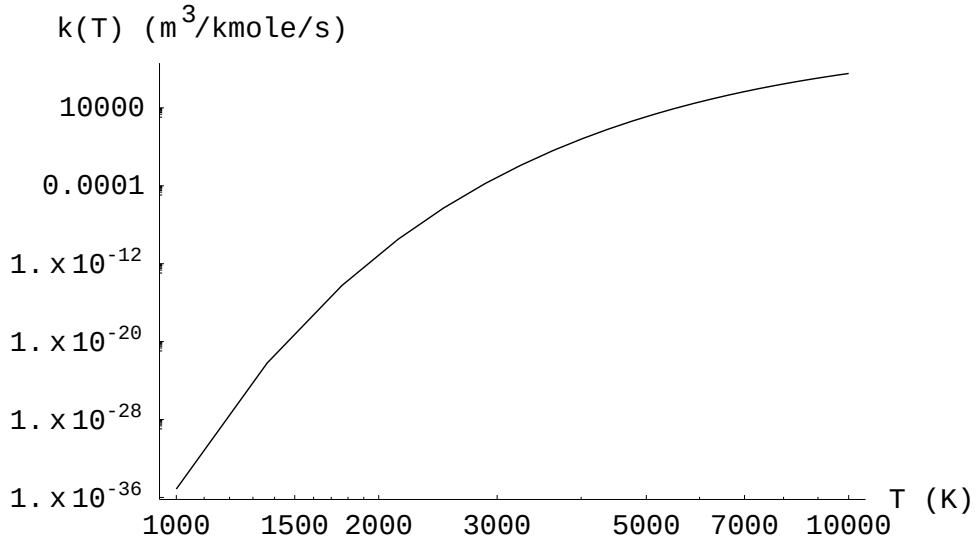

Figure 5.1: $k(T)$ for Nitrogen dissociation example.

Now the general equation for kinetics of a single reaction, Eq. (5.279), reduces for N_2 molar concentration to

$$\frac{d\overline{\rho}_{N_2}}{dt} = \nu_{N_2} a T^{\beta} \exp\left(\frac{-\overline{E}}{\overline{R}T}\right) (\overline{\rho}_{N_2})^{\nu'_{N_2}} (\overline{\rho}_N)^{\nu'_N} \left(1 - \frac{1}{K_c} (\overline{\rho}_{N_2})^{\nu_{N_2}} (\overline{\rho}_N)^{\nu_N}\right). \tag{5.302}$$

Realizing that $\nu'_{N_2} = 2$, $\nu'_N = 0$, $\nu_{N_2} = -1$, and $\nu_N = 2$, one gets

$$\frac{d\overline{\rho}_{N_2}}{dt} = -\underbrace{a T^{\beta} \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{=k(T)} \overline{\rho}_{N_2}^2 \left(1 - \frac{1}{K_c} \frac{\overline{\rho}_N^2}{\overline{\rho}_{N_2}}\right). \tag{5.303}$$

Examine the primary temperature dependency of the reaction

$$k(T) = a T^{\beta} \exp\left(\frac{-\overline{E}}{\overline{R}T}\right), \tag{5.304}$$

$$= \left(7.0 \times 10^{18} \ \frac{m^3 K^{1.6}}{kmole\ s}\right) T^{-1.6} \exp\left(\frac{-941550 \ \frac{kJ}{kmole}}{8.314 \ \frac{kJ}{kmole\ K} T}\right), \tag{5.305}$$

$$= \frac{7.0 \times 10^{18}}{T^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{T}\right). \tag{5.306}$$

Figure 5.1 gives a plot of $k(T)$ which shows its very strong dependency on temperature. For this problem, $T = 6000\ K$, so

$$k(6000) = \frac{7.0 \times 10^{18}}{6000^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{6000}\right), \tag{5.307}$$

$$= 40071.6 \ \frac{m^3}{kmole\ s}. \tag{5.308}$$

Now, the equilibrium constant K_c is needed. Recall

$$K_c = \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_i} \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right). \tag{5.309}$$

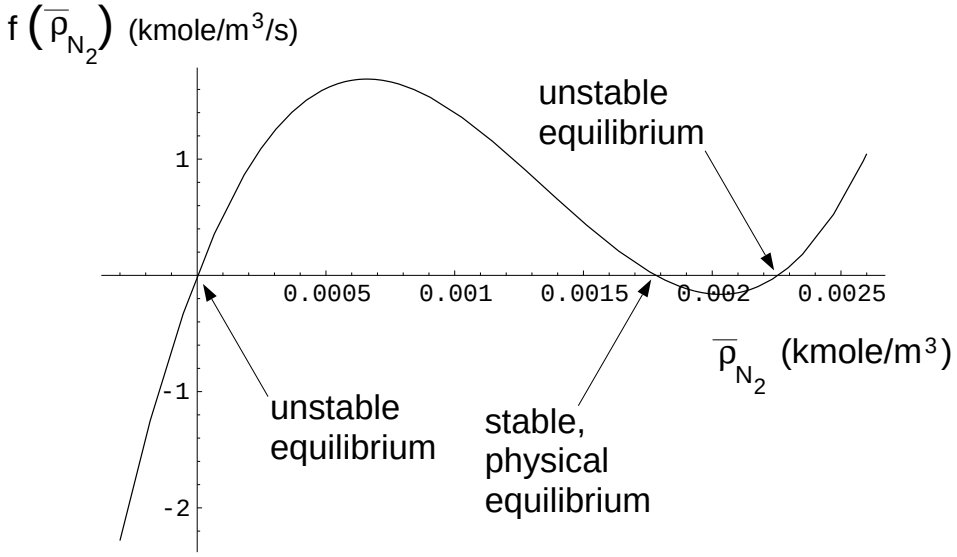

Figure 5.2: Forcing function, $f(\overline{\rho}_{N_2})$, which drives changes of $\overline{\rho}_{N_2}$ as a function of $\overline{\rho}_{N_2}$ in isothermal, isochoric problem.

For this system, since $\sum_{i=1}^{N} \nu_i = 1$, this reduces to

$$K_c = \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2\overline{g}^o_N - \overline{g}^o_{N_2})}{\overline{R}T}\right), \tag{5.310}$$

$$= \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2(\overline{h}^o_N - Ts^o_{T,N}) - (\overline{h}^o_{N_2} - Ts^o_{T,N_2}))}{\overline{R}T}\right), \tag{5.311}$$

$$= \left(\frac{100}{(8.314)(6000)}\right) \exp\left(\frac{-(2(597270 - (6000)216.926) - (205848 - (6000)292.984))}{(8.314)(6000)}\right), \tag{5.312}$$

$$= 0.000112112 \, \frac{kmole}{m^3}. \tag{5.313}$$

The differential equation for N_2 evolution is then given by

$$\frac{d\overline{\rho}_{N_2}}{dt} = \underbrace{-\left(40071.6 \, \frac{m^3}{kmole}\right) \overline{\rho}^2_{N_2} \left(1 - \frac{1}{0.000112112 \, \frac{kmole}{m^3}} \frac{\left(2\left(2.00465 \times 10^{-3} \, \frac{kmole}{m^3} - \overline{\rho}_{N_2}\right)\right)^2}{\overline{\rho}_{N_2}}\right)}_{\equiv f(\overline{\rho}_{N_2})}, \tag{5.314}$$

$$= f(\overline{\rho}_{N_2}). \tag{5.315}$$

The system is at equilibrium when $f(\overline{\rho}_{N_2}) = 0$. This is an algebraic function of $\overline{\rho}_{N_2}$ only, and can be plotted. Figure 5.2 gives a plot of $f(\overline{\rho}_{N_2})$ and shows that it has three potential equilibrium points. It is seen there are three roots. Solving for the equilibria requires solving

$$0 = -\left(40071.6 \, \frac{m^3}{kmole}\right) \overline{\rho}^2_{N_2} \left(1 - \frac{1}{0.000112112 \, \frac{kmole}{m^3}} \frac{\left(2\left(2.00465 \times 10^{-3} \, \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}\right)^2}{\overline{\rho}_{N_2}}\right). \tag{5.316}$$

The three roots are

$$\overline{\rho}_{N_2} = \underbrace{0\ \frac{kmole}{m^3}}_{\text{unstable}}, \qquad \underbrace{0.00178121\ \frac{kmole}{m^3}}_{\text{stable}}, \qquad \underbrace{0.00225611\ \frac{kmole}{m^3}}_{\text{unstable}}. \tag{5.317}$$

By inspection of the topology of Fig. 5.2, the only stable root is $0.00178121\ \frac{kmole}{m^3}$. This root agrees with the equilibrium value found in an earlier example for the same problem conditions. Small perturbations from this equilibrium induce the forcing function to supply dynamics which restore the system to its original equilibrium state. Small perturbations from the unstable equilibria induce non-restoring dynamics. For this root, one can then determine that the stable equilibrium value of $\overline{\rho}_N = 0.000446882\ \frac{kmole}{m^3}$.

One can examine this stability more formally. Define an equilibrium concentration $\overline{\rho}^{eq}_{N_2}$ such that

$$f(\overline{\rho}^{eq}_{N_2}) = 0. \tag{5.318}$$

Now perform a Taylor series of $f(\overline{\rho}_{N_2})$ about $\overline{\rho}_{N_2} = \overline{\rho}^{eq}_{N_2}$:

$$f(\overline{\rho}_{N_2}) \sim \underbrace{f(\overline{\rho}^{eq}_{N_2})}_{=0} + \left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} (\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2}) + \frac{1}{2}\frac{d^2 f}{d\overline{\rho}^2_{N_2}}(\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2})^2 + \ldots \tag{5.319}$$

Now the first term of the Taylor series is zero by construction. Next neglect all higher order terms as small so that the approximation becomes

$$f(\overline{\rho}_{N_2}) \sim \left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} (\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2}). \tag{5.320}$$

Thus, near equilibrium, one can write

$$\frac{d\overline{\rho}_{N_2}}{dt} \sim \left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} (\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2}). \tag{5.321}$$

Since the derivative of a constant is zero, one can also write the equation as

$$\frac{d}{dt}(\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2}) \sim \left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} (\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2}). \tag{5.322}$$

This has a solution, valid near the equilibrium point, of

$$(\overline{\rho}_{N_2} - \overline{\rho}^{eq}_{N_2}) = C \exp\left(\left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} t\right), \tag{5.323}$$

$$\overline{\rho}_{N_2} = \overline{\rho}^{eq}_{N_2} + C \exp\left(\left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} t\right). \tag{5.324}$$

Here C is some constant whose value is not important for this discussion. If the slope of f is positive, that is,

$$\left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} > 0, \qquad \text{unstable}, \tag{5.325}$$

the equilibrium will be *unstable*. That is a perturbation will grow without bound as $t \to \infty$. If the slope is zero,

$$\left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} = 0, \qquad \text{neutrally stable}, \tag{5.326}$$

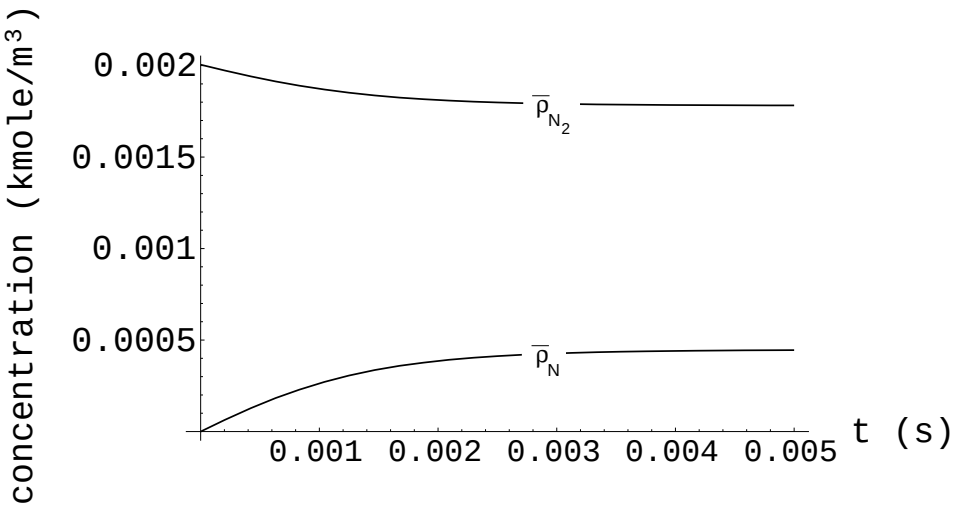

Figure 5.3: $\overline{\rho}_{N_2}(t)$ and $\overline{\rho}_N(t)$ in isothermal, isochoric nitrogen dissociation problem.

the solution is stable in that there is no unbounded growth, and moreover is known as *neutrally stable*. If the slope is negative,

$$\left.\frac{df}{d\overline{\rho}_{N_2}}\right|_{\overline{\rho}_{N_2}=\overline{\rho}^{eq}_{N_2}} < 0, \qquad \text{asymptotically stable,} \tag{5.327}$$

the solution is stable in that there is no unbounded growth, and moreover is known as *asymptotically stable*.

A numerical solution via an explicit technique such as a Runge-Kutta integration is found for Eq. (5.314). The solution for $\overline{\rho}_{N_2}$, along with $\overline{\rho}_N$ is plotted in Fig. 5.3.

Linearization of Eq. (5.314) about the equilibrium state gives rise to the locally linearly valid

$$\frac{d}{dt}\left(\overline{\rho}_{N_2} - 0.00178121\right) = -1209.39(\overline{\rho}_{N_2} - 0.00178121) + \ldots \tag{5.328}$$

This has local asymptotically stable solution

$$\overline{\rho}_{N_2} = 0.00178121 + C\exp\left(-1209.39t\right). \tag{5.329}$$

Here C is some integration constant whose value is irrelevant for this analysis. The time scale of relaxation τ is the time when the argument of the exponential is -1, which is

$$\tau = \frac{1}{1209.39\ s^{-1}} = 8.27 \times 10^{-4}\ s. \tag{5.330}$$

One usually finds this time scale to have high sensitivity to temperature, with high temperatures giving fast time constants and thus fast reactions.

The equilibrium values agree exactly with those found in the earlier example; see Eq. (4.469). Here the kinetics provide the details of *how much time it takes* to achieve equilibrium. This is one of the key questions of non-equilibrium thermodynamics.

5.5.2 Isobaric systems

The form of the previous section is the most important as it is easily extended to a Cartesian grid with fixed volume elements in fluid flow problems. However, there is another important spatially homogeneous problem in which the formulation needs slight modification: *isobaric* reaction, with P equal to a constant. Again, in this section only *isothermal* conditions will be considered.

In an isobaric problem, there can be volume change. Consider first the problem of isobaric expansion of an inert mixture. In such a mixture, the total number of moles of each species must be constant, so one gets

$$\frac{dn_i}{dt} = 0, \qquad \text{inert, isobaric mixture.} \tag{5.331}$$

Now carry out the sequence of operations, realizing the the total mass m is also constant:

$$\begin{aligned}
\frac{1}{m}\frac{d}{dt}\left(n_i\right) &= 0, && (5.332)\\
\frac{d}{dt}\left(\frac{n_i}{m}\right) &= 0, && (5.333)\\
\frac{d}{dt}\left(\frac{n_i}{V}\frac{V}{m}\right) &= 0, && (5.334)\\
\frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) &= 0, && (5.335)\\
\frac{1}{\rho}\frac{d\overline{\rho}_i}{dt} - \frac{\overline{\rho}_i}{\rho^2}\frac{d\rho}{dt} &= 0, && (5.336)\\
\frac{d\overline{\rho}_i}{dt} &= \frac{\overline{\rho}_i}{\rho}\frac{d\rho}{dt}. && (5.337)
\end{aligned}$$

So a global density decrease of the inert material due to volume increase of a fixed mass system induces a concentration decrease of each species. Extended to a material with a single reaction rate r, one could say either

$$\begin{aligned}
\frac{d\overline{\rho}_i}{dt} &= \nu_i r + \frac{\overline{\rho}_i}{\rho}\frac{d\rho}{dt}, \qquad \text{or} && (5.338)\\
\frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) &= \frac{1}{\rho}\nu_i r, \qquad \text{generally valid,} && (5.339)\\
&= \frac{\dot{\omega}_i}{\rho}. && (5.340)
\end{aligned}$$

Equation (5.339) is consistent with Eq. (5.275) and is actually valid for general systems with variable density, temperature, and pressure.

However, in this section, it is required that pressure and temperature be constant. Now

differentiate the isobaric, isothermal, ideal gas law to get the density derivative.

$$
\begin{aligned}
P &= \sum_{i=1}^{N} \overline{\rho}_i \overline{R} T, && (5.341)\\
0 &= \sum_{i=1}^{N} \overline{R} T \frac{d\overline{\rho}_i}{dt}, && (5.342)\\
0 &= \sum_{i=1}^{N} \frac{d\overline{\rho}_i}{dt}, && (5.343)\\
0 &= \sum_{i=1}^{N} \left(\nu_i r + \frac{\overline{\rho}_i}{\rho} \frac{d\rho}{dt} \right), && (5.344)\\
0 &= r \sum_{i=1}^{N} \nu_i + \frac{1}{\rho} \frac{d\rho}{dt} \sum_{i=1}^{N} \overline{\rho}_i, && (5.345)\\
\frac{d\rho}{dt} &= \frac{-r \sum_{i=1}^{N} \nu_i}{\sum_{i=1}^{N} \frac{\overline{\rho}_i}{\rho}}. && (5.346)\\
&= -\frac{\rho r \sum_{i=1}^{N} \nu_i}{\sum_{i=1}^{N} \overline{\rho}_i}, && (5.347)\\
&= -\frac{\rho r \sum_{i=1}^{N} \nu_i}{\frac{P}{\overline{R}T}}, && (5.348)\\
&= -\frac{\rho \overline{R} T r \sum_{i=1}^{N} \nu_i}{P}, && (5.349)\\
&= -\frac{\rho \overline{R} T r \sum_{k=1}^{N} \nu_k}{P}. && (5.350)
\end{aligned}
$$

Note that if there is no net number change in the reaction, $\sum_{k=1}^{N} \nu_k = 0$, the isobaric, isothermal reaction also guarantees there would be no density or volume change. It is convenient to define the net number change in the elementary reaction as $\Delta \mathsf{n}$:

$$
\boxed{\Delta \mathsf{n} \equiv \sum_{k=1}^{N} \nu_k.} \qquad (5.351)
$$

Here $\Delta \mathsf{n}$ is taken to be a dimensionless pure number. It is associated with the number change in the elementary reaction and not the actual mole change in a physical system; it is, however, proportional to the actual mole change.

Now use Eq. (5.350) to eliminate the density derivative in Eq. (5.338) to get

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r - \frac{\overline{\rho}_i}{\rho}\frac{\rho \overline{R} T r \sum_{k=1}^{N} \nu_k}{P}, \tag{5.352}$$

$$= r\left(\underbrace{\nu_i}_{\text{reaction effect}} - \underbrace{\frac{\overline{\rho}_i \overline{R} T}{P} \sum_{k=1}^{N} \nu_k}_{\text{expansion effect}} \right), \tag{5.353}$$

or

$$\boxed{\frac{d\overline{\rho}_i}{dt} = r\left(\underbrace{\nu_i}_{\text{reaction effect}} - \underbrace{y_i \Delta \mathsf{n}}_{\text{expansion effect}} \right).} \tag{5.354}$$

There are two terms dictating the rate change of species molar concentration. The first, a reaction effect, is precisely the same term that drove the isochoric reaction. The second is due to the fact that the volume can change if the number of moles change, and this induces an intrinsic change in concentration. Note that the term $\overline{\rho}_i \overline{R} T / P = y_i$, the mole fraction.

Example 5.14

Study a variant of the nitrogen dissociation problem considered in an earlier example, see p. 145, in which at $t = 0\ s$, $1\ kmole$ of N_2 exists at $P = 100\ kPa$ and $T = 6000\ K$. In this case, take the reaction to be *isothermal* and *isobaric*. Consider again the elementary nitrogen dissociation reaction

$$N_2 + N_2 \leftrightharpoons 2N + N_2, \tag{5.355}$$

which has kinetic rate parameters of

$$a = 7.0 \times 10^{21}\ \frac{cm^3\ K^{1.6}}{mole\ s}, \tag{5.356}$$

$$\beta = -1.6, \tag{5.357}$$

$$\overline{E} = 224928.4\ \frac{cal}{mole}. \tag{5.358}$$

In SI units, this becomes

$$a = \left(7.0 \times 10^{21}\ \frac{cm^3\ K^{1.6}}{mole\ s}\right)\left(\frac{1\ m}{100\ cm}\right)^3\left(\frac{1000\ mole}{kmole}\right) = 7.0 \times 10^{18}\ \frac{m^3\ K^{1.6}}{kmole\ s}, \tag{5.359}$$

$$\overline{E} = \left(224928.4\ \frac{cal}{mole}\right)\left(4.186\ \frac{J}{cal}\right)\left(\frac{kJ}{1000\ J}\right)\left(\frac{1000\ mole}{kmole}\right) = 941550\ \frac{kJ}{kmole}. \tag{5.360}$$

At the initial state, the material is all N_2, so $P_{N_2} = P = 100\ kPa$. The ideal gas law then gives at

$t = 0$

$$P = P_{N_2} = \overline{\rho}_{N_2}\overline{R}T, \tag{5.361}$$

$$\overline{\rho}_{N_2}\big|_{t=0} = \frac{P}{\overline{R}T}, \tag{5.362}$$

$$= \frac{100\ kPa}{\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}, \tag{5.363}$$

$$= 2.00465 \times 10^{-3}\ \frac{kmole}{m^3}. \tag{5.364}$$

Thus, the initial volume is

$$V|_{t=0} = \frac{n_{N_2}|_{t=0}}{\overline{\rho}_{N_2}\big|_{t=0}} = \frac{1\ kmole}{2.00465 \times 10^{-3}\ \frac{kmole}{m^3}} = 4.9884 \times 10^2\ m^3. \tag{5.365}$$

In this isobaric process, one always has $P = 100\ kPa$. Now, in general

$$P = \overline{R}T(\overline{\rho}_{N_2} + \overline{\rho}_N); \tag{5.366}$$

therefore, one can write $\overline{\rho}_N$ in terms of $\overline{\rho}_{N_2}$:

$$\overline{\rho}_N = \frac{P}{\overline{R}T} - \overline{\rho}_{N_2}, \tag{5.367}$$

$$= \frac{100\ kPa}{\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)} - \overline{\rho}_{N_2}, \tag{5.368}$$

$$= \left(2.00465 \times 10^{-3}\ \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}. \tag{5.369}$$

Then the equations for kinetics of a single isobaric isothermal reaction, Eq. (5.353) in conjunction with Eq. (5.280), reduce for N_2 molar concentration to

$$\frac{d\overline{\rho}_{N_2}}{dt} = \underbrace{\left(aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)(\overline{\rho}_{N_2})^{\nu'_{N_2}}(\overline{\rho}_N)^{\nu'_N}\left(1 - \frac{1}{K_c}(\overline{\rho}_{N_2})^{\nu_{N_2}}(\overline{\rho}_N)^{\nu_N}\right)\right)}_{=r}\left(\nu_{N_2} - \frac{\overline{\rho}_{N_2}\overline{R}T}{P}(\nu_{N_2} + \nu_N)\right). \tag{5.370}$$

Realizing that $\nu'_{N_2} = 2$, $\nu'_N = 0$, $\nu_{N_2} = -1$, and $\nu_N = 2$, one gets

$$\frac{d\overline{\rho}_{N_2}}{dt} = \underbrace{aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{=k(T)}\overline{\rho}_{N_2}^2\left(1 - \frac{1}{K_c}\frac{\overline{\rho}_N^2}{\overline{\rho}_{N_2}}\right)\left(-1 - \frac{\overline{\rho}_{N_2}\overline{R}T}{P}\right). \tag{5.371}$$

The temperature dependency of the reaction is unchanged from the previous reaction:

$$k(T) = aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right), \tag{5.372}$$

$$= \left(7.0 \times 10^{18}\ \frac{m^3 K^{1.6}}{kmole\ s}\right) T^{-1.6} \exp\left(\frac{-941550\ \frac{kJ}{kmole}}{8.314\ \frac{kJ}{kmole\ K}T}\right), \tag{5.373}$$

$$= \frac{7.0 \times 10^{18}}{T^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{T}\right). \tag{5.374}$$

For this problem, $T = 6000\ K$, so

$$k(6000) = \frac{7.0 \times 10^{18}}{6000^{1.6}} \exp\left(\frac{-1.1325 \times 10^5}{6000}\right), \tag{5.375}$$

$$= 40130.2\ \frac{m^3}{kmole\ s}. \tag{5.376}$$

The equilibrium constant K_c is also unchanged from the previous example. Recall

$$K_c = \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_i} \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right). \tag{5.377}$$

For this system, since $\sum_{i=1}^{N} \nu_i = \Delta \mathsf{n} = 1$, this reduces to

$$K_c = \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2\overline{g}^o_N - \overline{g}^o_{N_2})}{\overline{R}T}\right), \tag{5.378}$$

$$= \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2\overline{g}^o_N - \overline{g}^o_{N_2})}{\overline{R}T}\right), \tag{5.379}$$

$$= \left(\frac{P_o}{\overline{R}T}\right) \exp\left(\frac{-(2(\overline{h}^o_N - Ts^o_{T,N}) - (\overline{h}^o_{N_2} - Ts^o_{T,N_2}))}{\overline{R}T}\right), \tag{5.380}$$

$$= \left(\frac{100}{(8.314)(6000)}\right) \exp\left(\frac{-(2(597270 - (6000)216.926) - (205848 - (6000)292.984))}{(8.314)(6000)}\right), \tag{5.381}$$

$$= 0.000112112\ \frac{kmole}{m^3}. \tag{5.382}$$

The differential equation for N_2 evolution is then given by

$$\frac{d\overline{\rho}_{N_2}}{dt} = \left(40130.2\ \frac{m^3}{kmole}\right) \overline{\rho}^2_{N_2} \left(1 - \frac{1}{0.000112112\ \frac{kmole}{m^3}} \frac{\left(\left(2.00465 \times 10^{-3}\ \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}\right)^2}{\overline{\rho}_{N_2}}\right) \times \left(-1 - \frac{\overline{\rho}_{N_2}\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{100\ kPa}\right), \tag{5.383}$$

$$\equiv f(\overline{\rho}_{N_2}). \tag{5.384}$$

The system is at equilibrium when $f(\overline{\rho}_{N_2}) = 0$. This is an algebraic function of $\overline{\rho}_{N_2}$ only, and can be plotted. Figure 5.4 gives a plot of $f(\overline{\rho}_{N_2})$ and shows that it has four potential equilibrium points. It is seen there are four roots. Solving for the equilibria requires solving

$$0 = \left(40130.2\ \frac{m^3}{kmole}\right) \overline{\rho}^2_{N_2} \left(1 - \frac{1}{0.000112112\ \frac{kmole}{m^3}} \frac{\left(\left(2.00465 \times 10^{-3}\ \frac{kmole}{m^3}\right) - \overline{\rho}_{N_2}\right)^2}{\overline{\rho}_{N_2}}\right) \times \left(-1 - \frac{\overline{\rho}_{N_2}\left(8.314\ \frac{kJ}{kmole\ K}\right)(6000\ K)}{100\ kPa}\right). \tag{5.385}$$

The four roots are

$$\overline{\rho}_{N_2} = \underbrace{-0.002005\ \frac{kmole}{m^3}}_{\text{stable,non}-\text{physical}}, \quad \underbrace{0\ \frac{kmole}{m^3}}_{\text{unstable}}, \quad \underbrace{0.001583\ \frac{kmole}{m^3}}_{\text{stable,physical}}, \quad \underbrace{0.00254\ \frac{kmole}{m^3}}_{\text{unstable}}. \tag{5.386}$$

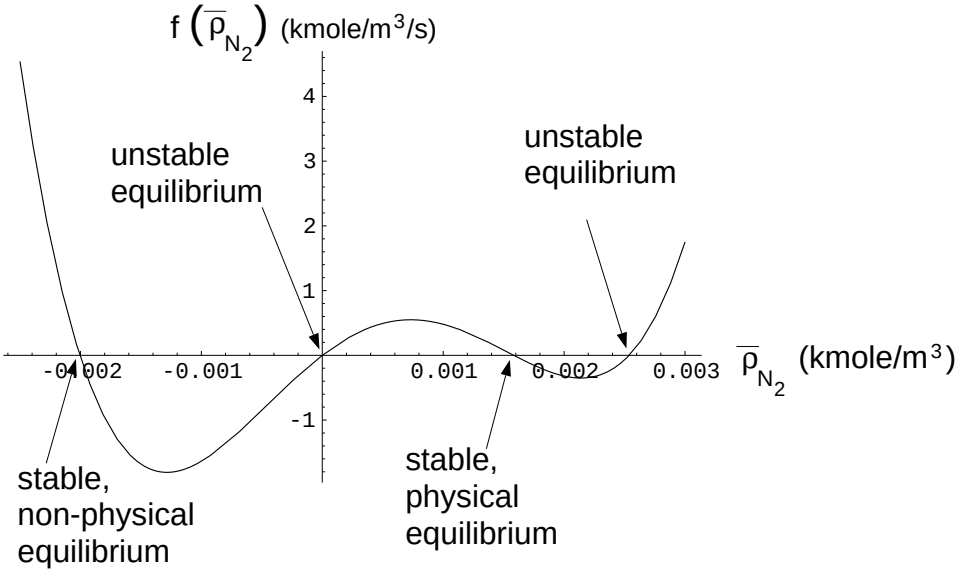

Figure 5.4: Forcing function, $f(\overline{\rho}_{N_2})$, which drives changes of $\overline{\rho}_{N_2}$ as a function of $\overline{\rho}_{N_2}$ in isothermal, isobaric problem.

By inspection of the topology of Fig. 5.2, the only stable, physical root is 0.001583 $\frac{kmole}{m^3}$. Small perturbations from this equilibrium induce the forcing function to supply dynamics which restore the system to its original equilibrium state. Small perturbations from the unstable equilibria induce non-restoring dynamics. For this root, one can then determine that the stable equilibrium value of $\overline{\rho}_N = 0.000421\ \frac{kmole}{m^3}$.

A numerical solution via an explicit technique such as a Runge-Kutta integration is found for Eq. (5.385). The solution for $\overline{\rho}_{N_2}$, along with $\overline{\rho}_N$ is plotted in Fig. 5.5.

Linearization of Eq. (5.385) about the equilibrium state gives rise to the locally linearly valid

$$\frac{d}{dt}\left(\overline{\rho}_{N_2} - 0.001583\right) = -967.073(\overline{\rho}_{N_2} - 0.001583) + \ldots \tag{5.387}$$

This has local solution

$$\overline{\rho}_{N_2} = 0.001583 + C\exp\left(-967.073t\right). \tag{5.388}$$

Again, C is an irrelevant integration constant. The time scale of relaxation τ is the time when the argument of the exponential is -1, which is

$$\tau = \frac{1}{967.073\ s^{-1}} = 1.03 \times 10^{-3}\ s. \tag{5.389}$$

Note that the time constant for the isobaric combustion is about a factor 1.25 greater than for isochoric combustion under the otherwise identical conditions.

The equilibrium values agree exactly with those found in the earlier example; see Eq. (4.514). Again, the kinetics provide the details of *how much time it takes* to achieve equilibrium.

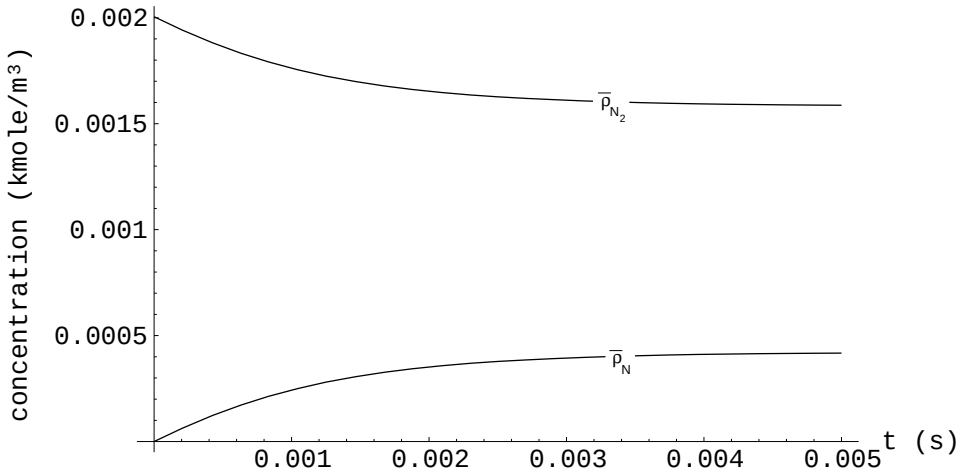

Figure 5.5: $\overline{\rho}_{N_2}(t)$ and $\overline{\rho}_N(t)$ in isobaric, isothermal nitrogen dissociation problem.

5.6 Some conservation and evolution equations

Here a few useful global conservation and evolution equations are presented for some key properties. Only some cases are considered, and one could develop more relations for other scenarios.

5.6.1 Total mass conservation: isochoric reaction

One can easily show that the isochoric reaction rate model, Eq. (5.279), satisfies the principle of mixture mass conservation. Begin with Eq. (5.279) in a compact form, using the definition of the reaction rate r, Eq. (5.281) and perform the following operations:

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r, \tag{5.390}$$

$$\frac{d}{dt}\left(\frac{\rho c_i}{M_i}\right) = \nu_i r, \tag{5.391}$$

$$\frac{d}{dt}\left(\rho c_i\right) = \nu_i M_i r, \tag{5.392}$$

$$\frac{d}{dt}\left(\rho c_i\right) = \nu_i \underbrace{\sum_{l=1}^{L} \mathcal{M}_l \phi_{li}}_{=M_i} r, \tag{5.393}$$

$$\frac{d}{dt}\left(\rho c_i\right) = \sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \nu_i r, \tag{5.394}$$

$$\sum_{i=1}^{N} \frac{d}{dt}\left(\rho c_i\right) = \sum_{i=1}^{N}\sum_{l=1}^{L} \mathcal{M}_l \phi_{li} \nu_i r, \tag{5.395}$$

$$\frac{d}{dt}\left(\rho \underbrace{\sum_{i=1}^{N} c_i}_{=1}\right) = \sum_{l=1}^{L}\sum_{i=1}^{N} \mathcal{M}_l \phi_{li} \nu_i r, \tag{5.396}$$

$$\frac{d\rho}{dt} = r \sum_{l=1}^{L} \mathcal{M}_l \underbrace{\sum_{i=1}^{N} \phi_{li}\nu_i}_{=0}. \tag{5.397}$$

Therefore, we get

$$\boxed{\frac{d\rho}{dt} = 0.} \tag{5.398}$$

Note the term $\sum_{i=1}^{N} \phi_{li}\nu_i = 0$ because of stoichiometry, Eq. (5.24).

5.6.2 Element mass conservation: isochoric reaction

Through a similar series of operations, one can show that the mass of each element, $l = 1, \ldots, L$, in conserved in this reaction, which is chemical, not nuclear. Once again, begin with Eq. (5.281) and perform a set of operations,

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r, \tag{5.399}$$

$$\phi_{li}\frac{d\overline{\rho}_i}{dt} = \phi_{li}\nu_i r, \qquad l = 1, \ldots, L, \tag{5.400}$$

$$\frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = r\phi_{li}\nu_i, \qquad l = 1, \ldots, L, \tag{5.401}$$

$$\sum_{i=1}^{N} \frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = \sum_{i=1}^{N} r\phi_{li}\nu_i, \qquad l = 1, \ldots, L, \tag{5.402}$$

$$\frac{d}{dt}\left(\sum_{i=1}^{N} \phi_{li}\overline{\rho}_i\right) = r\underbrace{\sum_{i=1}^{N} \phi_{li}\nu_i}_{=0}, \qquad l = 1, \ldots, L, \tag{5.403}$$

$$\frac{d}{dt}\left(\sum_{i=1}^{N} \phi_{li}\overline{\rho}_i\right) = 0, \qquad l = 1, \ldots, L. \tag{5.404}$$

The term $\sum_{i=1}^{N} \phi_{li} \overline{\rho}_i$ represents the number of moles of element l per unit volume, by the following analysis

$$\sum_{i=1}^{N} \phi_{li} \overline{\rho}_i = \sum_{i=1}^{N} \frac{moles\ element\ l}{moles\ species\ i} \frac{moles\ species\ i}{volume} = \frac{moles\ element\ l}{volume} \equiv \overline{\rho}_l{}^e. \tag{5.405}$$

Here the *elemental mole density*, $\overline{\rho}_l{}^e$, for element l has been defined. So the element concentration for each element remains constant in a constant volume reaction process:

$$\boxed{\frac{d\overline{\rho}_l{}^e}{dt} = 0,} \qquad l = 1, \ldots, L. \tag{5.406}$$

One can also multiply by the elemental mass, $\mathcal{M}_l$ to get the *elemental mass density*, ρ_l^e:

$$\rho_l^e \equiv \mathcal{M}_l \overline{\rho}_l{}^e, \qquad l = 1, \ldots, L. \tag{5.407}$$

Since $\mathcal{M}_l$ is a constant, one can incorporate this definition into Eq. (5.406) to get

$$\frac{d\rho_l^e}{dt} = 0, \qquad l = 1, \ldots, L. \tag{5.408}$$

The element mass density remains constant in the constant volume reaction. One could also simply say since the elements' density is constant, and the mixture is simply a sum of the elements, that the mixture density is conserved as well.

5.6.3 Energy conservation: adiabatic, isochoric reaction

Consider a simple application of the first law of thermodynamics to reaction kinetics: that of a closed, adiabatic, isochoric combustion process in a mixture of ideal gases. One may be interested in the rate of temperature change. First, because the system is closed, there can be no mass change, and because the system is isochoric, the total volume is a non-zero constant; hence,

$$\frac{dm}{dt} = 0, \tag{5.409}$$

$$\frac{d}{dt}(\rho V) = 0, \tag{5.410}$$

$$V\frac{d\rho}{dt} = 0, \tag{5.411}$$

$$\frac{d\rho}{dt} = 0. \tag{5.412}$$

For such a process, the first law of thermodynamics is

$$\frac{dU}{dt} = \dot{Q} - \dot{W}. \tag{5.413}$$

But there is no heat transfer or work in the adiabatic isochoric process, so one gets

$$\frac{dU}{dt} = 0, \tag{5.414}$$

$$\frac{d}{dt}(mu) = 0, \tag{5.415}$$

$$m\frac{du}{dt} + u\underbrace{\frac{dm}{dt}}_{=0} = 0, \tag{5.416}$$

$$\frac{du}{dt} = 0. \tag{5.417}$$

Thus for the mixture of ideal gases, $u(T, \overline{\rho}_1, \ldots, \overline{\rho}_N) = u_o$. One can see how reaction rates affect temperature changes by expanding the derivative in Eq. (5.417)

$$\frac{d}{dt}\left(\sum_{i=1}^{N} c_i u_i\right) = 0, \tag{5.418}$$

$$\sum_{i=1}^{N} \frac{d}{dt}\left(c_i u_i\right) = 0, \tag{5.419}$$

$$\sum_{i=1}^{N} \left(c_i \frac{du_i}{dt} + u_i \frac{dc_i}{dt}\right) = 0, \tag{5.420}$$

$$\sum_{i=1}^{N} \left(c_i \frac{du_i}{dT}\frac{dT}{dt} + u_i \frac{dc_i}{dt}\right) = 0, \tag{5.421}$$

$$\sum_{i=1}^{N} \left(c_i c_{vi} \frac{dT}{dt} + u_i \frac{dc_i}{dt}\right) = 0, \tag{5.422}$$

$$\frac{dT}{dt}\underbrace{\sum_{i=1}^{N} c_i c_{vi}}_{=c_v} = -\sum_{i=1}^{N} u_i \frac{dc_i}{dt}, \tag{5.423}$$

$$c_v \frac{dT}{dt} = -\sum_{i=1}^{N} u_i \frac{d}{dt}\left(\frac{M_i \overline{\rho}_i}{\rho}\right), \tag{5.424}$$

$$\rho c_v \frac{dT}{dt} = -\sum_{i=1}^{N} u_i M_i \frac{d\overline{\rho}_i}{dt}, \tag{5.425}$$

$$\rho c_v \frac{dT}{dt} = -\sum_{i=1}^{N} u_i M_i \nu_i r, \tag{5.426}$$

$$\frac{dT}{dt} = -\frac{r\sum_{i=1}^{N} \nu_i \overline{u}_i}{\rho c_v}. \tag{5.427}$$

If one defines the net energy change of the reaction as

$$\Delta U \equiv \sum_{i=1}^{N} \nu_i \overline{u}_i, \tag{5.428}$$

one then gets

$$\boxed{\frac{dT}{dt} = -\frac{r\Delta U}{\rho c_v}.} \tag{5.429}$$

The rate of temperature change is dependent on the absolute energies, not the energy differences. If the reaction is going forward, so $r > 0$, and that is a direction in which the net molar energy change is negative, then the temperature will rise.

5.6.4 Energy conservation: adiabatic, isobaric reaction

Solving for the reaction dynamics in an adiabatic isobaric system requires some non-obvious manipulations. First, the first law of thermodynamics says $dU = dQ - dW$. Since the process is adiabatic, one has $dQ = 0$, so $dU + PdV = 0$. Since it is isobaric, one gets $d(U + PV) = 0$, or $dH = 0$. So the total enthalpy is constant. Then

$$\begin{aligned}
\frac{d}{dt}H &= 0, & (5.430)\\
\frac{d}{dt}(mh) &= 0, & (5.431)\\
\frac{dh}{dt} &= 0, & (5.432)\\
\frac{d}{dt}\left(\sum_{i=1}^{N} c_i h_i\right) &= 0, & (5.433)\\
\sum_{i=1}^{N} \frac{d}{dt}\left(c_i h_i\right) &= 0, & (5.434)\\
\sum_{i=1}^{N} c_i \frac{dh_i}{dt} + h_i \frac{dc_i}{dt} &= 0, & (5.435)\\
\sum_{i=1}^{N} c_i \frac{dh_i}{dT}\frac{dT}{dt} + h_i \frac{dc_i}{dt} &= 0, & (5.436)
\end{aligned}$$

$$\sum_{i=1}^{N} c_i c_{Pi} \frac{dT}{dt} + \sum_{i=1}^{N} h_i \frac{dc_i}{dt} = 0, \tag{5.437}$$

$$\frac{dT}{dt} \underbrace{\sum_{i=1}^{N} c_i c_{Pi}}_{=c_P} + \sum_{i=1}^{N} h_i \frac{dc_i}{dt} = 0, \tag{5.438}$$

$$c_P \frac{dT}{dt} + \sum_{i=1}^{N} h_i \frac{d}{dt}\left(\frac{\overline{\rho}_i M_i}{\rho}\right) = 0, \tag{5.439}$$

$$c_P \frac{dT}{dt} + \sum_{i=1}^{N} h_i M_i \frac{d}{dt}\left(\frac{\overline{\rho}_i}{\rho}\right) = 0. \tag{5.440}$$

Now use Eq (5.339) to eliminate the term in Eq. (5.440) involving molar concentration derivatives to get

$$c_P \frac{dT}{dt} + \sum_{i=1}^{N} \overline{h}_i \frac{\nu_i r}{\rho} = 0, \tag{5.441}$$

$$\frac{dT}{dt} = -\frac{r \sum_{i=1}^{N} \overline{h}_i \nu_i}{\rho c_P}. \tag{5.442}$$

So the temperature derivative is known as an algebraic function. If one defines the net enthalpy change as

$$\Delta H \equiv \sum_{i=1}^{N} \overline{h}_i \nu_i, \tag{5.443}$$

one gets

$$\boxed{\frac{dT}{dt} = -\frac{r \Delta H}{\rho c_P}.} \tag{5.444}$$

Now differentiate the isobaric ideal gas law to get the density derivative.

$$P = \sum_{i=1}^{N} \overline{\rho}_i \overline{R} T, \tag{5.445}$$

$$0 = \sum_{i=1}^{N} \overline{\rho}_i \overline{R} \frac{dT}{dt} + \sum_{i=1}^{N} \overline{R} T \frac{d\overline{\rho}_i}{dt}, \tag{5.446}$$

$$0 = \frac{dT}{dt} \sum_{i=1}^{N} \overline{\rho}_i + \sum_{i=1}^{N} T \left(\nu_i r + \frac{\overline{\rho}_i}{\rho} \frac{d\rho}{dt}\right), \tag{5.447}$$

$$0 = \frac{1}{T} \frac{dT}{dt} \sum_{i=1}^{N} \overline{\rho}_i + r \sum_{i=1}^{N} \nu_i + \frac{1}{\rho} \frac{d\rho}{dt} \sum_{i=1}^{N} \overline{\rho}_i. \tag{5.448}$$

Solving, we get

$$\frac{d\rho}{dt} = \frac{-\frac{1}{T}\frac{dT}{dt}\sum_{i=1}^{N}\overline{\rho}_i - r\sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\rho}}. \tag{5.449}$$

One takes dT/dt from Eq. (5.442) to get

$$\frac{d\rho}{dt} = \frac{\frac{1}{T}\frac{r\sum_{i=1}^{N}\overline{h}_i\nu_i}{\rho c_P}\sum_{i=1}^{N}\overline{\rho}_i - r\sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\rho}}. \tag{5.450}$$

Now recall that $\overline{\rho} = \rho/M$ and $\overline{c}_P = c_P M$, so $\overline{\rho}\,\overline{c}_P = \rho c_P$. Then Equation (5.450) can be reduced slightly:

$$\frac{d\rho}{dt} = r\rho\frac{\frac{\sum_{i=1}^{N}\overline{h}_i\nu_i}{\overline{c}_P T}\overbrace{\sum_{i=1}^{N}\frac{\overline{\rho}_i}{\overline{\rho}}}^{=1} - \sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\overline{\rho}_i}, \tag{5.451}$$

$$= r\rho\frac{\sum_{i=1}^{N}\frac{\overline{h}_i\nu_i}{\overline{c}_P T} - \sum_{i=1}^{N}\nu_i}{\sum_{i=1}^{N}\overline{\rho}_i}, \tag{5.452}$$

$$= r\rho\frac{\sum_{i=1}^{N}\nu_i\left(\frac{\overline{h}_i}{\overline{c}_P T} - 1\right)}{\frac{P}{\overline{R}T}}, \tag{5.453}$$

$$= r\frac{\rho\overline{R}T}{P}\sum_{i=1}^{N}\nu_i\left(\frac{\overline{h}_i}{\overline{c}_P T} - 1\right), \tag{5.454}$$

$$= rM\sum_{i=1}^{N}\nu_i\left(\frac{\overline{h}_i}{\overline{c}_P T} - 1\right), \tag{5.455}$$

where M is the mean molecular mass. Note for exothermic reaction $\sum_{i=1}^{N}\nu_i\overline{h}_i < 0$, so exothermic reaction induces a density decrease as the increased temperature at constant pressure causes the volume to increase.

Then using Eq. (5.455) to eliminate the density derivative in Eq. (5.338), and changing the dummy index from i to k, one gets an explicit expression for concentration evolution:

$$\frac{d\overline{\rho}_i}{dt} = \nu_i r + \frac{\overline{\rho}_i}{\rho}rM\sum_{k=1}^{N}\nu_k\left(\frac{\overline{h}_k}{\overline{c}_P T} - 1\right), \tag{5.456}$$

$$= r\left(\nu_i + \underbrace{\frac{\overline{\rho}_i}{\rho}}_{=y_i}M\sum_{k=1}^{N}\nu_k\left(\frac{\overline{h}_k}{\overline{c}_P T} - 1\right)\right), \tag{5.457}$$

$$= r\left(\nu_i + y_i\sum_{k=1}^{N}\nu_k\left(\frac{\overline{h}_k}{\overline{c}_P T} - 1\right)\right). \tag{5.458}$$

Defining the change of enthalpy of the reaction as $\Delta H \equiv \sum_{k=1}^{N} \nu_k \overline{h}_k$, and the change of number of the reaction as $\Delta \mathsf{n} \equiv \sum_{k=1}^{N} \nu_k$, one can also say

$$\boxed{\frac{d\overline{\rho}_i}{dt} = r\left(\nu_i + y_i \left(\frac{\Delta H}{\overline{c}_P T} - \Delta \mathsf{n}\right)\right).} \tag{5.459}$$

Exothermic reaction, $\Delta H < 0$, and net number increases, $\Delta \mathsf{n} > 0$, both tend to decrease the molar concentrations of the species in the isobaric reaction.

Lastly, the evolution of the adiabatic, isobaric system, can be described by the simultaneous, coupled ordinary differential equations: Eqs. (5.442, 5.450, 5.458). These require numerical solution in general. Note also that one could also employ a more fundamental treatment as a differential algebraic system involving $H = H_1$, $P = P_1 = \overline{R}T \sum_{i=1}^{N} \overline{\rho}_i$ and Eq. (5.338).

5.6.5 Entropy evolution: Clausius-Duhem relation

Now consider whether the kinetics law that has been posed actually satisfies the second law of thermodynamics. Consider again Eq. (4.387). There is an algebraic relation on the right side. If it can be shown that this algebraic relation is positive semi-definite, then the second law is satisfied, and the algebraic relation is known as a Clausius-Duhem relation.

Now take Eq. (4.387) and perform some straightforward operations on it:

$$dS|_{U,V} = \underbrace{-\frac{1}{T}\sum_{i=1}^{N}\overline{\mu}_i dn_i}_{\text{irreversible entropy production}} \geq 0, \tag{5.460}$$

$$\left.\frac{dS}{dt}\right|_{U,V} = -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\frac{dn_i}{dt}\frac{1}{V} \geq 0, \tag{5.461}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\frac{d\overline{\rho}_i}{dt} \geq 0, \tag{5.462}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\nu_i \underbrace{\underbrace{aT^\beta \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{\equiv k(T)}\underbrace{\left(\prod_{k=1}^{N}\overline{\rho}_k{}^{\nu'_k}\right)}_{\text{forward reaction}}\left(1-\underbrace{\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k{}^{\nu_k}}_{\text{reverse reaction}}\right)}_{\equiv r} \geq 0, \tag{5.463}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\nu_i k(T)\left(\prod_{k=1}^{N}\overline{\rho}_k{}^{\nu'_k}\right)\left(1-\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k{}^{\nu_k}\right) \geq 0, \tag{5.464}$$

$$= -\frac{V}{T}k(T)\left(\prod_{k=1}^{N}\overline{\rho}_k{}^{\nu'_k}\right)\left(1-\frac{1}{K_c}\prod_{k=1}^{N}\overline{\rho}_k{}^{\nu_k}\right)\underbrace{\left(\sum_{i=1}^{N}\overline{\mu}_i\nu_i\right)}_{=-\overline{\alpha}} \geq 0, \tag{5.465}$$

Change the dummy index from k back to i,

$$= \frac{V}{T}k(T)\left(\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu'_i}\right)\left(1-\frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right)\overline{\alpha} \geq 0, \tag{5.466}$$

$$= \frac{V}{T}r\overline{\alpha}, \tag{5.467}$$

$$= \frac{\overline{\alpha}}{T}\frac{d\zeta}{dt}. \tag{5.468}$$

Consider now the affinity $\overline{\alpha}$ term in Eq. (5.466) and expand it so that it has a more useful form:

$$\overline{\alpha} = -\sum_{i=1}^{N}\overline{\mu}_i\nu_i = -\sum_{i=1}^{N}\overline{g}_i\nu_i, \tag{5.469}$$

$$= -\sum_{i=1}^{N}\left(\overline{g}^o_{T,i} + \overline{R}T\ln\left(\frac{P_i}{P_o}\right)\right)\nu_i, \tag{5.470}$$

$$= -\underbrace{\sum_{i=1}^{N} \overline{g}^o_{T,i}\nu_i}_{=\Delta G^o} - \overline{R}T \sum_{i=1}^{N} \ln\left(\frac{P_i}{P_o}\right)^{\nu_i}, \tag{5.471}$$

$$= \overline{R}T\left(\underbrace{\frac{-\Delta G^o}{\overline{R}T}}_{=\ln K_P} - \sum_{i=1}^{N} \ln\left(\frac{P_i}{P_o}\right)^{\nu_i}\right), \tag{5.472}$$

$$= \overline{R}T\left(\ln K_P - \ln \prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{\nu_i}\right), \tag{5.473}$$

$$= -\overline{R}T\left(\ln \frac{1}{K_P} + \ln \prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{\nu_i}\right), \tag{5.474}$$

$$= -\overline{R}T \ln\left(\frac{1}{K_P}\prod_{i=1}^{N}\left(\frac{P_i}{P_o}\right)^{\nu_i}\right), \tag{5.475}$$

$$= -\overline{R}T \ln\left(\frac{\left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N}\nu_i}}{K_c}\prod_{i=1}^{N}\left(\frac{\overline{\rho}_i\overline{R}T}{P_o}\right)^{\nu_i}\right), \tag{5.476}$$

$$= -\overline{R}T \ln\left(\frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right). \tag{5.477}$$

Equation (5.477) is the common definition of affinity. Another form can be found by employing the definition of K_c from Eq. (5.270) to get

$$\overline{\alpha} = -\overline{R}T \ln\left(\left(\frac{P_o}{\overline{R}T}\right)^{-\sum_{i=1}^{N}\nu_i} \exp\left(\frac{\Delta G^o}{\overline{R}T}\right)\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right), \tag{5.478}$$

$$= -\overline{R}T\left(\frac{\Delta G^o}{\overline{R}T} + \ln\left(\left(\frac{P_o}{\overline{R}T}\right)^{-\sum_{i=1}^{N}\nu_i}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right)\right), \tag{5.479}$$

$$= -\Delta G^o - \overline{R}T \ln\left(\left(\frac{P_o}{\overline{R}T}\right)^{-\sum_{i=1}^{N}\nu_i}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right). \tag{5.480}$$

To see clearly that the entropy production rate is positive semi-definite, substitute Eq. (5.477) into Eq. (5.466) to get

$$\left.\frac{dS}{dt}\right|_{U,V} = \frac{V}{T}k(T)\left(\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu'_i}\right)\left(1 - \frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right)\left(-\overline{R}T \ln\left(\frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right)\right) \geq 0, \tag{5.481}$$

$$= -\overline{R}Vk(T)\left(\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu'_i}\right)\left(1 - \frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right)\ln\left(\frac{1}{K_c}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu_i}\right) \geq 0. \tag{5.482}$$

Define forward and reverse reaction coefficients, $\mathcal{R}'$, and $\mathcal{R}''$, respectively, as

$$\mathcal{R}' \equiv k(T) \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i'}, \tag{5.483}$$

$$\mathcal{R}'' \equiv \frac{k(T)}{K_c} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i''}. \tag{5.484}$$

Both $\mathcal{R}'$ and $\mathcal{R}''$ have units of $kmole/m^3/s$. It is easy to see that

$$r = \mathcal{R}' - \mathcal{R}''. \tag{5.485}$$

Note that since $k(T) > 0$, $K_c > 0$, and $\overline{\rho}_i \geq 0$, that both $\mathcal{R}' \geq 0$ and $\mathcal{R}'' \geq 0$. Since $\nu_i = \nu_i'' - \nu_i'$, one finds that

$$\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i} = \frac{1}{K_c} \frac{k(T)}{k(T)} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i'' - \nu_i'} = \frac{\mathcal{R}''}{\mathcal{R}'}. \tag{5.486}$$

Then Eq. (5.482) reduces to

$$\left.\frac{dS}{dt}\right|_{U,V} = -\overline{R} V \mathcal{R}' \left(1 - \frac{\mathcal{R}''}{\mathcal{R}'}\right) \ln\left(\frac{\mathcal{R}''}{\mathcal{R}'}\right) \geq 0. \tag{5.487}$$

Finally, we get

$$\boxed{\left.\frac{dS}{dt}\right|_{U,V} = \overline{R} V \left(\mathcal{R}' - \mathcal{R}''\right) \ln\left(\frac{\mathcal{R}'}{\mathcal{R}''}\right) \geq 0.} \tag{5.488}$$

Obviously, if the forward rate is greater than the reverse rate $\mathcal{R}' - \mathcal{R}'' > 0$, $\ln(\mathcal{R}'/\mathcal{R}'') > 0$, and the entropy production is positive. If the forward rate is less than the reverse rate, $\mathcal{R}' - \mathcal{R}'' < 0$, $\ln(\mathcal{R}'/\mathcal{R}'') < 0$, and the entropy production is still positive. The production rate is zero when $\mathcal{R}' = \mathcal{R}''$.

Note that the affinity $\overline{\alpha}$ can be written as

$$\overline{\alpha} = \overline{R} T \ln\left(\frac{\mathcal{R}'}{\mathcal{R}''}\right). \tag{5.489}$$

And so when the forward reaction rate exceeds the reverse, the affinity is positive. It is zero at equilibrium, when the forward reaction rate equals the reverse.

5.7 Simple one-step kinetics

A common model in theoretical combustion is that of so-called simple one-step kinetics. Such a model, in which the molecular mass does not change, is quantitatively appropriate only

for isomerization reactions. However, as a pedagogical tool as well as a qualitative model for real chemistry, it can be valuable.

Consider the reversible reaction

$$\mathsf{A} \leftrightharpoons \mathsf{B}. \tag{5.490}$$

where chemical species A and B have identical molecular masses $M_{\mathsf{A}} = M_{\mathsf{B}} = M$. Consider further the case in which at the initial state, n_o moles of A only are present. Also take the reaction to be isochoric and isothermal. These assumptions can easily be relaxed for more general cases. Specializing then Eq. (5.240) for this case, one has

$$n_{\mathsf{A}} = \underbrace{\nu_A}_{=-1}\zeta + \underbrace{n_{\mathsf{A}o}}_{=n_o}, \tag{5.491}$$

$$n_{\mathsf{B}} = \underbrace{\nu_{\mathsf{B}}}_{=1}\zeta + \underbrace{n_{\mathsf{B}o}}_{=0}. \tag{5.492}$$

Thus

$$n_{\mathsf{A}} = -\zeta + n_o, \tag{5.493}$$

$$n_{\mathsf{B}} = \zeta. \tag{5.494}$$

Now n_o is constant throughout the reaction. Scale by this and define the dimensionless reaction progress as $\hat{\zeta} \equiv \zeta/n_o$ to get

$$\underbrace{\frac{n_{\mathsf{A}}}{n_o}}_{=y_{\mathsf{A}}} = -\hat{\zeta} + 1, \tag{5.495}$$

$$\underbrace{\frac{n_{\mathsf{B}}}{n_o}}_{=y_{\mathsf{B}}} = \hat{\zeta}. \tag{5.496}$$

In terms of the mole fractions then, one has

$$y_{\mathsf{A}} = 1 - \hat{\zeta}, \tag{5.497}$$

$$y_{\mathsf{B}} = \hat{\zeta}. \tag{5.498}$$

The reaction kinetics for each species reduce to

$$\frac{d\overline{\rho}_{\mathsf{A}}}{dt} = -r, \qquad \overline{\rho}_{\mathsf{A}}(0) = \frac{n_o}{V} \equiv \overline{\rho}_o, \tag{5.499}$$

$$\frac{d\overline{\rho}_{\mathsf{B}}}{dt} = r, \qquad \overline{\rho}_{\mathsf{B}}(0) = 0. \tag{5.500}$$

Addition of Eqs. (5.499) and (5.500) gives

$$\frac{d}{dt}\left(\overline{\rho}_{\mathsf{A}} + \overline{\rho}_{\mathsf{B}}\right) = 0, \tag{5.501}$$

$$\overline{\rho}_{\mathsf{A}} + \overline{\rho}_{\mathsf{B}} = \overline{\rho}_o, \tag{5.502}$$

$$\underbrace{\frac{\overline{\rho}_{\mathsf{A}}}{\overline{\rho}_o}}_{=y_{\mathsf{A}}} + \underbrace{\frac{\overline{\rho}_{\mathsf{B}}}{\overline{\rho}_o}}_{=y_{\mathsf{B}}} = 1. \tag{5.503}$$

In terms of the mole fractions y_i, one then has

$$y_{\mathsf{A}} + y_{\mathsf{B}} = 1. \tag{5.504}$$

The reaction rate r is then

$$\begin{aligned} r &= k\overline{\rho}_{\mathsf{A}}\left(1 - \frac{1}{K_c}\frac{\overline{\rho}_{\mathsf{B}}}{\overline{\rho}_{\mathsf{A}}}\right), && (5.505)\\ &= k\overline{\rho}_o\frac{\overline{\rho}_{\mathsf{A}}}{\overline{\rho}_o}\left(1 - \frac{1}{K_c}\frac{\overline{\rho}_{\mathsf{B}}/\overline{\rho}_o}{\overline{\rho}_{\mathsf{A}}/\overline{\rho}_o}\right), && (5.506)\\ &= k\overline{\rho}_o y_{\mathsf{A}}\left(1 - \frac{1}{K_c}\frac{y_{\mathsf{B}}}{y_{\mathsf{A}}}\right), && (5.507)\\ &= k\overline{\rho}_o(1-\hat{\zeta})\left(1 - \frac{1}{K_c}\frac{\hat{\zeta}}{1-\hat{\zeta}}\right). && (5.508) \end{aligned}$$

Now $r = (1/V)d\zeta/dt = (1/V)d(n_o\hat{\zeta})/dt = (n_o/V)d(\hat{\zeta})/dt = \overline{\rho}_o d\hat{\zeta}/dt$. So the reaction dynamics can be described by a single ordinary differential equation in a single unknown:

$$\begin{aligned} \overline{\rho}_o\frac{d\hat{\zeta}}{dt} &= k\overline{\rho}_o(1-\hat{\zeta})\left(1 - \frac{1}{K_c}\frac{\hat{\zeta}}{1-\hat{\zeta}}\right), && (5.509)\\ \frac{d\hat{\zeta}}{dt} &= k(1-\hat{\zeta})\left(1 - \frac{1}{K_c}\frac{\hat{\zeta}}{1-\hat{\zeta}}\right). && (5.510) \end{aligned}$$

Equation (5.510) is in equilibrium when

$$\hat{\zeta} = \frac{1}{1+\frac{1}{K_c}} \sim 1 - \frac{1}{K_c} + \ldots \tag{5.511}$$

As $K_c \to \infty$, the equilibrium value of $\hat{\zeta} \to 1$. In this limit, the reaction is irreversible. That is, the species B is preferred over A. Equation (5.510) has exact solution

$$\hat{\zeta} = \frac{1 - \exp\left(-k\left(1+\frac{1}{K_c}\right)t\right)}{1+\frac{1}{K_c}}. \tag{5.512}$$

For $k > 0$, $K_c > 0$, the equilibrium is stable. The time constant of relaxation τ is

$$\tau = \frac{1}{k\left(1+\frac{1}{K_c}\right)}. \tag{5.513}$$

For the isothermal, isochoric system, one should consider the second law in terms of the Helmholtz free energy. Combine then Eq. (4.394), $dA|_{T,V} \leq 0$, with Eq. (4.311), $dA =$

$-SdT - PdV + \sum_{i=1}^{N} \overline{\mu}_i dn_i$ and taking time derivatives, one finds

$$dA|_{T,V} = \left(-SdT - PdV + \sum_{i=1}^{N} \overline{\mu}_i dn_i \right) \Bigg|_{T,V} \leq 0, \tag{5.514}$$

$$\left. \frac{dA}{dt} \right|_{T,V} = \sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt} \leq 0, \tag{5.515}$$

$$-\frac{1}{T} \frac{dA}{dt} = -\frac{V}{T} \sum_{i=1}^{N} \overline{\mu}_i \frac{d\overline{\rho}_i}{dt} \geq 0. \tag{5.516}$$

This is exactly the same form as Eq. (5.482), which can be directly substituted into Eq. (5.516) to give

$$-\frac{1}{T} \left. \frac{dA}{dt} \right|_{T,V} = -\overline{R} V k(T) \left(\prod_{i=1}^{N} \overline{\rho}_i{}^{\nu'_i} \right) \left(1 - \frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i} \right) \ln \left(\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i} \right) \geq 0, \tag{5.517}$$

$$\left. \frac{dA}{dt} \right|_{T,V} = \overline{R} V T k(T) \left(\prod_{i=1}^{N} \overline{\rho}_i{}^{\nu'_i} \right) \left(1 - \frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i} \right) \ln \left(\frac{1}{K_c} \prod_{i=1}^{N} \overline{\rho}_i{}^{\nu_i} \right) \leq 0. \tag{5.518}$$

For the assumptions of this section, Eq. (5.518) reduces to

$$\left. \frac{dA}{dt} \right|_{T,V} = \overline{R} T k \overline{\rho}_o V (1 - \hat{\zeta}) \left(1 - \frac{1}{K_c} \frac{\hat{\zeta}}{1 - \hat{\zeta}} \right) \ln \left(\frac{1}{K_c} \frac{\hat{\zeta}}{1 - \hat{\zeta}} \right) \leq 0, \tag{5.519}$$

$$= k n_o \overline{R} T (1 - \hat{\zeta}) \left(1 - \frac{1}{K_c} \frac{\hat{\zeta}}{1 - \hat{\zeta}} \right) \ln \left(\frac{1}{K_c} \frac{\hat{\zeta}}{1 - \hat{\zeta}} \right) \leq 0. \tag{5.520}$$

Since the present analysis is nothing more than a special case of the previous section, Eq. (5.520) certainly holds. One questions however the behavior in the irreversible limit, $1/K_c \to 0$. Evaluating this limit, one finds

$$\lim_{1/K_c \to 0} \left. \frac{dA}{dt} \right|_{T,V} = k n_o \overline{R} T \left(\underbrace{(1 - \hat{\zeta})}_{>0} \underbrace{\ln \left(\frac{1}{K_c} \right)}_{\to -\infty} + (1 - \hat{\zeta}) \ln \hat{\zeta} - (1 - \hat{\zeta}) \ln (1 - \hat{\zeta}) + \ldots \right) \leq 0. \tag{5.521}$$

Now, performing the distinguished limit as $\hat{\zeta} \to 1$; that is the reaction goes to completion, one notes that all terms are driven to zero for small $1/K_c$. Recall that $1 - \hat{\zeta}$ goes to zero faster than $\ln(1 - \hat{\zeta})$ goes to $-\infty$. Note that the entropy inequality is ill-defined for a formally irreversible reaction with $1/K_c = 0$.

Chapter 6

Thermochemistry of multiple reactions

See Powers, Chapter 5
See Turns, Chapter 4, 5, 6
See Kuo, Chapters 1, 2
See Kondepudi and Prigogine, Chapter 16, 19

This chapter will extend notions associated with the thermodynamics of a single chemical reactions to systems in which many reactions occur simultaneously.

6.1 Summary of multiple reaction extensions

Consider now the reaction of N species, composed of L elements, in J reactions. This section will focus on the most common case in which $J \geq (N-L)$, which is usually the case in large chemical kinetic systems in use in engineering models. While much of the analysis will only require $J > 0$, certain results will depend on $J \geq (N-L)$. It is not difficult to study the complementary case where $0 < J < (N-L)$.

The molecular mass of species i is still given by Eq. (5.1):

$$M_i = \sum_{l=1}^{L} \mathcal{M}_l \phi_{li}, \qquad i = 1, \ldots, N. \tag{6.1}$$

However, each reaction has a stoichiometric coefficient. The j^{th} reaction can be summarized in the following ways:

$$\sum_{i=1}^{N} \chi_i \nu'_{ij} \quad \rightleftharpoons \quad \sum_{i=1}^{N} \chi_i \nu''_{ij}, \qquad j = 1, \ldots, J, \tag{6.2}$$

$$\sum_{i=1}^{N} \chi_i \nu_{ij} \quad = \quad 0, \qquad j = 1, \ldots, J. \tag{6.3}$$

Stoichiometry for the j^{th} reaction and l^{th} element is given by the extension of Eq. (5.24):

$$\boxed{\sum_{i=1}^{N} \phi_{li}\nu_{ij} = 0,} \qquad l = 1, \ldots, L, \quad j = 1, \ldots, J. \tag{6.4}$$

The net change in Gibbs free energy and equilibrium constants of the j^{th} reaction are defined by the extensions of Eqs. (5.268, 5.267, 5.270):

$$\boxed{\Delta G_j^o \equiv \sum_{i=1}^{N} \overline{g}_{T,i}^o \nu_{ij},} \qquad j = 1, \ldots, J, \tag{6.5}$$

$$\boxed{K_{P,j} \equiv \exp\left(\frac{-\Delta G_j^o}{\overline{R}T}\right),} \qquad j = 1, \ldots, J, \tag{6.6}$$

$$\boxed{K_{c,j} \equiv \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N}\nu_{ij}} \exp\left(\frac{-\Delta G_j^o}{\overline{R}T}\right),} \qquad j = 1, \ldots, J. \tag{6.7}$$

The equilibrium of the j^{th} reaction is given by the extension of Eq. (5.253):

$$\boxed{\sum_{i=1}^{N} \overline{\mu}_i \nu_{ij} = 0,} \qquad j = 1, \ldots, J, \tag{6.8}$$

or the extension of Eq. (5.255):

$$\sum_{i=1}^{N} \overline{g}_i \nu_{ij} \quad = \quad 0, \qquad j = 1, \ldots, J. \tag{6.9}$$

The multi-reaction extension of Eq. (4.521) for affinity is

$$\overline{\alpha}_j = -\sum_{i=1}^{N} \overline{\mu}_i \nu_{ij}, \qquad j = 1, \ldots, J. \tag{6.10}$$

In terms of the chemical affinity of each reaction, the equilibrium condition is simply the extension of Eq. (5.254):

$$\overline{\alpha}_j = 0, \qquad j = 1, \ldots, J. \tag{6.11}$$

At equilibrium, then the equilibrium constraints can be shown to reduce to the extension of Eq. (5.266):

$$\boxed{K_{P,j} = \prod_{i=1}^{N} \left(\frac{P_i}{P_o}\right)^{\nu_{ij}},} \qquad j = 1, \ldots, J, \tag{6.12}$$

or the extension of Eq. (5.274):

$$\boxed{K_{c,j} = \prod_{i=1}^{N} \overline{\rho}_i^{\,\nu_{ij}}, \qquad j = 1, \ldots, J.} \tag{6.13}$$

For isochoric reaction, the evolution of species concentration i due to the combined effect of J reactions is given by the extension of Eq. (5.279):

$$\boxed{\overbrace{\frac{d\overline{\rho}_i}{dt} = \sum_{j=1}^{J} \nu_{ij} \underbrace{a_j T^{\beta_j} \exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right)}_{\equiv k_j(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k^{\,\nu'_{kj}}\right)}_{\text{forward reaction}} \left(1 - \underbrace{\frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\,\nu_{kj}}}_{\text{reverse reaction}}\right)}^{\equiv \dot{\omega}_i}, \qquad i = 1, \ldots, N.} \tag{6.14}$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{\equiv r_j = (1/V) d\zeta_j/dt}$$

The extension to isobaric reactions is straightforward, and follows the same analysis as for a single reaction. Again, three intermediate variables which are in common usage have been defined. First one takes the reaction rate of the j^{th} reaction to be the extension of Eq. (5.280)

$$\boxed{r_j \equiv \underbrace{a_j T^{\beta_j} \exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right)}_{\equiv k_j(T)} \underbrace{\left(\prod_{k=1}^{N} \overline{\rho}_k^{\,\nu'_{kj}}\right)}_{\text{forward reaction}} \left(1 - \underbrace{\frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\,\nu_{kj}}}_{\text{reverse reaction}}\right), \quad j = 1, \ldots, J,} \tag{6.15}$$

or the extension of Eq. (5.281)

$$\boxed{r_j = \underbrace{a_j T^{\beta_j} \exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right)}_{\equiv k_j(T), \text{ Arrhenius rate}} \underbrace{\left(\underbrace{\prod_{k=1}^{N} \overline{\rho}_k^{\,\nu'_{kj}}}_{\text{forward reaction}} - \underbrace{\frac{1}{K_{c,j}} \prod_{k=1}^{N} \overline{\rho}_k^{\,\nu''_{kj}}}_{\text{reverse reaction}}\right)}_{\text{law of mass action}}, \qquad j = 1, \ldots, J,} \tag{6.16}$$

$$r_j = \frac{1}{V} \frac{d\zeta_j}{dt}. \tag{6.17}$$

Here ζ_j is the reaction progress variable for the j^{th} reaction.

Each reaction has a temperature-dependent rate function $k_j(T)$, which is an extension of Eq. (5.282):

$$\boxed{k_j(T) \equiv a_j T^{\beta_j} \exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right), \qquad j = 1, \ldots, J.} \tag{6.18}$$

The evolution rate of each species is given by $\dot{\omega}_i$, defined now as an extension of Eq. (5.284):

$$\boxed{\dot{\omega}_i \equiv \sum_{j=1}^{J} \nu_{ij} r_j,} \qquad i = 1, \ldots, N. \tag{6.19}$$

The multi-reaction extension of Eq. (5.239) for mole change in terms of progress variables is

$$\boxed{dn_i = \sum_{j=1}^{J} \nu_{ij} d\zeta_j,} \qquad i = 1, \ldots, N. \tag{6.20}$$

One also has Eq. (5.243):

$$\begin{aligned}
dG|_{T,P} &= \sum_{i=1}^{N} \overline{\mu}_i dn_i, && (6.21)\\
&= \sum_{i=1}^{N} \overline{\mu}_i \sum_{k=1}^{J} \nu_{ik} d\zeta_k, && (6.22)\\
\left.\frac{\partial G}{\partial \zeta_j}\right|_{\zeta_p} &= \sum_{i=1}^{N} \overline{\mu}_i \sum_{k=1}^{J} \nu_{ik} \frac{\partial \zeta_k}{\partial \zeta_j}, && (6.23)\\
&= \sum_{i=1}^{N} \overline{\mu}_i \sum_{j=1}^{J} \nu_{ik} \delta_{kj}, && (6.24)\\
&= \sum_{i=1}^{N} \overline{\mu}_i \nu_{ij}, && (6.25)\\
&= -\overline{\alpha}_j, \qquad j = 1, \ldots, J. && (6.26)
\end{aligned}$$

For a set of adiabatic, isochoric reactions, one can show the extension of Eq. (5.429) is

$$\boxed{\frac{dT}{dt} = -\frac{\sum_{j=1}^{J} r_j \Delta U_j}{\rho c_v},} \tag{6.27}$$

where the energy change for a reaction ΔU_j is defined as the extension of Eq. (5.428):

$$\boxed{\Delta U_j = \sum_{i=1}^{N} \overline{u}_i \nu_{ij},} \qquad j = 1, \ldots, J. \tag{6.28}$$

Similarly for a set of adiabatic, isobaric reactions, one can show the extension of Eq. (5.444):

$$\boxed{\frac{dT}{dt} = -\frac{\sum_{j=1}^{J} r_j \Delta H_j}{\rho c_P},} \tag{6.29}$$

where the enthalpy change for a reaction ΔH_j is defined as the extension of Eq. (5.443):

$$\boxed{\Delta H_j = \sum_{i=1}^{N} \overline{h}_i \nu_{ij},} \qquad j = 1, \ldots, J. \tag{6.30}$$

Moreover, the density and species concentration derivatives for an adiabatic, isobaric set can be shown to be extensions of Eqs. (5.455, 5.459):

$$\frac{d\rho}{dt} = M \sum_{j=1}^{J} r_j \sum_{i=1}^{N} \nu_{ij} \left(\frac{\overline{h}_i}{\overline{c}_P T} - 1 \right), \tag{6.31}$$

$$\frac{d\overline{\rho}_i}{dt} = \sum_{j=1}^{J} r_j \left(\nu_{ij} + y_i \left(\frac{\Delta H_j}{\overline{c}_P T} - \Delta \mathsf{n}_j \right) \right), \tag{6.32}$$

where

$$\Delta \mathsf{n}_j = \sum_{k=1}^{N} \nu_{kj}. \tag{6.33}$$

In a similar fashion to that shown for a single reaction, one can further sum over all reactions and prove that mixture mass is conserved, element mass and number are conserved.

Example 6.1

Show that element mass and number are conserved for the multi-reaction formulation.

Start with Eq. (6.14) and expand as follows:

$$\frac{d\overline{\rho}_i}{dt} = \sum_{j=1}^{J} \nu_{ij} r_j, \tag{6.34}$$

$$\phi_{li} \frac{d\overline{\rho}_i}{dt} = \phi_{li} \sum_{j=1}^{J} \nu_{ij} r_j, \tag{6.35}$$

$$\frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = \sum_{j=1}^{J} \phi_{li}\nu_{ij} r_j, \tag{6.36}$$

$$\sum_{i=1}^{N} \frac{d}{dt}\left(\phi_{li}\overline{\rho}_i\right) = \sum_{i=1}^{N}\sum_{j=1}^{J} \phi_{li}\nu_{ij} r_j, \tag{6.37}$$

$$\underbrace{\frac{d}{dt}\left(\sum_{i=1}^{N} \phi_{li}\overline{\rho}_i\right)}_{=\overline{\rho}_l{}^e} = \sum_{j=1}^{J}\sum_{i=1}^{N} \phi_{li}\nu_{ij} r_j, \tag{6.38}$$

$$\frac{d\overline{\rho}_l{}^e}{dt} = \sum_{j=1}^{J} r_j \underbrace{\sum_{i=1}^{N} \phi_{li}\nu_{ij}}_{=0}, \tag{6.39}$$

$$\frac{d\overline{\rho}_l{}^e}{dt} = 0, \qquad l = 1, \ldots, L, \tag{6.40}$$

$$\frac{d}{dt}\left(\mathcal{M}_l \overline{\rho}_l{}^e\right) = 0, \qquad l = 1, \ldots, L, \tag{6.41}$$

$$\frac{d\rho_l{}^e}{dt} = 0, \qquad l = 1, \ldots, L. \tag{6.42}$$

It is also straightforward to show that the mixture density is conserved for the multi-reaction, multi-component mixture:

$$\frac{d\rho}{dt} = 0. \tag{6.43}$$

The proof of the Clausius-Duhem relationship for the second law is an extension of the single reaction result. Start with Eq. (5.460) and operate much as for a single reaction model.

$$dS|_{U,V} = \underbrace{-\frac{1}{T}\sum_{i=1}^{N} \overline{\mu}_i dn_i}_{\text{irreversible entropy production}} \geq 0, \tag{6.44}$$

$$\left.\frac{dS}{dt}\right|_{U,V} = -\frac{V}{T}\sum_{i=1}^{N} \overline{\mu}_i \frac{dn_i}{dt}\frac{1}{V} \geq 0, \tag{6.45}$$

$$= -\frac{V}{T}\sum_{i=1}^{N} \overline{\mu}_i \frac{d\overline{\rho}_i}{dt} \geq 0, \tag{6.46}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\overline{\mu}_i\sum_{j=1}^{J}\nu_{ij}r_j \geq 0, \tag{6.47}$$

$$= -\frac{V}{T}\sum_{i=1}^{N}\sum_{j=1}^{J}\overline{\mu}_i\nu_{ij}r_j \geq 0, \tag{6.48}$$

$$= -\frac{V}{T}\sum_{j=1}^{J}r_j\sum_{i=1}^{N}\overline{\mu}_i\nu_{ij} \geq 0, \tag{6.49}$$

$$= -\frac{V}{T}\sum_{j=1}^{J}k_j\prod_{i=1}^{N}\overline{\rho}_i^{\nu'_{ij}}\left(1-\frac{1}{K_{c,j}}\prod_{i=1}^{N}\overline{\rho}_i^{\nu_{ij}}\right)\sum_{i=1}^{N}\overline{\mu}_i\nu_{ij} \geq 0, \tag{6.50}$$

$$= -\frac{V}{T}\sum_{j=1}^{J}k_j\prod_{i=1}^{N}\overline{\rho}_i^{\nu'_{ij}}\left(1-\frac{1}{K_{c,j}}\prod_{i=1}^{N}\overline{\rho}_i^{\nu_{ij}}\right)\left(\overline{R}T\ln\left(\frac{1}{K_{c,j}}\prod_{i=1}^{N}\overline{\rho}_i^{\nu_{ij}}\right)\right) \geq 0, \tag{6.51}$$

$$= -\overline{R}V\sum_{j=1}^{J}k_j\prod_{i=1}^{N}\overline{\rho}_i^{\nu'_{ij}}\left(1-\frac{1}{K_{c,j}}\prod_{i=1}^{N}\overline{\rho}_i^{\nu_{ij}}\right)\ln\left(\frac{1}{K_{c,j}}\prod_{i=1}^{N}\overline{\rho}_i^{\nu_{ij}}\right) \geq 0. \tag{6.52}$$

Note that Eq. (6.49) can also be written in terms of the affinities (see Eq. (6.10)) and reaction progress variables (see Eq. (6.17) as

$$\left.\frac{dS}{dt}\right|_{U,V} = \frac{1}{T}\sum_{j=1}^{J}\overline{\alpha}_j\frac{d\zeta_j}{dt} \geq 0. \tag{6.53}$$

Similar to the argument for a single reaction, if one defines extensions of Eqs. (5.483, 5.484) as

$$\mathcal{R}'_j = k_j\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu'_{ij}}, \tag{6.54}$$

$$\mathcal{R}''_j = \frac{k_j}{K_{c,j}}\prod_{i=1}^{N}\overline{\rho}_i{}^{\nu''_{ij}}, \tag{6.55}$$

then it is easy to show that

$$r_j = \mathcal{R}'_j - \mathcal{R}''_j, \tag{6.56}$$

and we get the equivalent of Eq. (5.488):

$$\boxed{\left.\frac{dS}{dt}\right|_{U,V} = \overline{R}V\sum_{j=1}^{J}\left(\mathcal{R}'_j-\mathcal{R}''_j\right)\ln\left(\frac{\mathcal{R}'_j}{\mathcal{R}''_j}\right) \geq 0.} \tag{6.57}$$

Since $k_j(T) > 0$, $\overline{R} > 0$, and $V \geq 0$, and each term in the summation combines to be positive semi-definite, one sees that the Clausius-Duhem inequality is guaranteed to be satisfied for multi-component reactions.

6.2 Equilibrium conditions

For multicomponent mixtures undergoing multiple reactions, determining the equilibrium condition is more difficult. There are two primary approaches, both of which are essentially equivalent. The most straightforward method requires formal minimization of the Gibbs free energy of the mixture. It can be shown that this actually finds the equilibrium associated with *all possible reactions*.

6.2.1 Minimization of G via Lagrange multipliers

Recall Eq. (4.395), $dG|_{T,P} \leq 0$. Recall also Eq. (4.397), $G = \sum_{i=1}^{N} \overline{g}_i n_i$. Since $\overline{\mu}_i = \overline{g}_i = \left.\frac{\partial G}{\partial n_i}\right|_{P,T,n_j}$, one also has $G = \sum_{i=1}^{N} \overline{\mu}_i n_i$. From Eq. (4.398), $dG|_{T,P} = \sum_{i=1}^{N} \overline{\mu}_i dn_i$. Now one must also demand for a system coming to equilibrium that the element numbers are conserved. This can be achieved by requiring

$$\sum_{i=1}^{N} \phi_{li}(n_{io} - n_i) = 0, \qquad l = 1, \ldots, L. \tag{6.58}$$

Here recall n_{io} is the initial number of moles of species i in the mixture, and ϕ_{li} is the number of moles of element l in species i. If one interprets $n_{io} - n_i$ as $-\nu_{ij}$, the negative of the net mole change, Eq. (6.58) becomes $-\sum_{i=1}^{N} \phi_{li}\nu_{ij} = 0$, equivalent to Eq. (6.4).

One can now use the method of constrained optimization given by the method of Lagrange multipliers to extremize G subject to the constraints of element conservation. The extremum will be a minimum; this will not be proved, but it will be demonstrated. Define a set of L Lagrange multipliers λ_l. Next define an augmented Gibbs free energy function G^*, which is simply G plus the product of the Lagrange multipliers and the constraints:

$$G^* = G + \sum_{l=1}^{L} \lambda_l \sum_{k=1}^{N} \phi_{lk}(n_{ko} - n_k). \tag{6.59}$$

Now when the constraints are satisfied, one has $G^* = G$, so assuming the constraints can be satisfied, extremizing G is equivalent to extremizing G^*. To extremize G^*, take its differential

with respect to n_i, with P, T and n_j constant and set it to zero for each species:

$$\left.\frac{\partial G^*}{\partial n_i}\right|_{T,P,n_j} = \underbrace{\left.\frac{\partial G}{\partial n_i}\right|_{T,P,n_j}}_{=\overline{\mu}_i} + \left.\frac{\partial}{\partial n_i}\right|_{T,P,n_j} \left(\sum_{l=1}^{L} \lambda_l \sum_{k=1}^{N} \phi_{lk}(n_{ko} - n_k)\right) = 0, \quad i = 1, \ldots, N, \tag{6.60}$$

$$= \overline{\mu}_i - \sum_{l=1}^{L} \lambda_l \sum_{k=1}^{N} \phi_{lk} \underbrace{\left.\frac{\partial n_k}{\partial n_i}\right|_{T,P,n_j}}_{\delta_{ki}} = 0, \quad i = 1, \ldots, N, \tag{6.61}$$

$$= \overline{\mu}_i - \sum_{l=1}^{L} \lambda_l \sum_{k=1}^{N} \phi_{lk}\delta_{ki} = 0, \quad i = 1, \ldots, N, \tag{6.62}$$

$$= \overline{\mu}_i - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \ldots, N. \tag{6.63}$$

Next, for an ideal gas, one can expand the chemical potential so as to get

$$\underbrace{\overline{\mu}^o_{T,i} + \overline{R}T \ln\left(\frac{P_i}{P_o}\right)}_{=\overline{\mu}_i} - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \ldots, N, \tag{6.64}$$

$$\overline{\mu}^o_{T,i} + \overline{R}T \ln\left(\underbrace{\left(\frac{n_i P}{\sum_{k=1}^{N} n_k}\right)}_{=P_i} \frac{1}{P_o}\right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \ldots, N. \tag{6.65}$$

Recalling that $\sum_{k=1}^{N} n_k = n$, in summary then, one has $N + L$ equations

$$\overline{\mu}^o_{T,i} + \overline{R}T \ln\left(\frac{n_i}{n}\frac{P}{P_o}\right) - \sum_{l=1}^{L} \lambda_l \phi_{li} = 0, \qquad i = 1, \ldots, N, \tag{6.66}$$

$$\sum_{i=1}^{N} \phi_{li}(n_{io} - n_i) = 0, \qquad l = 1, \ldots, L. \tag{6.67}$$

in $N + L$ unknowns: $n_i, i = 1, \ldots, N,\ \lambda_l, l = 1, \ldots, L$.

Example 6.2

Consider a previous example problem, see p. 145, in which

$$N_2 + N_2 \leftrightharpoons 2N + N_2. \tag{6.68}$$

Take the reaction to be isothermal and isobaric with $T = 6000\ K$ and $P = 100\ kPa$. Initially one has 1 $kmole$ of N_2 and 0 $kmole$ of N. Use the extremization of Gibbs free energy to find the equilibrium composition.

First find the chemical potentials at the reference pressure of each of the possible constituents.

$$\overline{\mu}^o_{T,i} = \overline{g}^o_i = \overline{h}^o_i - T\overline{s}^o_i = \overline{h}^o_{298,i} + \Delta\overline{h}^o_i - T\overline{s}^o_i. \tag{6.69}$$

For each species, one then finds

$$\overline{\mu}^o_{N_2} = 0 + 205848 - (6000)(292.984) = -1552056\ \frac{kJ}{kmole}, \tag{6.70}$$

$$\overline{\mu}^o_{N} = 472680 + 124590 - (6000)(216.926) = -704286\ \frac{kJ}{kmole}. \tag{6.71}$$

To each of these one must add

$$\overline{R}T \ln\left(\frac{n_i P}{n P_o}\right),$$

to get the full chemical potential. Now $P = P_o = 100\ kPa$ for this problem, so one only must consider $\overline{R}T = 8.314(6000) = 49884\ kJ/kmole$. So, the chemical potentials are

$$\overline{\mu}_{N_2} = -1552056 + 49884 \ln\left(\frac{n_{N_2}}{n_N + n_{N_2}}\right), \tag{6.72}$$

$$\overline{\mu}_{N} = -704286 + 49884 \ln\left(\frac{n_{N}}{n_N + n_{N_2}}\right). \tag{6.73}$$

Then one adds on the Lagrange multiplier and then considers element conservation to get the following coupled set of nonlinear algebraic equations:

$$-1552056 + 49884 \ln\left(\frac{n_{N_2}}{n_N + n_{N_2}}\right) - 2\lambda_N = 0, \tag{6.74}$$

$$-704286 + 49884 \ln\left(\frac{n_{N}}{n_N + n_{N_2}}\right) - \lambda_N = 0, \tag{6.75}$$

$$n_N + 2n_{N_2} = 2. \tag{6.76}$$

These non-linear equations are solved numerically to get

$$n_{N_2} = 0.88214\ kmole, \tag{6.77}$$

$$n_N = 0.2357\ kmole, \tag{6.78}$$

$$\lambda_N = -781934\ \frac{kJ}{kmole}. \tag{6.79}$$

These agree with results found in the earlier example problem, see p. 145.

Example 6.3

Consider a mixture of 2 $kmole$ of H_2 and 1 $kmole$ of O_2 at $T = 3000\ K$ and $P = 100\ kPa$. Assuming an isobaric and isothermal equilibration process with the products consisting of H_2, O_2, H_2O, OH, H, and O, find the equilibrium concentrations. Consider the same mixture at $T = 298\ K$ and $T = 1000\ K$.

The first task is to find the chemical potentials of each species at the reference pressure and $T = 3000\ K$. Here one can use the standard tables along with the general equation

$$\overline{\mu}^o_{T,i} = \overline{g}^o_i = \overline{h}^o_i - T\overline{s}^o_i = \overline{h}^o_{298,i} + \Delta\overline{h}^o_i - T\overline{s}^o_i. \tag{6.80}$$

For each species, one then finds

$$\begin{aligned}
\overline{\mu}^o_{H_2} &= 0 + 88724 - 3000(202.989) = -520242\ \frac{kJ}{kmole}, && (6.81)\\
\overline{\mu}^o_{O_2} &= 0 + 98013 - 3000(284.466) = -755385\ \frac{kJ}{kmole}, && (6.82)\\
\overline{\mu}^o_{H_2O} &= -241826 + 126548 - 3000(286.504) = -974790\ \frac{kJ}{kmole}, && (6.83)\\
\overline{\mu}^o_{OH} &= 38987 + 89585 - 3000(256.825) = -641903\ \frac{kJ}{kmole}, && (6.84)\\
\overline{\mu}^o_{H} &= 217999 + 56161 - 3000(162.707) = -213961\ \frac{kJ}{kmole}, && (6.85)\\
\overline{\mu}^o_{O} &= 249170 + 56574 - 3000(209.705) = -323371\ \frac{kJ}{kmole}. && (6.86)
\end{aligned}$$

To each of these one must add

$$\overline{R}T \ln\left(\frac{n_i P}{n P_o}\right),$$

to get the full chemical potential. Now $P = P_o = 100\ kPa$ for this problem, so one must only consider $\overline{R}T = 8.314(3000) = 24942\ kJ/kmole$. So, the chemical potentials are

$$\begin{aligned}
\overline{\mu}_{H_2} &= -520243 + 24942 \ln\left(\frac{n_{H_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), && (6.87)\\
\overline{\mu}_{O_2} &= -755385 + 24942 \ln\left(\frac{n_{O_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), && (6.88)\\
\overline{\mu}_{H_2O} &= -974790 + 24942 \ln\left(\frac{n_{H_2O}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), && (6.89)\\
\overline{\mu}_{OH} &= -641903 + 24942 \ln\left(\frac{n_{OH}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), && (6.90)\\
\overline{\mu}_{H} &= -213961 + 24942 \ln\left(\frac{n_{H}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right), && (6.91)\\
\overline{\mu}_{O} &= -323371 + 24942 \ln\left(\frac{n_{O}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right). && (6.92)
\end{aligned}$$

Then one adds on the Lagrange multipliers and then considers element conservation to get the following

coupled set of nonlinear equations:

$$-520243 + 24942 \ln\left(\frac{n_{H_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right) - 2\lambda_H = 0, \quad (6.93)$$

$$-755385 + 24942 \ln\left(\frac{n_{O_2}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right) - 2\lambda_O = 0, \quad (6.94)$$

$$-974790 + 24942 \ln\left(\frac{n_{H_2O}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right) - 2\lambda_H - \lambda_O = 0, \quad (6.95)$$

$$-641903 + 24942 \ln\left(\frac{n_{OH}}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right) - \lambda_H - \lambda_O = 0, \quad (6.96)$$

$$-213961 + 24942 \ln\left(\frac{n_H}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right) - \lambda_H = 0, \quad (6.97)$$

$$-323371 + 24942 \ln\left(\frac{n_O}{n_{H_2} + n_{O_2} + n_{H_2O} + n_{OH} + n_H + n_O}\right) - \lambda_O = 0, \quad (6.98)$$

$$2n_{H_2} + 2n_{H_2O} + n_{OH} + n_H = 4, \quad (6.99)$$

$$2n_{O_2} + n_{H_2O} + n_{OH} + n_O = 2. \quad (6.100)$$

These non-linear algebraic equations can be solved numerically via a Newton-Raphson technique. The equations are sensitive to the initial guess, and one can use ones intuition to help guide the selection. For example, one might expect to have n_{H_2O} somewhere near 2 *kmole*. Application of the Newton-Raphson iteration yields

$$n_{H_2} = 3.19 \times 10^{-1} \; kmole, \quad (6.101)$$

$$n_{O_2} = 1.10 \times 10^{-1} \; kmole, \quad (6.102)$$

$$n_{H_2O} = 1.50 \times 10^{0} \; kmole, \quad (6.103)$$

$$n_{OH} = 2.20 \times 10^{-1} \; kmole, \quad (6.104)$$

$$n_H = 1.36 \times 10^{-1} \; kmole, \quad (6.105)$$

$$n_O = 5.74 \times 10^{-2} \; kmole, \quad (6.106)$$

$$\lambda_H = -2.85 \times 10^{5} \; \frac{kJ}{kmole}, \quad (6.107)$$

$$\lambda_O = -4.16 \times 10^{5} \; \frac{kJ}{kmole}. \quad (6.108)$$

At this relatively high value of temperature, all species considered have a relatively major presence. That is, there are no truly minor species.

Unless a very good guess is provided, it may be difficult to find a solution for this set of non-linear equations. Straightforward algebra allows the equations to be recast in a form which sometimes

converges more rapidly:

$$\frac{n_{H_2}}{n_{H_2}+n_{O_2}+n_{H_2O}+n_{OH}+n_H+n_O} = \exp\left(\frac{520243}{24942}\right)\left(\exp\left(\frac{\lambda_H}{24942}\right)\right)^2, \quad (6.109)$$

$$\frac{n_{O_2}}{n_{H_2}+n_{O_2}+n_{H_2O}+n_{OH}+n_H+n_O} = \exp\left(\frac{755385}{24942}\right)\left(\exp\left(\frac{\lambda_O}{24942}\right)\right)^2, \quad (6.110)$$

$$\frac{n_{H_2O}}{n_{H_2}+n_{O_2}+n_{H_2O}+n_{OH}+n_H+n_O} = \exp\left(\frac{974790}{24942}\right)\exp\left(\frac{\lambda_O}{24942}\right)\left(\exp\left(\frac{\lambda_H}{24942}\right)\right)^2, \quad (6.111)$$

$$\frac{n_{OH}}{n_{H_2}+n_{O_2}+n_{H_2O}+n_{OH}+n_H+n_O} = \exp\left(\frac{641903}{24942}\right)\exp\left(\frac{\lambda_O}{24942}\right)\exp\left(\frac{\lambda_H}{24942}\right), \quad (6.112)$$

$$\frac{n_H}{n_{H_2}+n_{O_2}+n_{H_2O}+n_{OH}+n_H+n_O} = \exp\left(\frac{213961}{24942}\right)\exp\left(\frac{\lambda_H}{24942}\right), \quad (6.113)$$

$$\frac{n_O}{n_{H_2}+n_{O_2}+n_{H_2O}+n_{OH}+n_H+n_O} = \exp\left(\frac{323371}{24942}\right)\exp\left(\frac{\lambda_O}{24942}\right), \quad (6.114)$$

$$2n_{H_2}+2n_{H_2O}+n_{OH}+n_H = 4, \quad (6.115)$$

$$2n_{O_2}+n_{H_2O}+n_{OH}+n_O = 2. \quad (6.116)$$

Then solve these considering n_i, $\exp(\lambda_O/24942)$, and $\exp(\lambda_H/24942)$ as unknowns. The same result is recovered, but a broader range of initial guesses converge to the correct solution.

One can verify that this choice extremizes G by direct computation; moreover, this will show that the extremum is actually a minimum. In so doing, one must exercise care to see that element conservation is retained. As an example, perturb the equilibrium solution above for n_{H_2} and n_H such that

$$n_{H_2} = 3.19\times10^{-1}+\xi, \quad (6.117)$$

$$n_H = 1.36\times10^{-1}-2\xi. \quad (6.118)$$

Leave all other species mole numbers the same. In this way, when $\xi = 0$, one has the original equilibrium solution. For $\xi \neq 0$, the solution moves off the equilibrium value in such a way that elements are conserved. Then one has $G = \sum_{i=1}^{N}\overline{\mu}_i n_i = G(\xi)$.

The difference $G(\xi) - G(0)$ is plotted in Fig. 6.1. When $\xi = 0$, there is no deviation from the value predicted by the Newton-Raphson iteration. Clearly when $\xi = 0$, $G(\xi) - G(0)$, takes on a minimum value, and so then does $G(\xi)$. So the procedure works.

At the lower temperature, $T = 298\ K$, application of the same procedure yields very different results:

$$n_{H_2} = 4.88\times10^{-27}\ kmole, \quad (6.119)$$

$$n_{O_2} = 2.44\times10^{-27}\ kmole, \quad (6.120)$$

$$n_{H_2O} = 2.00\times10^{0}\ kmole, \quad (6.121)$$

$$n_{OH} = 2.22\times10^{-29}\ kmole, \quad (6.122)$$

$$n_H = 2.29\times10^{-49}\ kmole, \quad (6.123)$$

$$n_O = 1.67\times10^{-54}\ kmole, \quad (6.124)$$

$$\lambda_H = -9.54\times10^{4}\ \frac{kJ}{kmole}, \quad (6.125)$$

$$\lambda_O = -1.07\times10^{5}\ \frac{kJ}{kmole}. \quad (6.126)$$

At the intermediate temperature, $T = 1000\ K$, application of the same procedure shows the minor

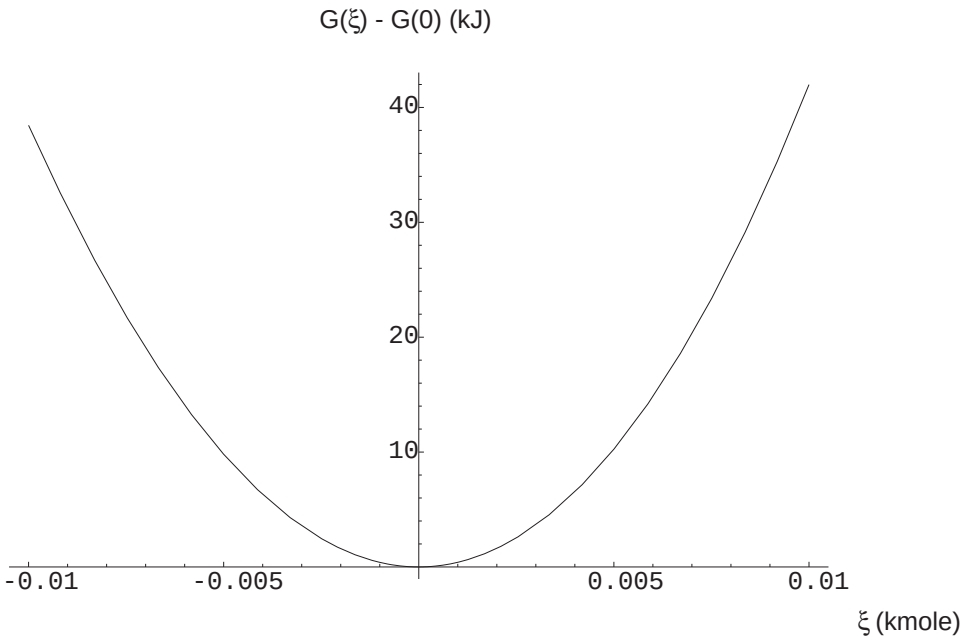

Figure 6.1: Gibbs free energy variation as mixture composition is varied maintaining element conservation for mixture of H_2, O_2, H_2O, OH, H, and O at $T = 3000\ K$, $P = 100\ kPa$.

species become slightly more prominent:

$$n_{H_2} = 4.99 \times 10^{-7}\ kmole, \tag{6.127}$$
$$n_{O_2} = 2.44 \times 10^{-7}\ kmole, \tag{6.128}$$
$$n_{H_2O} = 2.00 \times 10^{0}\ kmole, \tag{6.129}$$
$$n_{OH} = 2.09 \times 10^{-8}\ kmole, \tag{6.130}$$
$$n_{H} = 2.26 \times 10^{-12}\ kmole, \tag{6.131}$$
$$n_{O} = 1.10 \times 10^{-13}\ kmole, \tag{6.132}$$
$$\lambda_H = -1.36 \times 10^{5}\ \frac{kJ}{kmole}, \tag{6.133}$$
$$\lambda_O = -1.77 \times 10^{5}\ \frac{kJ}{kmole}. \tag{6.134}$$

6.2.2 Equilibration of all reactions

In another equivalent method, if one commences with a multi-reaction model, one can require each reaction to be in equilibrium. This leads to a set of algebraic equations for $r_j = 0$, which

from Eq. (6.16) leads to

$$K_{c,j} = \left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N}\nu_{ij}} \exp\left(\frac{-\Delta G_j^o}{\overline{R}T}\right) = \prod_{k=1}^{N} \overline{\rho}_k{}^{\nu_{kj}}, \qquad j = 1, \ldots, J. \tag{6.135}$$

With some effort it can be shown that not all of the J equations are linearly independent. Moreover, they do not possess a unique solution. However, for closed systems, only one of the solutions is physical, as will be shown in the following section. The others typically involve non-physical, negative concentrations.

Nevertheless, Eqs. (6.135) are entirely consistent with the predictions of the $N + L$ equations which arise from extremization of Gibbs free energy while enforcing element number constraints. This can be shown by beginning with Eq. (6.65), rewritten in terms of molar concentrations, and performing the following sequence of operations:

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln\left(\frac{n_i/V}{\sum_{k=1}^{N} n_k/V}\frac{P}{P_o}\right) - \sum_{l=1}^{L}\lambda_l\phi_{li} = 0, \qquad i = 1, \ldots, N, \tag{6.136}$$

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln\left(\frac{\overline{\rho}_i}{\sum_{k=1}^{N} \overline{\rho}_k}\frac{P}{P_o}\right) - \sum_{l=1}^{L}\lambda_l\phi_{li} = 0, \qquad i = 1, \ldots, N, \tag{6.137}$$

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln\left(\frac{\overline{\rho}_i}{\overline{\rho}}\frac{P}{P_o}\right) - \sum_{l=1}^{L}\lambda_l\phi_{li} = 0, \qquad i = 1, \ldots, N, \tag{6.138}$$

$$\overline{\mu}_{T,i}^o + \overline{R}T \ln\left(\overline{\rho}_i\frac{\overline{R}T}{P_o}\right) - \sum_{l=1}^{L}\lambda_l\phi_{li} = 0, \qquad i = 1, \ldots, N, \tag{6.139}$$

$$\nu_{ij}\overline{\mu}_{T,i}^o + \nu_{ij}\overline{R}T \ln\left(\overline{\rho}_i\frac{\overline{R}T}{P_o}\right) - \nu_{ij}\sum_{l=1}^{L}\lambda_l\phi_{li} = 0, \qquad i = 1, \ldots, N, \quad j = 1, \ldots, J, \tag{6.140}$$

$$\underbrace{\sum_{i=1}^{N}\nu_{ij}\overline{\mu}_{T,i}^o}_{=\Delta G_j^o} + \sum_{i=1}^{N}\nu_{ij}\overline{R}T \ln\left(\overline{\rho}_i\frac{\overline{R}T}{P_o}\right) - \sum_{i=1}^{N}\nu_{ij}\sum_{l=1}^{L}\lambda_l\phi_{li} = 0, \qquad j = 1, \ldots, J, \tag{6.141}$$

$$\Delta G_j^o + \overline{R}T\sum_{i=1}^{N}\nu_{ij} \ln\left(\overline{\rho}_i\frac{\overline{R}T}{P_o}\right) - \sum_{l=1}^{L}\lambda_l\underbrace{\sum_{i=1}^{N}\phi_{li}\nu_{ij}}_{=0} = 0, \qquad j = 1, \ldots, J, \tag{6.142}$$

$$\Delta G_j^o + \overline{R}T\sum_{i=1}^{N}\nu_{ij} \ln\left(\overline{\rho}_i\frac{\overline{R}T}{P_o}\right) = 0, \qquad j = 1, \ldots, J. \tag{6.143}$$

Here, the stoichiometry for each reaction has been employed to remove the Lagrange multi-

pliers. Continue to find

$$\sum_{i=1}^{N} \ln\left(\overline{\rho}_i \frac{\overline{R}T}{P_o}\right)^{\nu_{ij}} = -\frac{\Delta G_j^o}{\overline{R}T}, \qquad j = 1, \ldots, J, \tag{6.144}$$

$$\exp\left(\sum_{i=1}^{N} \ln\left(\overline{\rho}_i \frac{\overline{R}T}{P_o}\right)^{\nu_{ij}}\right) = \exp\left(-\frac{\Delta G_j^o}{\overline{R}T}\right), \qquad j = 1, \ldots, J, \tag{6.145}$$

$$\prod_{i=1}^{N} \left(\overline{\rho}_i \frac{\overline{R}T}{P_o}\right)^{\nu_{ij}} = \exp\left(-\frac{\Delta G_j^o}{\overline{R}T}\right), \qquad j = 1, \ldots, J, \tag{6.146}$$

$$\left(\frac{\overline{R}T}{P_o}\right)^{\sum_{i=1}^{N} \nu_{ij}} \prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}} = \exp\left(-\frac{\Delta G_j^o}{\overline{R}T}\right), \qquad j = 1, \ldots, J, \tag{6.147}$$

$$\prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}} = \underbrace{\left(\frac{P_o}{\overline{R}T}\right)^{\sum_{i=1}^{N} \nu_{ij}} \exp\left(-\frac{\Delta G_j^o}{\overline{R}T}\right)}_{=K_{c,j}}, \qquad j = 1, \ldots, J, \tag{6.148}$$

In summary,

$$\boxed{\prod_{i=1}^{N} \overline{\rho}_i^{\nu_{ij}} = K_{c,j},} \qquad j = 1, \ldots, J, \tag{6.149}$$

which is identical to Eq. (6.135), obtained by equilibrating each of the J reactions. Thus, extremization of Gibbs free energy is consistent with equilibrating each of the J reactions.

6.3 Concise reaction rate law formulations

One can additional analysis to obtain a more efficient representation of the reaction rate law for multiple reactions. There are two important cases: 1) $J \geq (N - L)$; this is most common for large chemical kinetic systems, and 2) $J < (N - L)$; this is common for simple chemistry models.

The species production rate is given by Eq. (6.14), which reduces to

$$\frac{d\overline{\rho}_i}{dt} = \frac{1}{V} \sum_{j=1}^{J} \nu_{ij} \frac{d\zeta_j}{dt}, \qquad i = 1, \ldots, N. \tag{6.150}$$

Now recalling Eq. (5.99), one has

$$dn_i = \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N. \tag{6.151}$$

Comparing then Eq. (6.151) to Eq. (6.20), one sees that

$$\sum_{j=1}^{J} \nu_{ij} d\zeta_j = \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N, \tag{6.152}$$

$$\frac{1}{V} \sum_{j=1}^{J} \nu_{ij} d\zeta_j = \frac{1}{V} \sum_{k=1}^{N-L} \mathcal{D}_{ik} d\xi_k, \qquad i = 1, \ldots, N. \tag{6.153}$$

6.3.1 Reaction dominant: $J \geq (N - L)$

Consider first the most common case in which $J \geq (N - L)$. One can say the species production rate is given

$$\frac{d\overline{\rho}_i}{dt} = \frac{1}{V} \sum_{k=1}^{N-L} \mathcal{D}_{ik} \frac{d\xi_k}{dt} = \sum_{j=1}^{J} \nu_{ij} r_j, \qquad i = 1, \ldots, N. \tag{6.154}$$

One would like to invert and solve directly for $d\xi_k/dt$. However, $\mathcal{D}_{ik}$ is non-square and has no inverse. But since $\sum_{i=1}^{N} \phi_{li} \mathcal{D}_{ip} = 0$, and $\sum_{i=1}^{N} \phi_{li} \nu_{ij} = 0$, L of the equations N equations in Eq. (6.154) are redundant.

At this point, it is more convenient to go to a Gibbs vector notation, where there is an obvious correspondence between the bold vectors and the indicial counterparts:

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \frac{1}{V} \mathbf{D} \cdot \frac{d\boldsymbol{\xi}}{dt} = \boldsymbol{\nu} \cdot \mathbf{r}, \tag{6.155}$$

$$\mathbf{D}^T \cdot \mathbf{D} \cdot \frac{d\boldsymbol{\xi}}{dt} = V \mathbf{D}^T \cdot \boldsymbol{\nu} \cdot \mathbf{r}, \tag{6.156}$$

$$\frac{d\boldsymbol{\xi}}{dt} = V (\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T \cdot \boldsymbol{\nu} \cdot \mathbf{r}. \tag{6.157}$$

Because of the L linear dependencies, there is no loss of information in this matrix projection. This system of $N - L$ equations is the smallest number of differential equations that can be solved for a general system in which $J > (N - L)$.

Lastly, one recovers the original system when forming

$$\mathbf{D} \cdot \frac{d\boldsymbol{\xi}}{dt} = V \underbrace{\mathbf{D} \cdot (\mathbf{D}^T \cdot \mathbf{D})^{-1} \cdot \mathbf{D}^T}_{=\mathbf{P}} \cdot \boldsymbol{\nu} \cdot \mathbf{r}. \tag{6.158}$$

Here, the $N \times N$ projection matrix $\mathbf{P}$ is symmetric, has norm of unity, has rank of $N - L$, has $N - L$ eigenvalues of value unity, and L eigenvalues of value zero. And, while application of a general projection matrix to $\boldsymbol{\nu} \cdot \mathbf{r}$ filters some of the information in $\boldsymbol{\nu} \cdot \mathbf{r}$, because the $N \times (N - L)$ matrix $\mathbf{D}$ spans the same column space as the $N \times J$ matrix $\boldsymbol{\nu}$, no information is lost in Eq. (6.158) relative to the original Eq. (6.155). Mathematically, one can say

$$\mathbf{P} \cdot \boldsymbol{\nu} = \boldsymbol{\nu}. \tag{6.159}$$

6.3.2 Species dominant: $J < (N - L)$

Next consider the case in which $J < (N-L)$. This often arises in models of simple chemistry, for example one- or two-step kinetics.

The fundamental reaction dynamics are most concisely governed by the J equations which form

$$\boxed{\frac{1}{V}\frac{d\boldsymbol{\zeta}}{dt} = \mathbf{r}.} \tag{6.160}$$

However, $\mathbf{r}$ is a function of the concentrations; one must therefore recover $\overline{\boldsymbol{\rho}}$ as a function of reaction progress $\boldsymbol{\zeta}$. In vector form, Eq. (6.150) is written as

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \frac{1}{V}\boldsymbol{\nu} \cdot \frac{d\boldsymbol{\zeta}}{dt}. \tag{6.161}$$

Take as an initial condition that the reaction progress is zero at $t = 0$ and that there are an appropriate set of initial conditions on the species concentrations $\overline{\boldsymbol{\rho}}$:

$$\boldsymbol{\zeta} = \mathbf{0}, \qquad t = 0, \tag{6.162}$$

$$\overline{\boldsymbol{\rho}} = \overline{\boldsymbol{\rho}}_o, \qquad t = 0. \tag{6.163}$$

Then, since $\boldsymbol{\nu}$ is a constant, Eq. (6.161) is easily integrated. After applying the initial conditions, Eq. (6.163), one gets

$$\overline{\boldsymbol{\rho}} = \overline{\boldsymbol{\rho}}_o + \frac{1}{V}\boldsymbol{\nu} \cdot \boldsymbol{\zeta}. \tag{6.164}$$

Last, if $J = (N-L)$, either approach yields the same number of equations, and is equally concise.

6.4 Adiabatic, isochoric kinetics

Here an example which uses multiple reactions for an adiabatic isochoric system is given.

Example 6.4

Consider the full time-dependency of a problem considered in a previous example in which the equilibrium state was found; see Sec. 5.3.3.4,. A closed, fixed, adiabatic volume contains at $t = 0\ s$ a stoichiometric mixture of 2 $kmole$ of H_2, 1 $kmole$ of O_2, and 8 $kmole$ of N_2 at 100 kPa and 1000 K. Find the reaction dynamics as the system proceeds from its initial state to its final state.

This problem requires a detailed numerical solution. Such a solution was performed by solving Eq. (6.14) along with the associated calorically imperfect species state equations for a mixture of eighteen interacting species: H_2, H, O, O_2, OH, H_2O, HO_2, H_2O_2, N, NH_2, NH_3, N_2H, NO, NO_2, N_2O, HNO, and N_2. The equilibrium values were reported in a previous example.

The dynamics of the reaction process are reflected in Fig. 6.2. At early time, $t < 4 \times 10^{-4}\ s$, the pressure, temperature, and major reactant species concentrations ($H_2,\ O_2,\ N_2$) are nearly constant.

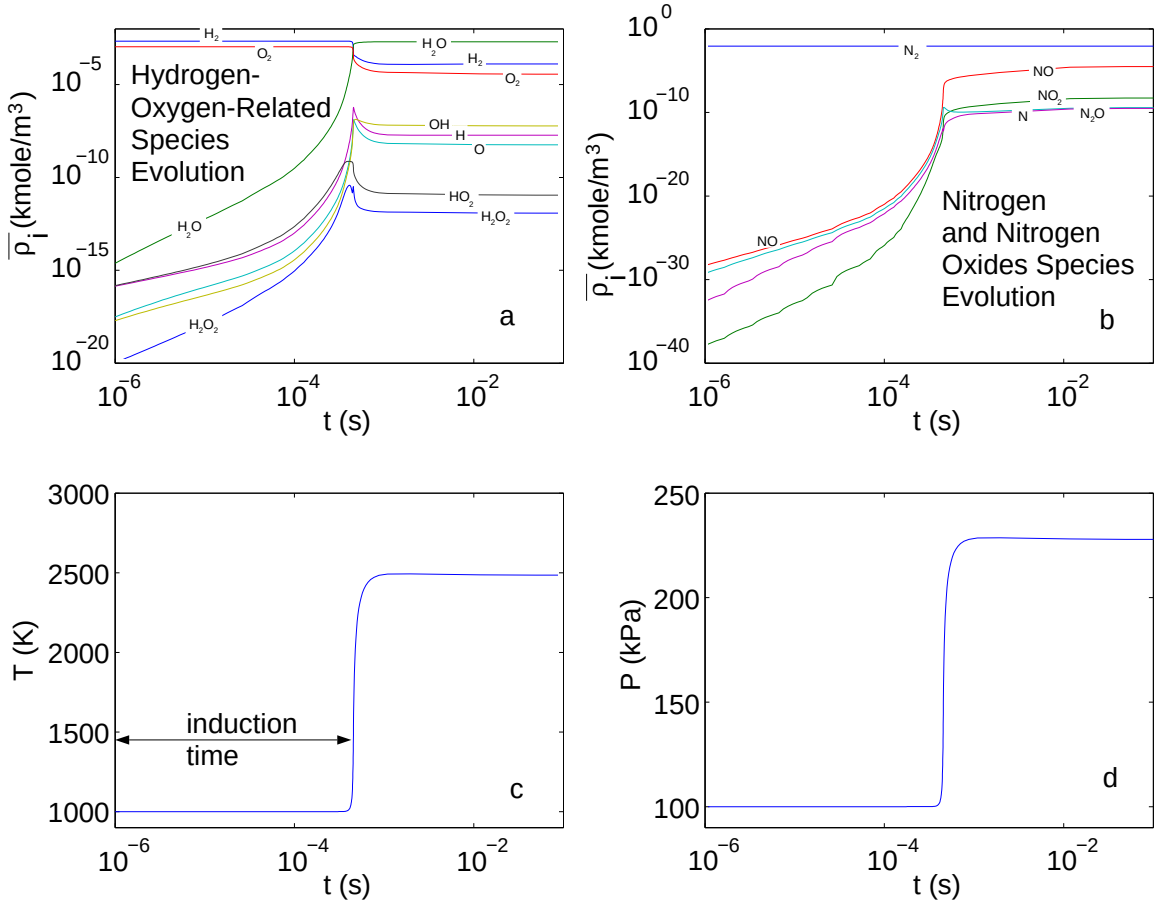

Figure 6.2: Plot of a) $\overline{\rho}_{H_2}(t)$, $\overline{\rho}_H(t)$, $\overline{\rho}_O(t)$, $\overline{\rho}_{O_2}(t)$, $\overline{\rho}_{OH}(t)$, $\overline{\rho}_{H_2O}(t)$, $\overline{\rho}_{HO_2}(t)$, $\overline{\rho}_{H_2O_2}(t)$, b) $\overline{\rho}_N(t)$, $\overline{\rho}_{NO}(t)$, $\overline{\rho}_{NO2}(t)$, $\overline{\rho}_{N_2O}(t)$, $\overline{\rho}_{N_2}(t)$, c) $T(t)$, and d) $P(t)$ for adiabatic, isochoric combustion of a mixture of $2H_2 + O_2 + 8N_2$ initially at $T = 1000\ K$, $P = 100\ kPa$.

However, the minor species, e.g. OH, NO, HO_2 and the major product, H_2O, are undergoing very rapid growth, albeit concentrations whose value remains small. In this period, the material is in what is known as the *induction period*.

After a certain critical mass of minor species has accumulated, exothermic recombination of these minor species to form the major product H_2O induces the temperature to rise, which accelerates further the reaction rates. This is manifested in a *thermal explosion*. A common definition of the end of the induction period is the *induction time*, $t = t_{ind}$, the time when dT/dt goes through a maximum. Here one finds

$$t_{ind} = 4.53 \times 10^{-4}\ s. \tag{6.165}$$

At the end of the induction zone, there is a final relaxation to equilibrium.

Chapter 7

Kinetics in some more detail

See Powers, Chapter 1

Here we give further details of kinetics. These notes are also used to introduce a separate combustion course and have some overlap with previous chapters.

Let us consider the reaction of N molecular chemical species composed of L elements via J chemical reactions. Let us assume the gas is an ideal mixture of ideal gases that satisfies Dalton's law of partial pressures. The reaction will be considered to be driven by *molecular collisions*. We will not model individual collisions, but instead attempt to capture their collective effect.

An example of a model of such a reaction is listed in Table 7.1. There we find a $N = 9$ species, $J = 37$ step irreversible reaction mechanism for an $L = 3$ hydrogen-oxygen-argon mixture from Maas and Warnatz,[1] with corrected f_{H_2} from Maas and Pope.[2] The model has also been utilized by Fedkiw, *et al.*[3] We need not worry yet about f_{H_2}, which is known as a collision efficiency factor. The one-sided arrows indicate that each individual reaction is considered to be irreversible. Note that for nearly each reaction, a separate reverse reaction is listed; thus, pairs of irreversible reactions can in some sense be considered to model reversible reactions.

In this model a set of elementary reactions are hypothesized. For the j^{th} reaction we have the collision frequency factor a_j, the temperature-dependency exponent β_j and the activation energy $\overline{E}_j$. These will be explained in short order. Other common forms exist. Often reactions systems are described as being composed of reversible reactions. Such reactions are usually notated by two sided arrows. One such system is reported by Powers and Paolucci[4] reported here in Table 7.2. Both overall models are complicated.

[1]Maas, U., and Warnatz, J., 1988, "Ignition Processes in Hydrogen-Oxygen Mixtures," *Combustion and Flame*, 74(1): 53-69.

[2]Maas, U., and Pope, S. B., 1992, "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combustion and Flame*, 88(3-4): 239-264.

[3]Fedkiw, R. P., Merriman, B., and Osher, S., 1997, "High Accuracy Numerical Methods for Thermally Perfect Gas Flows with Chemistry," *Journal of Computational Physics*, 132(2): 175-190.

[4]Powers, J. M., and Paolucci, S., 2005, "Accurate Spatial Resolution Estimates for Reactive Supersonic

j	Reaction	$a_j \left(\frac{(mol/cm^3)^{\left(1-\nu'_{M,j}-\sum_{i=1}^{N}\nu'_{ij}\right)}}{s\ K^{\beta_j}} \right)$	β_j	$\overline{E}_j \ \left(\frac{kJ}{mole}\right)$
1	$O_2 + H \rightarrow OH + O$	2.00×10^{14}	0.00	70.30
2	$OH + O \rightarrow O_2 + H$	1.46×10^{13}	0.00	2.08
3	$H_2 + O \rightarrow OH + H$	5.06×10^{4}	2.67	26.30
4	$OH + H \rightarrow H_2 + O$	2.24×10^{4}	2.67	18.40
5	$H_2 + OH \rightarrow H_2O + H$	1.00×10^{8}	1.60	13.80
6	$H_2O + H \rightarrow H_2 + OH$	4.45×10^{8}	1.60	77.13
7	$OH + OH \rightarrow H_2O + O$	1.50×10^{9}	1.14	0.42
8	$H_2O + O \rightarrow OH + OH$	1.51×10^{10}	1.14	71.64
9	$H + H + M \rightarrow H_2 + M$	1.80×10^{18}	-1.00	0.00
10	$H_2 + M \rightarrow H + H + M$	6.99×10^{18}	-1.00	436.08
11	$H + OH + M \rightarrow H_2O + M$	2.20×10^{22}	-2.00	0.00
12	$H_2O + M \rightarrow H + OH + M$	3.80×10^{23}	-2.00	499.41
13	$O + O + M \rightarrow O_2 + M$	2.90×10^{17}	-1.00	0.00
14	$O_2 + M \rightarrow O + O + M$	6.81×10^{18}	-1.00	496.41
15	$H + O_2 + M \rightarrow HO_2 + M$	2.30×10^{18}	-0.80	0.00
16	$HO_2 + M \rightarrow H + O_2 + M$	3.26×10^{18}	-0.80	195.88
17	$HO_2 + H \rightarrow OH + OH$	1.50×10^{14}	0.00	4.20
18	$OH + OH \rightarrow HO_2 + H$	1.33×10^{13}	0.00	168.30
19	$HO_2 + H \rightarrow H_2 + O_2$	2.50×10^{13}	0.00	2.90
20	$H_2 + O_2 \rightarrow HO_2 + H$	6.84×10^{13}	0.00	243.10
21	$HO_2 + H \rightarrow H_2O + O$	3.00×10^{13}	0.00	7.20
22	$H_2O + O \rightarrow HO_2 + H$	2.67×10^{13}	0.00	242.52
23	$HO_2 + O \rightarrow OH + O_2$	1.80×10^{13}	0.00	-1.70
24	$OH + O_2 \rightarrow HO_2 + O$	2.18×10^{13}	0.00	230.61
25	$HO_2 + OH \rightarrow H_2O + O_2$	6.00×10^{13}	0.00	0.00
26	$H_2O + O_2 \rightarrow HO_2 + OH$	7.31×10^{14}	0.00	303.53
27	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.50×10^{11}	0.00	-5.20
28	$OH + OH + M \rightarrow H_2O_2 + M$	3.25×10^{22}	-2.00	0.00
29	$H_2O_2 + M \rightarrow OH + OH + M$	2.10×10^{24}	-2.00	206.80
30	$H_2O_2 + H \rightarrow H_2 + HO_2$	1.70×10^{12}	0.00	15.70
31	$H_2 + HO_2 \rightarrow H_2O_2 + H$	1.15×10^{12}	0.00	80.88
32	$H_2O_2 + H \rightarrow H_2O + OH$	1.00×10^{13}	0.00	15.00
33	$H_2O + OH \rightarrow H_2O_2 + H$	2.67×10^{12}	0.00	307.51
34	$H_2O_2 + O \rightarrow OH + HO_2$	2.80×10^{13}	0.00	26.80
35	$OH + HO_2 \rightarrow H_2O_2 + O$	8.40×10^{12}	0.00	84.09
36	$H_2O_2 + OH \rightarrow H_2O + HO_2$	5.40×10^{12}	0.00	4.20
37	$H_2O + HO_2 \rightarrow H_2O_2 + OH$	1.63×10^{13}	0.00	132.71

Table 7.1: Third body collision efficiencies with M are $f_{H_2} = 1.00$, $f_{O_2} = 0.35$, and $f_{H_2O} = 6.5$.

j	Reaction	$a_j \left(\frac{(mol/cm^3)^{\left(1-\nu'_{M,j}-\sum_{i=1}^{N}\nu'_{ij}\right)}}{s\ K^{\beta_j}} \right)$	β_j	$\overline{E}_j \ \left(\frac{cal}{mole}\right)$
1	$H_2 + O_2 \rightleftharpoons OH + OH$	1.70×10^{13}	0.00	47780
2	$OH + H_2 \rightleftharpoons H_2O + H$	1.17×10^{9}	1.30	3626
3	$H + O_2 \rightleftharpoons OH + O$	5.13×10^{16}	-0.82	16507
4	$O + H_2 \rightleftharpoons OH + H$	1.80×10^{10}	1.00	8826
5	$H + O_2 + M \rightleftharpoons HO_2 + M$	2.10×10^{18}	-1.00	0
6	$H + O_2 + O_2 \rightleftharpoons HO_2 + O_2$	6.70×10^{19}	-1.42	0
7	$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	6.70×10^{19}	-1.42	0
8	$OH + HO_2 \rightleftharpoons H_2O + O_2$	5.00×10^{13}	0.00	1000
9	$H + HO_2 \rightleftharpoons OH + OH$	2.50×10^{14}	0.00	1900
10	$O + HO_2 \rightleftharpoons O_2 + OH$	4.80×10^{13}	0.00	1000
11	$OH + OH \rightleftharpoons O + H_2O$	6.00×10^{8}	1.30	0
12	$H_2 + M \rightleftharpoons H + H + M$	2.23×10^{12}	0.50	92600
13	$O_2 + M \rightleftharpoons O + O + M$	1.85×10^{11}	0.50	95560
14	$H + OH + M \rightleftharpoons H_2O + M$	7.50×10^{23}	-2.60	0
15	$H + HO_2 \rightleftharpoons H_2 + O_2$	2.50×10^{13}	0.00	700
16	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	2.00×10^{12}	0.00	0
17	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.30×10^{17}	0.00	45500
18	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$	1.60×10^{12}	0.00	3800
19	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.00×10^{13}	0.00	1800

Table 7.2: Nine species, nineteen step reversible reaction mechanism for an $H_2/O_2/N_2$ mixture. Third body collision efficiencies with M are $f_5(H_2O) = 21$, $f_5(H_2) = 3.3$, $f_{12}(H_2O) = 6$, $f_{12}(H) = 2$, $f_{12}(H_2) = 3$, $f_{14}(H_2O) = 20$.

7.1 Isothermal, isochoric kinetics

For simplicity, we will first focus attention on cases in which the temperature T and volume V are both constant. Such assumptions are known as "isothermal" and "isochoric," respectively. A nice fundamental treatment of elementary reactions of this type is given by Vincenti and Kruger in their detailed monograph.[5]

7.1.1 $O - O_2$ dissociation

One of the simplest physical examples is provided by the dissociation of O_2 into its atomic component O.

7.1.1.1 Pair of irreversible reactions

To get started, let us focus for now only on reactions 13 and 14 from Table 7.1 in the limiting case in which temperature T and volume V are constant.

7.1.1.1.1 Mathematical model The reactions describe oxygen dissociation and recombination in a pair of *irreversible* reactions:

$$13 : O + O + M \rightarrow O_2 + M, \tag{7.1}$$

$$14 : O_2 + M \rightarrow O + O + M, \tag{7.2}$$

with

$$a_{13} = 2.90 \times 10^{17} \left(\frac{mole}{cm^3}\right)^{-2} \frac{K}{s}, \quad \beta_{13} = -1.00, \quad \overline{E}_{13} = 0 \ \frac{kJ}{mole} \tag{7.3}$$

$$a_{14} = 6.81 \times 10^{18} \left(\frac{mole}{cm^3}\right)^{-1} \frac{K}{s}, \quad \beta_{14} = -1.00, \quad \overline{E}_{14} = 496.41 \ \frac{kJ}{mole}. \tag{7.4}$$

The irreversibility is indicated by the one-sided arrow. Though they participate in the overall hydrogen oxidation problem, these two reactions are in fact self-contained as well. So let us just consider that we have only oxygen in our box with $N = 2$ species, O_2 and O, $J = 2$ reactions (those being 13 and 14), and $L = 1$ element, that being O.

Recall that in the *cgs* system, common in thermochemistry, that $1\ erg = 1\ dyne\ cm = 10^{-7}\ J = 10^{-10}\ kJ$. Recall also that the *cgs* unit of force is the *dyne* and that $1\ dyne = 1\ g\ cm/s^2 = 10^{-5}\ N$. So for *cgs* we have

$$\overline{E}_{13} = 0 \ \frac{erg}{mole}, \qquad \overline{E}_{14} = 496.41 \ \frac{kJ}{mole} \left(\frac{10^{10}\ erg}{kJ}\right) = 4.96 \times 10^{12} \ \frac{erg}{mole}. \tag{7.5}$$

Flow with Detailed Chemistry," *AIAA Journal*, 43(5): 1088-1099.

[5] W. G. Vincenti and C. H. Kruger, 1965, *Introduction to Physical Gas Dynamics*, Wiley, New York.

The standard model for chemical reaction induces the following two ordinary differential equations for the evolution of O and O_2 molar concentrations:

$$\frac{d\overline{\rho}_O}{dt} = \underbrace{\underbrace{-2\,\underbrace{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M}_{=r_{13}} + \underbrace{2\,\underbrace{a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)}_{=k_{14}(T)}\overline{\rho}_{O_2}\overline{\rho}_M}_{=r_{14}}}, \tag{7.6}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = \underbrace{\underbrace{\underbrace{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M}_{=r_{13}} - \underbrace{\underbrace{a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)}_{=k_{14}(T)}\overline{\rho}_{O_2}\overline{\rho}_M}_{=r_{14}}}. \tag{7.7}$$

Here we use the notation $\overline{\rho}_i$ as the molar concentration of species i. Also a common usage for molar concentration is given by square brackets, e.g. $\overline{\rho}_{O_2} = [O_2]$. The symbol M represents an arbitrary third body and is an inert participant in the reaction. We also use the common notation of a temperature-dependent portion of the reaction rate for reaction j, $k_j(T)$, where

$$k_j(T) = a_j T^{\beta_j}\exp\left(\frac{\overline{E}_j}{\overline{R}T}\right). \tag{7.8}$$

The reaction rates for reactions 13 and 14 are defined as

$$r_{13} = k_{13}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M, \tag{7.9}$$

$$r_{14} = k_{14}\overline{\rho}_{O_2}\overline{\rho}_M. \tag{7.10}$$

We will give details of how to generalize this form later. The system Eq. (7.6-7.7) can be written simply as

$$\frac{d\overline{\rho}_O}{dt} = -2r_{13} + 2r_{14}, \tag{7.11}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = r_{13} - r_{14}. \tag{7.12}$$

Even more simply, in vector form, Eqs. (7.11-7.12) can be written as

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \boldsymbol{\nu}\cdot\mathbf{r}. \tag{7.13}$$

Here we have taken

$$\overline{\boldsymbol{\rho}} = \begin{pmatrix}\overline{\rho}_O\\ \overline{\rho}_{O_2}\end{pmatrix}, \tag{7.14}$$

$$\boldsymbol{\nu} = \begin{pmatrix}-2 & 2\\ 1 & -1\end{pmatrix}, \tag{7.15}$$

$$\mathbf{r} = \begin{pmatrix}r_{13}\\ r_{14}\end{pmatrix}. \tag{7.16}$$

In general, we will have $\overline{\boldsymbol{\rho}}$ be a column vector of dimension $N \times 1$, $\boldsymbol{\nu}$ will be a rectangular matrix of dimension $N \times J$ of rank R, and $\mathbf{r}$ will be a column vector of length $J \times 1$. So Eqs. (7.11-7.12) take the form

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_O \\ \overline{\rho}_{O_2}\end{pmatrix} = \begin{pmatrix}-2 & 2 \\ 1 & -1\end{pmatrix}\begin{pmatrix}r_{13} \\ r_{14}\end{pmatrix}. \tag{7.17}$$

Note here that the rank R of $\boldsymbol{\nu}$ is $R = L = 1$. Let us also define a stoichiometric matrix $\boldsymbol{\phi}$ of dimension $L \times N$. The component of $\boldsymbol{\phi}$, ϕ_{li} represents the number of element l in species i. Generally $\boldsymbol{\phi}$ will be full rank, which will vary since we can have $L < N$, $L = N$, or $L > N$. Here we have $L < N$ and $\boldsymbol{\phi}$ is of dimension 1×2:

$$\boldsymbol{\phi} = \begin{pmatrix}1 & 2\end{pmatrix}. \tag{7.18}$$

Element conservation is guaranteed by insisting that $\boldsymbol{\nu}$ be constructed such that

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}. \tag{7.19}$$

So we can say that each of the column vectors of $\boldsymbol{\nu}$ lies in the right null space of $\boldsymbol{\phi}$.

For our example, we see that Eq. (7.19) holds:

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \begin{pmatrix}1 & 2\end{pmatrix} \cdot \begin{pmatrix}-2 & 2 \\ 1 & -1\end{pmatrix} = \begin{pmatrix}0 & 0\end{pmatrix}. \tag{7.20}$$

The symbol $\overline{R}$ is the universal gas constant, where

$$\overline{R} = 8.31441 \ \frac{J}{mole \ K}\left(\frac{10^7 \ erg}{J}\right) = 8.31441 \times 10^7 \frac{erg}{mole \ K}. \tag{7.21}$$

Let us take as initial conditions

$$\overline{\rho}_O(t=0) = \widehat{\overline{\rho}}_O, \qquad \overline{\rho}_{O_2}(t=0) = \widehat{\overline{\rho}}_{O_2}. \tag{7.22}$$

Now M represents an arbitrary third body, so here

$$\overline{\rho}_M = \overline{\rho}_{O_2} + \overline{\rho}_O. \tag{7.23}$$

Thus, the ordinary differential equations of the reaction dynamics reduce to

$$\begin{aligned}\frac{d\overline{\rho}_O}{dt} &= -2a_{13}T^{\beta_{13}} \exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O\overline{\rho}_O\left(\overline{\rho}_{O_2} + \overline{\rho}_O\right) \\ &\quad +2a_{14}T^{\beta_{14}} \exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}\left(\overline{\rho}_{O_2} + \overline{\rho}_O\right), \qquad (7.24) \\ \frac{d\overline{\rho}_{O_2}}{dt} &= a_{13}T^{\beta_{13}} \exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O\overline{\rho}_O\left(\overline{\rho}_{O_2} + \overline{\rho}_O\right) \\ &\quad -a_{14}T^{\beta_{14}} \exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}\left(\overline{\rho}_{O_2} + \overline{\rho}_O\right). \qquad (7.25)\end{aligned}$$

Equations (7.24-7.25) with Eqs. (7.22) represent two non-linear ordinary differential equations with initial conditions in two unknowns $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$. We seek the behavior of these two species concentrations as a function of time.

Systems of non-linear equations are generally difficult to integrate analytically and generally require numerical solution. Before embarking on a numerical solution, we simplify as much as we can. Note that

$$\frac{d\overline{\rho}_O}{dt} + 2\frac{d\overline{\rho}_{O_2}}{dt} = 0, \tag{7.26}$$

$$\frac{d}{dt}\left(\overline{\rho}_O + 2\overline{\rho}_{O_2}\right) = 0. \tag{7.27}$$

We can integrate and apply the initial conditions (7.22) to get

$$\overline{\rho}_O + 2\overline{\rho}_{O_2} = \widehat{\overline{\rho}}_O + 2\widehat{\overline{\rho}}_{O_2} = constant. \tag{7.28}$$

The fact that this algebraic constraint exists for all time is a consequence of the conservation of mass of each O element. It can also be thought of as the conservation of number of O atoms. Such notions always hold for chemical reactions. They do not hold for nuclear reactions.

Standard linear algebra provides a robust way to find the constraint of Eq. (7.28). We can use elementary row operations to cast Eq. (7.16) into a row-echelon form. Here our goal is to get a linear combination which on the right side has an upper triangular form. To achieve this add twice the second equation with the first to form a new equation to replace the second equation. This gives

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_O + 2\overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -2 & 2 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} r_{13} \\ r_{14} \end{pmatrix}. \tag{7.29}$$

Obviously the second equation is one we obtained earlier, $d/dt(\overline{\rho}_O + 2\overline{\rho}_{O_2}) = 0$, and this induces our algebraic constraint. We also note the system can be recast as

$$\begin{pmatrix} 1 & 0 \\ 1 & 2 \end{pmatrix}\frac{d}{dt}\begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -2 & 2 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} r_{13} \\ r_{14} \end{pmatrix}. \tag{7.30}$$

This is of the matrix form

$$\mathbf{L}^{-1}\cdot\mathbf{P}\cdot\frac{d\overline{\boldsymbol{\rho}}}{dt} = \mathbf{U}\cdot\mathbf{r}. \tag{7.31}$$

Here $\mathbf{L}$ and $\mathbf{L}^{-1}$ are $N \times N$ lower triangular matrices of full rank N, and thus invertible. The matrix $\mathbf{U}$ is upper triangular of dimension $N \times J$ and with the same rank as $\boldsymbol{\nu}$, $R \geq L$. The matrix $\mathbf{P}$ is a permutation matrix of dimension $N \times N$. It is never singular and thus always invertable. It is used to effect possible row exchanges to achieve the desired form; often row exchanges are not necessary, in which case $\mathbf{P} = \mathbf{I}$, the $N \times N$ identity matrix. Equation (7.31) can be manipulated to form the original equation via

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \underbrace{\mathbf{P}^{-1}\cdot\mathbf{L}\cdot\mathbf{U}}_{=\boldsymbol{\nu}}\cdot\mathbf{r}. \tag{7.32}$$

What we have done is the standard linear algebra decomposition of $\boldsymbol{\nu} = \mathbf{P}^{-1} \cdot \mathbf{L} \cdot \mathbf{U}$.

We can also decompose the algebraic constraint, Eq. (7.28), in a non-obvious way that is more readily useful for larger systems. We can write

$$\overline{\rho}_{O_2} = \widehat{\overline{\rho}}_{O_2} - \frac{1}{2}\left(\overline{\rho}_O - \widehat{\overline{\rho}}_O\right). \tag{7.33}$$

Defining now $\overline{\xi}_O = \overline{\rho}_O - \widehat{\overline{\rho}}_O$, we can say

$$\underbrace{\begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}}_{=\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\overline{\rho}}_O \\ \widehat{\overline{\rho}}_{O_2} \end{pmatrix}}_{=\widehat{\overline{\boldsymbol{\rho}}}} + \underbrace{\begin{pmatrix} 1 \\ -\frac{1}{2} \end{pmatrix}}_{=\mathbf{D}} \underbrace{\left(\overline{\xi}_O\right)}_{=\overline{\boldsymbol{\xi}}}. \tag{7.34}$$

This gives the dependent variables in terms of a smaller number of transformed dependent variables in a way which satisfies the linear constraints. In vector form, the equation becomes

$$\overline{\boldsymbol{\rho}} = \widehat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}. \tag{7.35}$$

Here $\mathbf{D}$ is a full rank matrix which spans the same column space as does $\boldsymbol{\nu}$. Note that $\boldsymbol{\nu}$ may or may not be full rank. Since $\mathbf{D}$ spans the same column space as does $\boldsymbol{\nu}$, we must also have in general

$$\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}. \tag{7.36}$$

We see here this is true:

$$\begin{pmatrix} 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ -\frac{1}{2} \end{pmatrix} = (0). \tag{7.37}$$

We also note that the term $\exp(-\overline{E}_j/\overline{R}T)$ is a modulating factor to the dynamics. Let us see how this behaves for high and low temperatures. First for low temperature, we have

$$\lim_{T \to 0} \exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right) = 0. \tag{7.38}$$

At high temperature, we have

$$\lim_{T \to \infty} \exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right) = 1. \tag{7.39}$$

And lastly, at intermediate temperature, we have

$$\exp\left(\frac{-\overline{E}_j}{\overline{R}T}\right) \sim \mathcal{O}(1) \qquad \text{when} \qquad T = \mathcal{O}\left(\frac{\overline{E}_j}{\overline{R}}\right). \tag{7.40}$$

A sketch of this modulating factor is given in Figure 7.1. Note

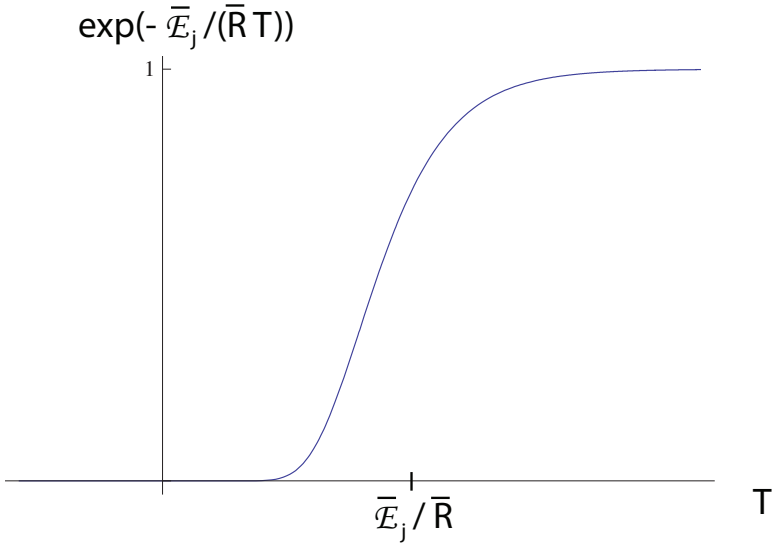

Figure 7.1: Plot of $\exp(-\overline{E}_j/\overline{R}/T)$ versus T; transition occurs at $T \sim \overline{E}_j/\overline{R}$.

- for small T, the modulation is extreme, and the reaction rate is *very* small,
- for $T \sim \overline{E}_j/\overline{R}$, the reaction rate is extremely sensitive to temperature, and
- for $T \to \infty$, the modulation is unity, and the reaction rate is limited only by molecular collision frequency.

Now $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$ represent molar concentrations which have standard units of $mole/cm^3$. So the reaction rates

$$\frac{d\overline{\rho}_O}{dt} \qquad \text{and} \qquad \frac{d\overline{\rho}_{O_2}}{dt}$$

have units of $mole/cm^3/s$.

Note that after conversion of $\overline{E}_j$ from $kJ/mole$ to $erg/mole$ we find the units of the argument of the exponential to be unitless. That is

$$\left[\frac{\overline{E}_j}{\overline{R}T}\right] = \frac{erg}{mole}\frac{mole\ K}{erg}\frac{1}{K} \Rightarrow \qquad \text{dimensionless.} \tag{7.41}$$

Here the brackets denote the units of a quantity, and not molar concentration. Let us get units for the collision frequency factor of reaction 13, a_{13}. We know the units of the rate $(mole/cm^3/s)$. Reaction 13 involves three molar species. Since $\beta_{13} = -1$, it also has an extra temperature dependency. The exponential of a unitless number is unitless, so we need not worry about that. For units to match, we must have

$$\left(\frac{mole}{cm^3\ s}\right) = [a_{13}]\left(\frac{mole}{cm^3}\right)\left(\frac{mole}{cm^3}\right)\left(\frac{mole}{cm^3}\right)K^{-1}. \tag{7.42}$$

So the units of a_{13} are

$$[a_{13}] = \left(\frac{mole}{cm^3}\right)^{-2} \frac{K}{s}. \tag{7.43}$$

For a_{14} we find a different set of units! Following the same procedure, we get

$$\left(\frac{mole}{cm^3\ s}\right) = [a_{14}] \left(\frac{mole}{cm^3}\right) \left(\frac{mole}{cm^3}\right) K^{-1}. \tag{7.44}$$

So the units of a_{14} are

$$[a_{14}] = \left(\frac{mole}{cm^3}\right)^{-1} \frac{K}{s}. \tag{7.45}$$

This discrepancy in the units of a_j the molecular collision frequency factor is a burden of traditional chemical kinetics, and causes many difficulties when classical non-dimensionalization is performed. With much effort, a cleaner theory could be formulated; however, this would require significant work to re-cast the now-standard a_j values for literally thousands of reactions which are well established in the literature.

7.1.1.1.2 Example calculation Let us consider an example problem. Let us take $T = 5000\ K$, and initial conditions $\widehat{\overline{\rho}}_O = 0.001\ mole/cm^3$ and $\widehat{\overline{\rho}}_{O_2} = 0.001\ mole/cm^3$. The initial temperature is very hot, and is near the temperature of the surface of the sun. This is also realizable in laboratory conditions, but uncommon in most combustion engineering environments.

We can solve these in a variety of ways. I chose here to solve both Eqs. (7.24-7.25) without the reduction provided by Eq. (7.28). However, we can check after numerical solution to see if Eq. (7.28) is actually satisfied. Substituting numerical values for all the constants to get

$$\begin{aligned}
-2a_{13}T^{\beta_{13}} \exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right) &= -2\left(2.9 \times 10^7\ \left(\frac{mole}{cm^3}\right)^{-2} \frac{K}{s}\right)(5000\ K)^{-1} \exp(0), \\
&= -1.16 \times 10^{14}\ \left(\frac{mole}{cm^3}\right)^{-2} \frac{1}{s}, \qquad (7.46) \\
2a_{14}T^{\beta_{14}} \exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right) &= 2\left(6.81 \times 10^{18}\ \left(\frac{mole}{cm^3}\right)^{-1} \frac{K}{s}\right)(5000\ K)^{-1} \\
&\quad \times \exp\left(\frac{-4.96 \times 10^{12}\ \frac{erg}{mole}}{8.31441 \times 10^7\ \frac{erg}{mole\ K}(5000\ K)}\right), \\
&= 1.77548 \times 10^{10}\ \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}, \qquad (7.47) \\
a_{13}T^{\beta_{13}} \exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right) &= 5.80 \times 10^{13}\ \left(\frac{mole}{cm^3}\right)^{-2} \frac{1}{s}, \qquad (7.48) \\
-a_{14}T^{\beta_{14}} \exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right) &= -8.8774 \times 10^9\ \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}. \qquad (7.49)
\end{aligned}$$

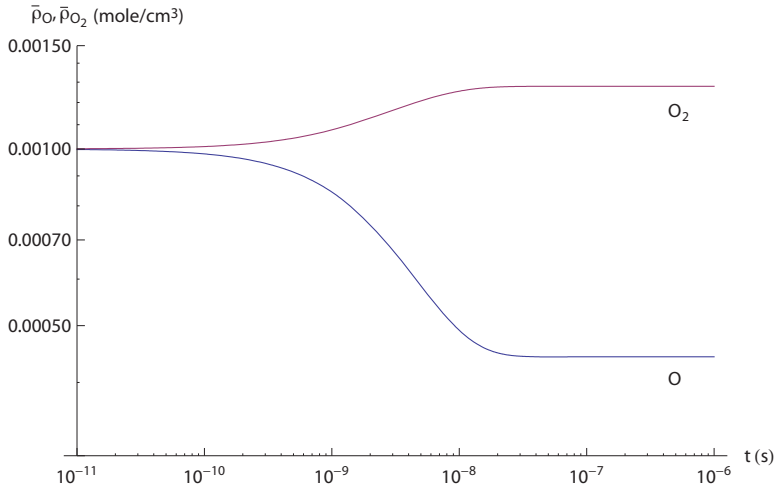

Figure 7.2: Molar concentrations versus time for oxygen dissociation problem.

Then the differential equation system becomes

$$\frac{d\overline{\rho}_O}{dt} = -(1.16 \times 10^{14})\overline{\rho}_O^2(\overline{\rho}_O + \overline{\rho}_{O_2}) + (1.77548 \times 10^{10})\overline{\rho}_{O_2}(\overline{\rho}_O + \overline{\rho}_{O_2}), \tag{7.50}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = (5.80 \times 10^{13})\overline{\rho}_O^2(\overline{\rho}_O + \overline{\rho}_{O_2}) - (8.8774 \times 10^{9})\overline{\rho}_{O_2}(\overline{\rho}_O + \overline{\rho}_{O_2}), \tag{7.51}$$

$$\overline{\rho}_O(0) = 0.001\ \frac{mole}{cm^3}, \tag{7.52}$$

$$\overline{\rho}_{O_2}(0) = 0.001\ \frac{mole}{cm^3}. \tag{7.53}$$

These non-linear ordinary differential equations are in a standard form for a wide variety of numerical software tools. Solution of such equations are not the topic of these notes.

7.1.1.1.2.1 Species concentration versus time A solution was obtained numerically, and a plot of $\overline{\rho}_O(t)$ and $\overline{\rho}_{O_2}(t)$ is given in Figure 7.2. Note that significant reaction does not commence until $t \sim 10^{-10}\ s$. This can be shown to be very close to the time between molecular collisions. For $10^{-9}\ s < t < 10^{-8}\ s$, there is a vigorous reaction. For $t > 10^{-7}\ s$, the reaction appears to be equilibrated. The calculation gives the equilibrium values $\overline{\rho}_O^e$ and $\overline{\rho}_{O_2}^e$, as

$$\lim_{t\to\infty} \overline{\rho}_O = \overline{\rho}_O^e = 0.0004424\ \frac{mole}{cm^3}, \tag{7.54}$$

$$\lim_{t\to\infty} \overline{\rho}_{O_2} = \overline{\rho}_{O_2}^e = 0.00127\ \frac{mole}{cm^3}, \tag{7.55}$$

Note that at this high temperature, O_2 is preferred over O, but there are definitely O molecules present at equilibrium.

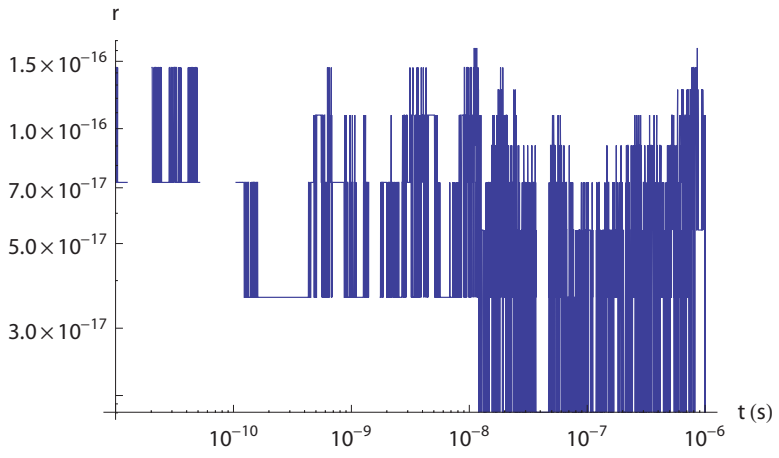

Figure 7.3: Dimensionless residual numerical error r in satisfying the element conservation constraint in the oxygen dissociation example.

We can check how well the numerical solution satisfied the algebraic constraint of element conservation by plotting the dimensionless residual error r

$$r = \left| \frac{\overline{\rho}_O + 2\overline{\rho}_{O_2} - \widehat{\overline{\rho}}_O - 2\widehat{\overline{\rho}}_{O_2}}{\widehat{\overline{\rho}}_O + 2\widehat{\overline{\rho}}_{O_2}} \right|, \tag{7.56}$$

as a function of time. If the constraint is exactly satisfied, we will have $r = 0$. Any non-zero r will be related to the numerical method we have chosen. It may contain roundoff error and have a sporadic nature. A plot of $r(t)$ is given in Figure 7.3. Clearly the error is small, and has the character of a roundoff error. In fact it is possible to drive r to be smaller by controlling the error tolerance in the numerical method.

7.1.1.1.2.2 Pressure versus time We can use the ideal gas law to calculate the pressure. Recall that the ideal gas law for molecular species i is

$$P_i V = n_i \overline{R} T. \tag{7.57}$$

Here P_i is the partial pressure of molecular species i, and n_i is the number of moles of molecular species i. Note that we also have

$$P_i = \frac{n_i}{V} \overline{R} T. \tag{7.58}$$

Note that by our definition of molecular species concentration that

$$\overline{\rho}_i = \frac{n_i}{V}. \tag{7.59}$$

So we also have the ideal gas law as

$$P_i = \overline{\rho}_i \overline{R} T. \tag{7.60}$$

Now in the Dalton mixture model, all species share the same T and V. So the mixture temperature and volume are the same for each species $V_i = V$, $T_i = T$. But the mixture pressure is taken to be the sum of the partial pressures:

$$P = \sum_{i=1}^{N} P_i. \tag{7.61}$$

Substituting from Eq. (7.60) into Eq. (7.61), we get

$$P = \sum_{i=1}^{N} \overline{\rho}_i \overline{R} T = \overline{R} T \sum_{i=1}^{N} \overline{\rho}_i. \tag{7.62}$$

For our example, we only have two species, so

$$P = \overline{R} T (\overline{\rho}_O + \overline{\rho}_{O_2}). \tag{7.63}$$

The pressure at the initial state $t = 0$ is

$$\begin{aligned} P(t=0) &= \overline{R} T (\widehat{\overline{\rho}}_O + \widehat{\overline{\rho}}_{O_2}), & (7.64)\\ &= \left(8.31441 \times 10^7 \frac{erg}{mole\ K}\right) (5000\ K) \left(0.001\ \frac{mole}{cm^3} + 0.001\ \frac{mole}{cm^3}\right), & (7.65)\\ &= 8.31441 \times 10^8\ \frac{dyne}{cm^2}, & (7.66)\\ &= 8.31441 \times 10^2\ bar. & (7.67) \end{aligned}$$

This pressure is over 800 atmospheres. It is actually a little too high for good experimental correlation with the underlying data, but we will neglect that for this exercise.

At the equilibrium state we have more O_2 and less O. And we have a different number of molecules, so we expect the pressure to be different. At equilibrium, the pressure is

$$\begin{aligned} P(t \to \infty) &= \lim_{t \to \infty} \overline{R} T (\overline{\rho}_O + \overline{\rho}_{O_2}), & (7.68)\\ &= \left(8.31441 \times 10^7 \frac{erg}{mole\ K}\right) (5000\ K) \left(0.0004424\ \frac{mole}{cm^3} + 0.00127\ \frac{mole}{cm^3}\right), & (7.69)\\ &= 7.15 \times 10^8\ \frac{dyne}{cm^2}, & (7.70)\\ &= 7.15 \times 10^2\ bar. & (7.71) \end{aligned}$$

The pressure has dropped because much of the O has recombined to form O_2. Thus there are fewer molecules at equilibrium. The temperature and volume have remained the same. A plot of $P(t)$ is given in Figure 7.4.

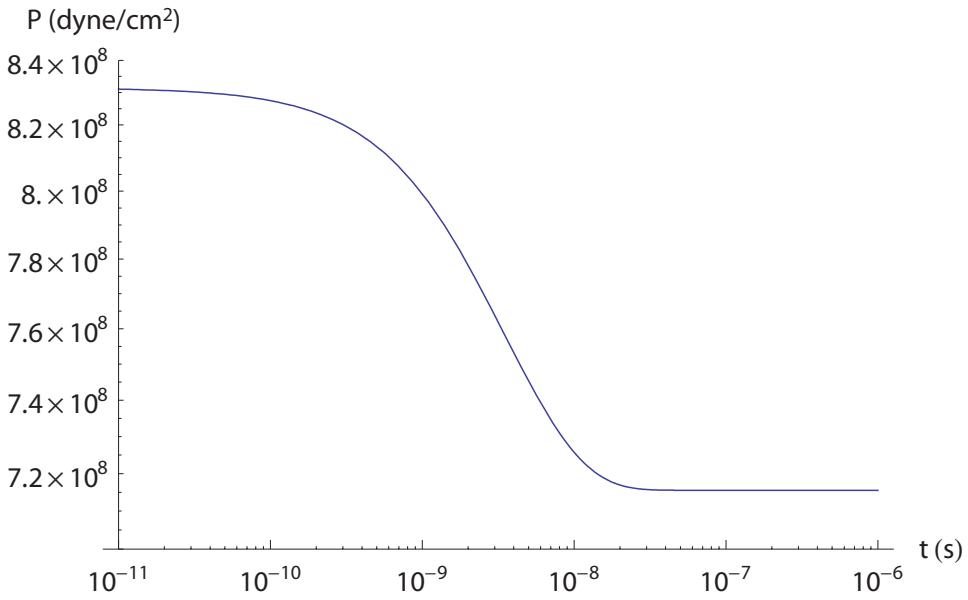

Figure 7.4: Pressure versus time for oxygen dissociation example.

7.1.1.1.2.3 Dynamical system form Now Eqs. (7.50-7.51) are of the standard form for an autonomous dynamical system:

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y}). \tag{7.72}$$

Here $\mathbf{y}$ is the vector of state variables $(\overline{\rho}_O, \overline{\rho}_{O_2})^T$. And $\mathbf{f}$ is an algebraic function of the state variables. For the isothermal system, the algebraic function is in fact a polynomial.

Equilibrium

The dynamical system is in equilibrium when

$$\mathbf{f}(\mathbf{y}) = \mathbf{0}. \tag{7.73}$$

This non-linear set of algebraic equations can be difficult to solve for large systems. For common chemical kinetics systems, such as the one we are dealing with, there is a guarantee of a unique equilibrium for which all state variables are physical. There are certainly other equilibria for which at least one of the state variables is non-physical. Such equilibria can be quite mathematically complicated.

Solving Eq. (7.73) for our oxygen dissociation problem gives us symbolically from Eq. (7.6-

7.7)

$$-2a_{13}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O^e\overline{\rho}_O^e\overline{\rho}_M^e T^{\beta_{13}} + 2a_{14}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}^e\overline{\rho}_M^e T^{\beta_{14}} = 0, \quad (7.74)$$

$$a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O^e\overline{\rho}_O^e\overline{\rho}_M^e - a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}^e\overline{\rho}_M^e = 0. \quad (7.75)$$

We notice that $\overline{\rho}_M^e$ cancels. This so-called third body will in fact never affect the equilibrium state. It will however influence the dynamics. Removing $\overline{\rho}_M^e$ and slightly rearranging Eqs. (7.74-7.75) gives

$$a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O^e\overline{\rho}_O^e = a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}^e, \quad (7.76)$$

$$a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O^e\overline{\rho}_O^e = a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\overline{\rho}_{O_2}^e. \quad (7.77)$$

These are the same equations! So we really have two unknowns for the equilibrium state $\overline{\rho}_O^e$ and $\overline{\rho}_{O_2}^e$ but seemingly only one equation. Note that rearranging either Eq. (7.76) or (7.77) gives the result

$$\frac{\overline{\rho}_O^e\overline{\rho}_O^e}{\overline{\rho}_{O_2}^e} = \frac{a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)}{a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)} = K(T). \quad (7.78)$$

That is, for the net reaction (excluding the inert third body), $O_2 \rightarrow O+O$, at equilibrium the product of the concentrations of the products divided by the product of the concentrations of the reactants is a function of temperature T. And for constant T, this is the so-called equilibrium constant. This is a famous result from basic chemistry. It is actually not complete yet, as we have not taken advantage of a connection with thermodynamics. But for now, it will suffice.

We still have a problem: Eq. (7.78) is still one equation for two unknowns. We solve this be recalling we have not yet taken advantage of our algebraic constraint of element conservation, Eq. (7.28). Let us use the equation to eliminate $\overline{\rho}_{O_2}^e$ in favor of $\overline{\rho}_O^e$:

$$\overline{\rho}_{O_2}^e = \frac{1}{2}\left(\widehat{\overline{\rho}}_O - \overline{\rho}_O^e\right) + \widehat{\overline{\rho}}_{O_2}. \quad (7.79)$$

So Eq. (7.76) reduces to

$$a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)\overline{\rho}_O^e\overline{\rho}_O^e = a_{14}T^{\beta_{14}}\exp\left(\frac{-\overline{E}_{14}}{\overline{R}T}\right)\underbrace{\left(\frac{1}{2}\left(\widehat{\overline{\rho}}_O - \overline{\rho}_O^e\right) + \widehat{\overline{\rho}}_{O_2}\right)}_{=\overline{\rho}_{O_2}^e}. \quad (7.80)$$

Equation (7.80) is one algebraic equation in one unknown. Its solution gives the equilibrium value $\overline{\rho}_O^e$. It is a quadratic equation for $\overline{\rho}_O^e$. Of its two roots, one will be physical. *We note*

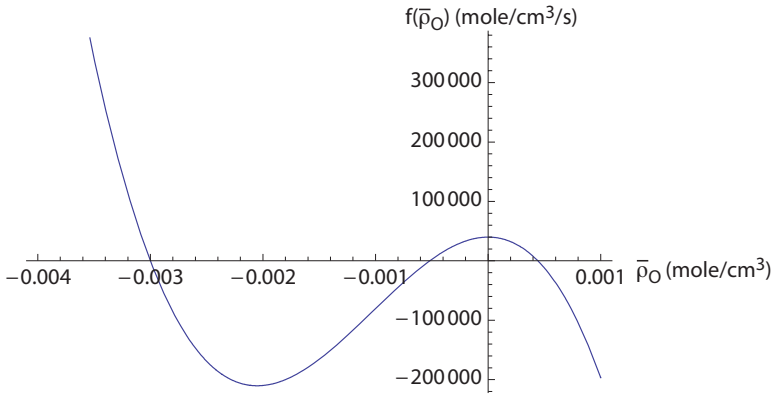

Figure 7.5: Equilibria for oxygen dissociation example.

that the equilibrium state will be a function of the initial conditions. Mathematically this is because our system is really best posed as a system of differential-algebraic equations. Systems which are purely differential equations will have equilibria which are independent of their initial conditions. Most of the literature of mathematical physics focuses on such systems of those. One of the foundational complications of chemical dynamics is the the equilibria is a function of the initial conditions, and this renders many common mathematical notions from traditional dynamic system theory to be invalid Fortunately, after one accounts for the linear constraints of element conservation, one can return to classical notions from traditional dynamic systems theory.

Consider the dynamics of Eq. (7.24) for the evolution of $\overline{\rho}_O$. Equilibrating the right hand side of this equation, gives Eq. (7.74). Eliminating $\overline{\rho}_M$ and then $\overline{\rho}_{O_2}$ in Eq. (7.74) then substituting in numerical parameters gives the cubic algebraic equation

$$33948.3 - (1.78439 \times 10^{11})(\overline{\rho}_O)^2 - (5.8 \times 10^{13})(\overline{\rho}_O)^3 = f(\overline{\rho}_O) = 0. \tag{7.81}$$

This equation is cubic because we did not remove the effect of $\overline{\rho}_M$. This will not affect the equilibrium, but will affect the dynamics. We can get an idea of where the roots are by plotting $f(\overline{\rho}_O)$ as seen in Figure 7.5. Zero crossings of $f(\overline{\rho}_O)$ in Figure 7.5 represent equilibria of the system, $\overline{\rho}_O^e$, $f(\overline{\rho}_O^e) = 0$. The cubic equation has three roots

$$\overline{\rho}_O^e = -0.003 \ \frac{mole}{cm^3}, \qquad \text{non-physical,} \tag{7.82}$$

$$\overline{\rho}_O^e = -0.000518944 \ \frac{mole}{cm^3}, \qquad \text{non-physical,} \tag{7.83}$$

$$\overline{\rho}_O^e = 0.000442414 \ \frac{mole}{cm^3}, \qquad \text{physical.} \tag{7.84}$$

Note the physical root found by our algebraic analysis is identical to that which was identified by our numerical integration of the ordinary differential equations of reaction kinetics.

Stability of equilibria

We can get a simple estimate of the stability of the equilibria by considering the slope of f near $f = 0$. Our dynamic system is of the form

$$\frac{d\overline{\rho}_O}{dt} = f(\overline{\rho}_O). \tag{7.85}$$

- Near the first non-physical root at $\overline{\rho}_O^e = -0.003$, a positive perturbation from equilibrium induces $f < 0$, which induces $d\overline{\rho}_O/dt < 0$, so $\overline{\rho}_O$ returns to its equilibrium. Similarly, a negative perturbation from equilibrium induces $d\overline{\rho}_O/dt > 0$, so the system returns to equilibrium. This non-physical equilibrium point is *stable*. Note stability does not imply physicality!

- Perform the same exercise for the non-physical root at $\overline{\rho}_O^e = -0.000518944$. We find this root is *unstable*.

- Perform the same exercise for the physical root at $\overline{\rho}_O^e = 0.000442414$. We find this root is *stable*.

In general if f crosses zero with a positive slope, the equilibrium is unstable. Otherwise, it is stable.

Consider a formal Taylor series expansion of Eq. (7.85) in the neighborhood of an equilibrium point $\overline{\rho}_O^3$:

$$\frac{d}{dt}\left(\overline{\rho}_O - \overline{\rho}_O^e\right) = \underbrace{f(\overline{\rho}_O^e)}_{=0} + \left.\frac{df}{d\overline{\rho}_O}\right|_{\overline{\rho}_O = \overline{\rho}_O^e} \left(\overline{\rho}_O - \overline{\rho}_O^e\right) + \ldots \tag{7.86}$$

We find $df/d\overline{\rho}_O$ by differentiating Eq. (7.81) to get

$$\frac{df}{d\overline{\rho}_O} = -(3.56877 \times 10^{11})\overline{\rho}_O - (1.74 \times 10^{14})\overline{\rho}_O^2. \tag{7.87}$$

We evaluate $df/d\overline{\rho}_O$ near the physical equilibrium point at $\overline{\rho}_O = 0.0004442414$ to get

$$\begin{aligned} \frac{df}{d\overline{\rho}_O} &= -(3.56877 \times 10^{11})(0.0004442414) - (1.74 \times 10^{14})(0.0004442414)^2, \\ &= -1.91945 \times 10^8 \ \frac{1}{s}. \end{aligned} \tag{7.88}$$

Thus the Taylor series expansion of Eq. (7.24) in the neighborhood of the physical equilibrium gives the local kinetics to be driven by

$$\frac{d}{dt}\left(\overline{\rho}_O - 0.000442414\right) = -(1.91945 \times 10^8)\left(\overline{\rho}_O - 0.0004442414\right) + \ldots. \tag{7.89}$$

So in the neighborhood of the physical equilibrium we have

$$\overline{\rho}_O = 0.0004442414 + A \exp\left(-1.91945 \times 10^8 t\right). \tag{7.90}$$

Here A is an arbitrary constant of integration. The local time constant which governs the times scales of local evolution is τ where

$$\tau = \frac{1}{1.91945 \times 10^8} = 5.20983 \times 10^{-9}\ s. \tag{7.91}$$

This nano-second time scale is very fast. It can be shown to be correlated with the mean time between collisions of molecules.

7.1.1.1.3 Effect of temperature Let us perform four case studies to see the effect of T on the system's equilibria and it dynamics near equilibrium.

- $T = 3000\ K$. Here we have significantly reduced the temperature, but it is still higher than typically found in ordinary combustion engineering environments. Here we find

$$\begin{aligned} \overline{\rho}_O^e &= 8.9371 \times 10^{-6}\ \frac{mole}{cm^3}, & (7.92)\\ \tau &= 1.92059 \times 10^{-7}\ s. & (7.93) \end{aligned}$$

  The equilibrium concentration of O dropped by two orders of magnitude relative to $T = 5000\ K$, and the time scale of the dynamics near equilibrium slowed by two orders of magnitude.

- $T = 1000\ K$. Here we reduce the temperature more. This temperature is common in combustion engineering environments. We find

$$\begin{aligned} \overline{\rho}_O^e &= 2.0356 \times 10^{-14}\ \frac{mole}{cm^3}, & (7.94)\\ \tau &= 2.82331 \times 10^{1}\ s. & (7.95) \end{aligned}$$

  The O concentration at equilibrium is greatly diminished to the point of being difficult to detect by standard measurement techniques. And the time scale of combustion has significantly slowed.

- $T = 300\ K$. This is obviously near room temperature. We find

$$\begin{aligned} \overline{\rho}_O^e &= 1.14199 \times 10^{-44}\ \frac{mole}{cm^3}, & (7.96)\\ \tau &= 1.50977 \times 10^{31}\ s. & (7.97) \end{aligned}$$

  The O concentration is effectively zero at room temperature, and the relaxation time is effectively infinite. As the oldest star in our galaxy has an age of $4.4 \times 10^{17}\ s$, we see that at this temperature, our mathematical model cannot be experimentally validated, so it loses its meaning. At such a low temperature, the theory becomes qualitatively correct, but not quantitatively predictive.

- $T = 10000\ K$. Such high temperature could be achieved in an atmospheric re-entry environment.

$$\overline{\rho}_O^e = 2.74807 \times 10^{-3}\ \frac{mole}{cm^3}, \tag{7.98}$$

$$\tau = 1.69119 \times 10^{-10}\ s. \tag{7.99}$$

At this high temperature, O become preferred over O_2, and the time scales of reaction become extremely small, under a nanosecond.

7.1.1.2 Single reversible reaction

The two irreversible reactions studied in the previous section are of a class that is common in combustion modeling. However, the model suffers a defect in that its link to classical equilibrium thermodynamics is missing. A better way to model essentially the same physics and guarantee consistency with classical equilibrium thermodynamics is to model the process as a single *reversible* reaction, with a suitably modified reaction rate term.

7.1.1.2.1 Mathematical model

7.1.1.2.1.1 Kinetics For the reversible $O - O_2$ reaction, let us only consider reaction 13 from Table 7.2 for which

$$13 : O_2 + M \leftrightharpoons O + O + M. \tag{7.100}$$

For this system, we have $N = 2$ molecular species in $L = 1$ elements reacting in $J = 1$ reaction. Here

$$a_{13} = 1.85 \times 10^{11}\ \left(\frac{mole}{cm^3}\right)^{-1} (K)^{-0.5}, \qquad \beta_{13} = 0.5, \qquad \overline{E}_{13} = 95560\ \frac{cal}{mole}. \tag{7.101}$$

Units of cal are common in chemistry, but we need to convert to erg, which is achieved via

$$\overline{E}_{13} = \left(95560\ \frac{cal}{mole}\right)\left(\frac{4.186\ J}{cal}\right)\left(\frac{10^7\ erg}{J}\right) = 4.00014 \times 10^{12}\ \frac{erg}{mole}. \tag{7.102}$$

For this reversible reaction, we slightly modify the kinetics equations to

$$\frac{d\overline{\rho}_O}{dt} = \underbrace{2\,\underbrace{a_{13}T^{\beta_{13}} \exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\left(\overline{\rho}_{O_2}\overline{\rho}_M - \frac{1}{K_{c,13}}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M\right)}_{=r_{13}}, \tag{7.103}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = \underbrace{-\underbrace{a_{13}T^{\beta_{13}} \exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right)}_{=k_{13}(T)}\left(\overline{\rho}_{O_2}\overline{\rho}_M - \frac{1}{K_{c,13}}\overline{\rho}_O\overline{\rho}_O\overline{\rho}_M\right)}_{=r_{13}}. \tag{7.104}$$

Here we have used equivalent definitions for $k_{13}(T)$ and r_{13}, so that Eqs. (7.103-7.104) can be written compactly as

$$\frac{d\overline{\rho}_O}{dt} = 2r_{13}, \tag{7.105}$$

$$\frac{d\overline{\rho}_{O_2}}{dt} = -r_{13}. \tag{7.106}$$

In matrix form, we can simplify to

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_O \\ \overline{\rho}_{O_2}\end{pmatrix} = \underbrace{\begin{pmatrix}2 \\ -1\end{pmatrix}}_{=\boldsymbol{\nu}}(r_{13}). \tag{7.107}$$

Here the $N \times J$ or 2×1 matrix $\boldsymbol{\nu}$ is

$$\boldsymbol{\nu} = \begin{pmatrix}2 \\ -1\end{pmatrix}. \tag{7.108}$$

Performing row operations, the matrix form reduces to

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_O \\ \overline{\rho}_O + 2\overline{\rho}_{O_2}\end{pmatrix} = \begin{pmatrix}2 \\ 0\end{pmatrix}(r_{13}), \tag{7.109}$$

or

$$\begin{pmatrix}1 & 0 \\ 1 & 2\end{pmatrix}\frac{d}{dt}\begin{pmatrix}\overline{\rho}_O \\ \overline{\rho}_{O_2}\end{pmatrix} = \begin{pmatrix}2 \\ 0\end{pmatrix}(r_{13}). \tag{7.110}$$

So here the $N \times N$ or 2×2 matrix $\mathbf{L}^{-1}$ is

$$\mathbf{L}^{-1} = \begin{pmatrix}1 & 0 \\ 1 & 2\end{pmatrix}. \tag{7.111}$$

The $N \times N$ or 2×2 permutation matrix $\mathbf{P}$ is the identity matrix. And the $N \times J$ or 2×1 upper triangular matrix $\mathbf{U}$ is

$$\mathbf{U} = \begin{pmatrix}2 \\ 0\end{pmatrix}. \tag{7.112}$$

Note that $\boldsymbol{\nu} = \mathbf{L} \cdot \mathbf{U}$ or equivalently $\mathbf{L}^{-1} \cdot \boldsymbol{\nu} = \mathbf{U}$:

$$\underbrace{\begin{pmatrix}1 & 0 \\ 1 & 2\end{pmatrix}}_{=\mathbf{L}^{-1}} \cdot \underbrace{\begin{pmatrix}2 \\ -1\end{pmatrix}}_{=\boldsymbol{\nu}} = \underbrace{\begin{pmatrix}2 \\ 0\end{pmatrix}}_{=\mathbf{U}}. \tag{7.113}$$

Once again the stoichiometric matrix $\boldsymbol{\phi}$ is

$$\boldsymbol{\phi} = \begin{pmatrix}1 & 2\end{pmatrix}. \tag{7.114}$$

And we see that $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}$ is satisfied:

$$\begin{pmatrix} 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} 2 \\ -1 \end{pmatrix} = \begin{pmatrix} 0 \end{pmatrix}. \tag{7.115}$$

As for the irreversible reactions, the reversible reaction rates are constructed to conserve O atoms. We have

$$\frac{d}{dt}\left(\overline{\rho}_O + 2\overline{\rho}_{O_2}\right) = 0. \tag{7.116}$$

Thus, we once again find

$$\overline{\rho}_O + 2\overline{\rho}_{O_2} = \widehat{\overline{\rho}}_O + 2\widehat{\overline{\rho}}_{O_2} = constant. \tag{7.117}$$

As before, we can say

$$\underbrace{\begin{pmatrix} \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}}_{=\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\overline{\rho}}_O \\ \widehat{\overline{\rho}}_{O_2} \end{pmatrix}}_{=\widehat{\overline{\boldsymbol{\rho}}}} + \underbrace{\begin{pmatrix} 1 \\ -\frac{1}{2} \end{pmatrix}}_{=\mathbf{D}} \underbrace{\left(\overline{\xi}_O\right)}_{=\overline{\boldsymbol{\xi}}}. \tag{7.118}$$

This gives the dependent variables in terms of a smaller number of transformed dependent variables in a way which satisfies the linear constraints. In vector form, the equation becomes

$$\overline{\boldsymbol{\rho}} = \widehat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}. \tag{7.119}$$

Once again $\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}$.

7.1.1.2.1.2 Thermodynamics Equations (7.103-7.104) are supplemented by an expression for the thermodynamics-based equilibrium constant $K_{c,13}$ which is:

$$K_{c,13} = \frac{P_o}{\overline{R}T} \exp\left(\frac{-\Delta G^o_{13}}{\overline{R}T}\right). \tag{7.120}$$

Here $P_o = 1.01326 \times 10^6\ dyne/cm^2 = 1\ atm$ is the reference pressure. The net change of Gibbs free energy at the reference pressure for reaction 13, ΔG^o_{13} is defined as

$$\Delta G^o_{13} = 2\overline{g}^o_O - \overline{g}^o_{O_2}. \tag{7.121}$$

We further recall that the Gibbs free energy for species i at the reference pressure is defined in terms of the enthalpy and entropy as

$$\overline{g}^o_i = \overline{h}^o_i - T\overline{s}^o_i. \tag{7.122}$$

It is common to find $\overline{h}^o_i$ and $\overline{s}^o_i$ in thermodynamic tables tabulated as functions of T.

We further note that both Eqs. (7.103) and (7.104) are in equilibrium when

$$\overline{\rho}^e_{O_2}\overline{\rho}^e_M = \frac{1}{K_{c,13}}\overline{\rho}^e_O\overline{\rho}^e_O\overline{\rho}^e_M. \tag{7.123}$$

We rearrange Eq. (7.123) to find the familiar

$$K_{c,13} = \frac{\overline{\rho}^e_O\overline{\rho}^e_O}{\overline{\rho}^e_{O_2}} = \frac{\prod[products]}{\prod[reactants]}. \tag{7.124}$$

If $K_{c,13} > 1$, the products are preferred. If $K_{c,13} < 1$, the reactants are preferred.

Now, $K_{c,13}$ is a function of T only, so it is known. But Eq. (7.124) once again is one equation in two unknowns. We can use the element conservation constraint, Eq. (7.117) to reduce to one equation and one unknown, valid at equilibrium:

$$K_{c,13} = \frac{\overline{\rho}^e_O\overline{\rho}^e_O}{\widehat{\overline{\rho}}_{O_2} + \frac{1}{2}(\widehat{\overline{\rho}}_O - \overline{\rho}^e_O)} \tag{7.125}$$

Using the element constraint, Eq. (7.117), we can recast the dynamics of our system by modifying Eq. (7.103) into one equation in one unknown:

$$\begin{aligned}\frac{d\overline{\rho}_O}{dt} &= 2a_{13}T^{\beta_{13}}\exp\left(\frac{-\overline{E}_{13}}{\overline{R}T}\right) \\ &\times\left(\underbrace{(\widehat{\overline{\rho}}_{O_2} + \frac{1}{2}(\widehat{\overline{\rho}}_O - \overline{\rho}_O))}_{=\overline{\rho}_{O_2}}\underbrace{(\widehat{\overline{\rho}}_{O_2} + \frac{1}{2}(\widehat{\overline{\rho}}_O - \overline{\rho}_O) + \overline{\rho}_O)}_{=\overline{\rho}_M} - \frac{1}{K_{c,13}}\overline{\rho}_O\overline{\rho}_O\underbrace{(\widehat{\overline{\rho}}_{O_2} + \frac{1}{2}(\widehat{\overline{\rho}}_O - \overline{\rho}_O) + \overline{\rho}_O)}_{=\overline{\rho}_M}\right),\end{aligned} \tag{7.126}$$

7.1.1.2.2 Example calculation Let us consider the same example as the previous section with $T = 5000\ K$. We need numbers for all of the parameters of Eq. (7.126). For O, we find at $T = 5000\ K$ that

$$\overline{h}^o_O = 3.48382 \times 10^{12}\ \frac{erg}{mole}, \tag{7.127}$$

$$\overline{s}^o_O = 2.20458 \times 10^9\ \frac{erg}{mole\ K}. \tag{7.128}$$

So

$$\begin{aligned}\overline{g}^o_O &= \left(3.48382 \times 10^{12}\ \frac{erg}{mole}\right) - (5000\ K)\left(2.20458 \times 10^9\ \frac{erg}{mole\ K}\right), \\ &= -7.53908 \times 10^{12}\ \frac{erg}{mole}.\end{aligned} \tag{7.129}$$

For O_2, we find at $T = 5000\ K$ that

$$\overline{h}^o_{O_2} = 1.80749 \times 10^{12}\ \frac{erg}{mole}, \tag{7.130}$$

$$\overline{s}^o_{O_2} = 3.05406 \times 10^9\ \frac{erg}{mole\ K}. \tag{7.131}$$

So

$$\begin{aligned}\overline{g}^o_{O_2} &= \left(1.80749 \times 10^{12}\ \frac{erg}{mole}\right) - (5000\ K)\left(3.05406 \times 10^9\ \frac{erg}{mole\ K}\right) \\ &= -1.34628 \times 10^{13}\ \frac{erg}{mole}. \end{aligned} \tag{7.132}$$

Thus, by Eq. (7.121), we have

$$\Delta G^o_{13} = 2(-7.53908 \times 10^{12}) - (-1.34628 \times 10^{13}) = -1.61536 \times 10^{12}\ \frac{erg}{mole}. \tag{7.133}$$

Thus, by Eq. (7.120) we get for our system

$$\begin{aligned} K_{c,13} &= \frac{1.01326 \times 10^6\ \frac{dyne}{cm^2}}{\left(8.31441 \times 10^7\ \frac{erg}{mole\ K}\right)(5000\ K)} \\ &\quad \times \exp\left(-\left(\frac{-1.61536 \times 10^{12}\ \frac{erg}{mole}}{\left(8.31441 \times 10^7\ \frac{erg}{mole\ K}\right)(5000\ K)}\right)\right), \end{aligned} \tag{7.134}$$

$$= 1.187 \times 10^{-4}\ \frac{mole}{cm^3}. \tag{7.135}$$

Substitution of all numerical parameters into Eq. (7.126) and expansion yields the following

$$\frac{d\overline{\rho}_O}{dt} = 3899.47 - (2.23342 \times 10^{10})\overline{\rho}^2_O - (7.3003 \times 10^{12})\overline{\rho}^3_O = f(\overline{\rho}_O),\ \overline{\rho}_O(0) = 0.001. \tag{7.136}$$

A plot of the time-dependent behavior of $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$ from solution of Eq. (7.136) is given in Figure 7.6. The behavior is similar to the predictions given by the pair of irreversible reactions in Fig. 7.1. Here direct calculation of the equilibrium from time integration reveals

$$\overline{\rho}^e_O = 0.000393328\ \frac{mole}{cm^3}. \tag{7.137}$$

Using Eq. (7.117) we find this corresponds to

$$\overline{\rho}^e_{O_2} = 0.00130334\ \frac{mole}{cm^3}. \tag{7.138}$$

We note the system begins significant reaction for $t \sim 10^{-9}\ s$ and is equilibrated for $t \sim 10^{-7}\ s$.

The equilibrium is verified by solving the algebraic equation

$$f(\overline{\rho}_O) = 3899.47 - (2.23342 \times 10^{10})\overline{\rho}^2_O - (7.3003 \times 10^{12})\overline{\rho}^3_O = 0. \tag{7.139}$$

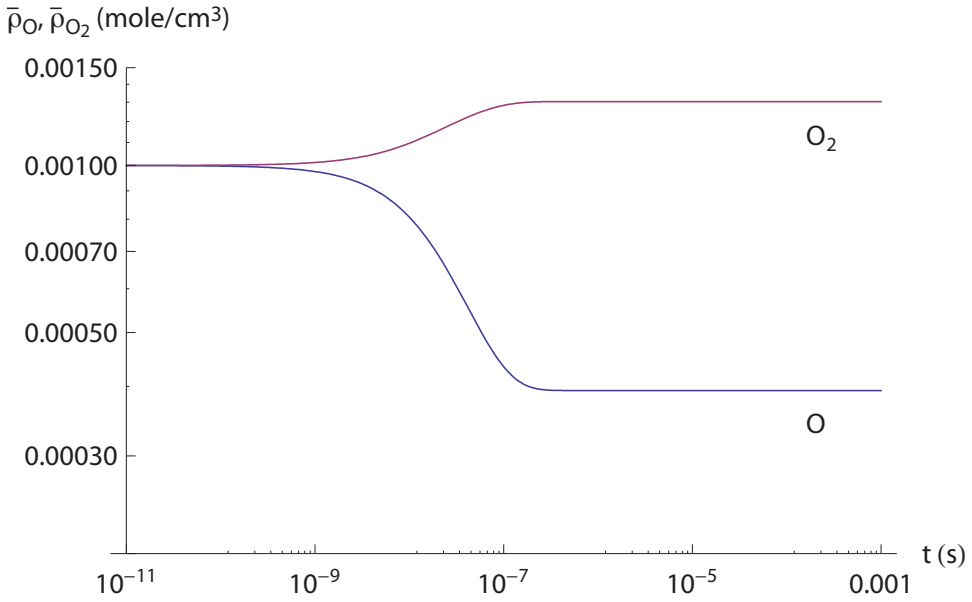

Figure 7.6: Plot of $\overline{\rho}_O(t)$ and $\overline{\rho}_{O_2}(t)$ for oxygen dissociation with reversible reaction.

This yields three roots:

$$\overline{\rho}_O^e = -0.003 \, \frac{mole}{cm^3}, \qquad \text{non-physical,} \tag{7.140}$$

$$\overline{\rho}_O^e = -0.000452678 \, \frac{mole}{cm^3}, \qquad \text{non-physical,} \tag{7.141}$$

$$\overline{\rho}_O^e = 0.000393328 \, \frac{mole}{cm^3}, \qquad \text{physical,} \tag{7.142}$$

$$\tag{7.143}$$

is given in Figure 7.6.

Linearizing Eq. (7.136) in the neighborhood of the physical equilibrium yields the equation

$$\frac{d}{dt}\left(\overline{\rho}_O - 0.000393328\right) = -(2.09575 \times 10^7)\left(\overline{\rho}_O - 0.000393328\right) + \ldots \tag{7.144}$$

This has solution

$$\overline{\rho}_O = 0.000393328 + A \exp\left(-2.09575 \times 10^7 t\right). \tag{7.145}$$

Again, A is an arbitrary constant. Obviously the equilibrium is stable. Moreover the time constant of relaxation to equilibrium is

$$\tau = \frac{1}{2.09575 \times 10^7} = 4.77156 \times 10^{-8} \; s. \tag{7.146}$$

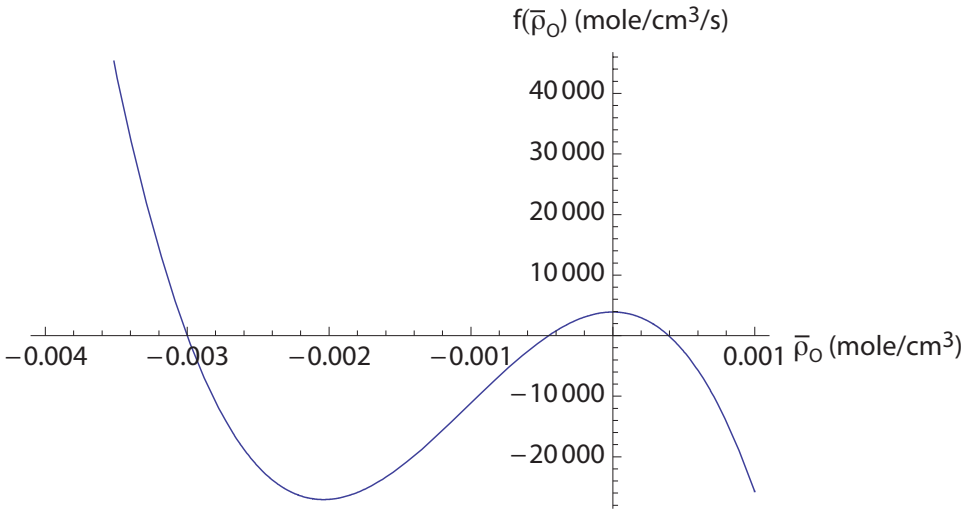

Figure 7.7: Plot of $f(\overline{\rho}_O)$ versus $\overline{\rho}_O$ for oxygen dissociation with reversible reaction.

This is consistent with the time scale to equilibrium which comes from integrating the full equation.

7.1.2 Zel'dovich mechanism of NO production

Let us consider next a more complicated reaction system: that of NO production known as the Zel'dovich[6] mechanism. This is an important model for the production of a major pollutant from combustion processes. It is most important for high temperature applications.

7.1.2.1 Mathematical model

The model has several versions. One is

$$1: \quad N + NO \leftrightharpoons N_2 + O, \tag{7.147}$$

$$2: \quad N + O_2 \leftrightharpoons NO + O. \tag{7.148}$$

similar to our results for O_2 dissociation, N_2 and O_2 are preferred at low temperature. As the temperature rises N and O begin to appear, and it is possible when they are mixed for NO to appear as a product.

[6]Yakov Borisovich Zel'dovich, 1915-1987, prolific Soviet physicist and father of thermonuclear weapons.

7.1.2.1.1 Standard model form Here we have the reaction of $N = 5$ molecular species with

$$\overline{\boldsymbol{\rho}} = \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_{N} \\ \overline{\rho}_{N_2} \\ \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix}. \tag{7.149}$$

We have $L = 2$ with N and O as the 2 elements. The stoichiometric matrix $\boldsymbol{\phi}$ of dimension $L \times N = 2 \times 5$ is

$$\boldsymbol{\phi} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix}. \tag{7.150}$$

The first row of $\boldsymbol{\phi}$ is for the N atom; the second row is for the O atom.

And we have $J = 2$ reactions. The reaction vector of length $J = 2$ is

$$\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} a_1 T^{\beta_1} \exp\left(-\frac{T_{a,1}}{T}\right) \left(\overline{\rho}_N \overline{\rho}_{NO} - \frac{1}{K_{c,1}} \overline{\rho}_{N_2} \overline{\rho}_O\right) \\ a_2 T^{\beta_2} \exp\left(-\frac{T_{a,2}}{T}\right) \left(\overline{\rho}_N \overline{\rho}_{O_2} - \frac{1}{K_{c,2}} \overline{\rho}_{NO} \overline{\rho}_O\right) \end{pmatrix}, \tag{7.151}$$

$$= \begin{pmatrix} k_1 \left(\overline{\rho}_N \overline{\rho}_{NO} - \frac{1}{K_{c,1}} \overline{\rho}_{N_2} \overline{\rho}_O\right) \\ k_2 \left(\overline{\rho}_N \overline{\rho}_{O_2} - \frac{1}{K_{c,2}} \overline{\rho}_{NO} \overline{\rho}_O\right) \end{pmatrix}. \tag{7.152}$$

Here, we have

$$k_1 = a_1 T^{\beta_1} \exp\left(-\frac{T_{a,1}}{T}\right), \tag{7.153}$$

$$k_2 = a_2 T^{\beta_2} \exp\left(-\frac{T_{a,2}}{T}\right). \tag{7.154}$$

In matrix form, the model can be written as

$$\frac{d}{dt} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_{N} \\ \overline{\rho}_{N_2} \\ \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & 0 \\ 1 & 1 \\ 0 & -1 \end{pmatrix}}_{=\boldsymbol{\nu}} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.155}$$

Here the matrix $\boldsymbol{\nu}$ has dimension $N \times J$ which is 5×2. The model is of our general form

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \boldsymbol{\nu} \cdot \mathbf{r}. \tag{7.156}$$

Note that our stoichiometric constraint on element conservation for each reaction $\boldsymbol{\phi}\cdot\boldsymbol{\nu} = \mathbf{0}$ holds here:

$$\boldsymbol{\phi}\cdot\boldsymbol{\nu} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & 0 \\ 1 & 1 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{7.157}$$

We get 4 zeros because there are 2 reactions each with 2 element constraints.

7.1.2.1.2 Reduced form Here we describe non-traditional, but useful reductions, using standard techniques from linear algebra to bring the model equations into a reduced form in which all of the linear constraints have been explicitly removed.

Let us perform a series of row operations to find all of the linear dependencies. Our aim is to convert the $\boldsymbol{\nu}$ matrix into an upper triangular form. The lower left corner of $\boldsymbol{\nu}$ already has a zero, so there is no need to worry about it. Let us add the first and fourth equations to eliminate the 1 in the $4,1$ slot. This gives

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_{N} \\ \overline{\rho}_{N_2} \\ \overline{\rho}_{NO} + \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 1 & 0 \\ 0 & 2 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.158}$$

Next, add the first and third equations to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_{N} \\ \overline{\rho}_{NO} + \overline{\rho}_{N_2} \\ \overline{\rho}_{NO} + \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ -1 & -1 \\ 0 & 1 \\ 0 & 2 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.159}$$

Now multiply the first equation by -1 and add it to the second to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ -\overline{\rho}_{NO} + \overline{\rho}_{N} \\ \overline{\rho}_{NO} + \overline{\rho}_{N_2} \\ \overline{\rho}_{NO} + \overline{\rho}_{O} \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 1 \\ 0 & 2 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.160}$$

Next multiply the fifth equation by -2 and add it to the second to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ -\overline{\rho}_{NO} + \overline{\rho}_{N} \\ \overline{\rho}_{NO} + \overline{\rho}_{N_2} \\ \overline{\rho}_{NO} + \overline{\rho}_{O} \\ -\overline{\rho}_{NO} + \overline{\rho}_{N} - 2\overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 1 \\ 0 & 2 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.161}$$

Next add the second and fourth equations to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ -\overline{\rho}_{NO} + \overline{\rho}_N \\ \overline{\rho}_{NO} + \overline{\rho}_{N_2} \\ \overline{\rho}_N + \overline{\rho}_O \\ -\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.162}$$

Next multiply the third equation by 2 and add it to the second to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ -\overline{\rho}_{NO} + \overline{\rho}_N \\ \overline{\rho}_{NO} + \overline{\rho}_N + 2\overline{\rho}_{N_2} \\ \overline{\rho}_N + \overline{\rho}_O \\ -\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.163}$$

Rewritten, this becomes

$$\underbrace{\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 2 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 & -2 \end{pmatrix}}_{=\mathbf{L}^{-1}} \frac{d}{dt}\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \underbrace{\begin{pmatrix} -1 & 1 \\ 0 & -2 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix}}_{=\mathbf{U}} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}. \tag{7.164}$$

A way to think of this type of row echelon form is that it defines two free variables, those associated with the non-zero pivots of $\mathbf{U}$: $\overline{\rho}_{NO}$ and $\overline{\rho}_N$. The remain three variables $\overline{\rho}_{N_2}$, $\overline{\rho}_O$ and $\overline{\rho}_{O_2}$ are bound variables which can be expressed in terms of the free variables.

The last three of the ordinary differential equations are homogeneous and can be integrated to form

$$\overline{\rho}_{NO} + \overline{\rho}_N + 2\overline{\rho}_{N_2} = C_1, \tag{7.165}$$

$$\overline{\rho}_N + \overline{\rho}_O = C_2, \tag{7.166}$$

$$-\overline{\rho}_{NO} + \overline{\rho}_N - 2\overline{\rho}_{O_2} = C_3. \tag{7.167}$$

The constants C_1, C_2 and C_3 are determined from the initial conditions on all five state variables. In matrix form, we can say

$$\begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}. \tag{7.168}$$

Considering the free variables, $\overline{\rho}_{NO}$ and $\overline{\rho}_N$, to be known, we move them to the right side to get

$$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} C_1 - \overline{\rho}_{NO} - \overline{\rho}_N \\ C_2 - \overline{\rho}_N \\ C_3 + \overline{\rho}_{NO} - \overline{\rho}_N \end{pmatrix}. \tag{7.169}$$

Solving, for the bound variables, we find

$$\begin{pmatrix} \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}C_1 - \frac{1}{2}\overline{\rho}_{NO} - \frac{1}{2}\overline{\rho}_N \\ C_2 - \overline{\rho}_N \\ -\frac{1}{2}C_3 - \frac{1}{2}\overline{\rho}_{NO} + \frac{1}{2}\overline{\rho}_N \end{pmatrix}. \tag{7.170}$$

We can rewrite this as

$$\begin{pmatrix} \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}C_1 \\ C_2 \\ -\frac{1}{2}C_3 \end{pmatrix} + \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \end{pmatrix}. \tag{7.171}$$

We can get a more elegant form by defining $\xi_{NO} = \overline{\rho}_{NO}$ and $\xi_N = \overline{\rho}_N$. Thus we can say our state variables have the form

$$\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2}C_1 \\ C_2 \\ -\frac{1}{2}C_3 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \xi_{NO} \\ \xi_N \end{pmatrix}. \tag{7.172}$$

By translating via $\xi_{NO} = \overline{\xi}_{NO} + \widehat{\overline{\rho}}_{NO}$ and $\xi_N = \overline{\xi}_N + \widehat{\overline{\rho}}_N$ and choosing the constants C_1, C_2 and C_3 appropriately, we can arrive at

$$\underbrace{\begin{pmatrix} \overline{\rho}_{NO} \\ \overline{\rho}_N \\ \overline{\rho}_{N_2} \\ \overline{\rho}_O \\ \overline{\rho}_{O_2} \end{pmatrix}}_{=\overline{\boldsymbol{\rho}}} = \underbrace{\begin{pmatrix} \widehat{\overline{\rho}}_{NO} \\ \widehat{\overline{\rho}}_N \\ \widehat{\overline{\rho}}_{N_2} \\ \widehat{\overline{\rho}}_O \\ \widehat{\overline{\rho}}_{O_2} \end{pmatrix}}_{=\widehat{\overline{\boldsymbol{\rho}}}} + \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix}}_{=\mathbf{D}} \underbrace{\begin{pmatrix} \overline{\xi}_{NO} \\ \overline{\xi}_N \end{pmatrix}}_{=\overline{\boldsymbol{\xi}}}. \tag{7.173}$$

This takes the form of

$$\overline{\boldsymbol{\rho}} = \widehat{\overline{\boldsymbol{\rho}}} + \mathbf{D} \cdot \overline{\boldsymbol{\xi}}. \tag{7.174}$$

Here the matrix $\mathbf{D}$ is of dimension $N \times R$, which here is 5×2. It spans the same column space as does the $N \times J$ matrix $\boldsymbol{\nu}$ which is of rank R. Here in fact $R = J = 2$, so $\mathbf{D}$ has the same dimension as $\boldsymbol{\nu}$. In general it will not. If $\mathbf{c}_1$ and $\mathbf{c}_2$ are the column vectors of $\mathbf{D}$, we

see that $-\mathbf{c}_1 - \mathbf{c}_2$ forms the first column vector of $\boldsymbol{\nu}$ and $\mathbf{c}_1 - \mathbf{c}_2$ forms the second column vector of $\boldsymbol{\nu}$. Note that $\boldsymbol{\phi} \cdot \mathbf{D} = \mathbf{0}$:

$$\boldsymbol{\phi} \cdot \mathbf{D} = \begin{pmatrix} 1 & 1 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -\frac{1}{2} & -\frac{1}{2} \\ 0 & -1 \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{7.175}$$

Equations (7.165-7.167) can also be linearly combined in a way which has strong physical relevance. We rewrite the system as three equations in which the first is identical to Eq. (7.165); the second is the difference of Eqs. (7.166) and (7.167); and the third is half of Eq. (7.165) minus half of Eq. (7.167) plus Eq. (7.166):

$$\begin{aligned} \overline{\rho}_{NO} + \overline{\rho}_N + 2\overline{\rho}_{N_2} &= C_1, & (7.176) \\ \overline{\rho}_O + \overline{\rho}_{NO} + 2\overline{\rho}_{O_2} &= C_2 - C_3, & (7.177) \\ \overline{\rho}_{NO} + \overline{\rho}_N + \overline{\rho}_{N_2} + \overline{\rho}_O + \overline{\rho}_{O_2} &= \frac{1}{2}(C_1 - C_3) + C_2. & (7.178) \end{aligned}$$

Equation (7.176) insists that the number of nitrogen elements be constant; Eq. (7.177) demands the number of oxygen elements be constant; and Eq. (7.178) requires the number of moles of molecular species be constant. For general reactions, including the earlier studied oxygen dissociation problem, the number of moles of molecular species will not be constant. Here because each reaction considered has two molecules reacting to form two molecules, we are guaranteed the number of moles will be constant. Hence, we get an additional linear constraint beyond the two for element conservation. Note that since our reaction is isothermal, isochoric and mole-preserving, it will also be isobaric.

7.1.2.1.3 Example calculation Let us consider an isothermal reaction at

$$T = 6000\ K. \tag{7.179}$$

The high temperature is useful in generating results which are easily visualized. It insures that there will be significant concentrations of all molecular species. Let us also take as an initial condition

$$\widehat{\overline{\rho}}_{NO} = \widehat{\overline{\rho}}_N = \widehat{\overline{\rho}}_{N_2} = \widehat{\overline{\rho}}_O = \widehat{\overline{\rho}}_{O_2} = 1 \times 10^{-6}\ \frac{mole}{cm^3}. \tag{7.180}$$

For this temperature and concentrations, the pressure, which will remain constant through the reaction, is $P = 2.4942 \times 10^6\ dyne/cm^2$. This is a little greater than atmospheric.

Kinetic data for this reaction is adopted from Baulch, *et al.*[7] The data for reaction 1 is

$$a_1 = 2.107 \times 10^{13}\ \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}, \qquad \beta_1 = 0, \qquad T_{a1} = 0\ K. \tag{7.181}$$

[7]Baulch, *et al.*, 2005, "Evaluated Kinetic Data for Combustion Modeling: Supplement II," *Journal of Physical and Chemical Reference Data*, 34(3): 757-1397.

For reaction 2, we have

$$a_2 = 5.8394 \times 10^9 \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{K^{1.01}\ s}, \qquad \beta_2 = 1.01, \qquad T_{a2} = 3120\ K. \tag{7.182}$$

Here the so-called activation temperature $T_{a,j}$ for reaction j is really the activation energy scaled by the universal gas constant:

$$T_{a,j} = \frac{\overline{E}_j}{\overline{R}}. \tag{7.183}$$

Substituting numbers we obtain for the reaction rates

$$k_1 = (2.107 \times 10^{13})(6000)^0 \exp\left(\frac{-0}{6000}\right) = 2.107 \times 10^{13} \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}, \tag{7.184}$$

$$k_2 = (5.8394 \times 10^9)(6000)^{1.01} \exp\left(\frac{-3120}{6000}\right) = 2.27231 \times 10^{13} \left(\frac{mole}{cm^3}\right)^{-1} \frac{1}{s}. \tag{7.185}$$

We will also need thermodynamic data. The data here will be taken from the Chemkin database.[8] Thermodynamic data for common materials is also found in most thermodynamic texts. For our system at 6000 K, we find

$$\overline{g}^o_{NO} = -1.58757 \times 10^{13}\ \frac{erg}{mole}, \tag{7.186}$$

$$\overline{g}^o_{N} = -7.04286 \times 10^{12}\ \frac{erg}{mole}, \tag{7.187}$$

$$\overline{g}^o_{N_2} = -1.55206 \times 10^{13}\ \frac{erg}{mole}, \tag{7.188}$$

$$\overline{g}^o_{O} = -9.77148 \times 10^{12}\ \frac{erg}{mole}, \tag{7.189}$$

$$\overline{g}^o_{O_2} = -1.65653 \times 10^{13}\ \frac{erg}{mole}. \tag{7.190}$$

Thus for each reaction, we find ΔG^o_j:

$$\Delta G^o_1 = \overline{g}^o_{N_2} + \overline{g}^o_{O} - \overline{g}^o_{N} - \overline{g}^o_{NO}, \tag{7.191}$$

$$= -1.55206 \times 10^{13} - 9.77148 \times 10^{12} + 7.04286 \times 10^{12} + 1.58757 \times 10^{13}, \tag{7.192}$$

$$= -2.37351 \times 10^{12}\ \frac{erg}{mole}, \tag{7.193}$$

$$\Delta G^o_2 = \overline{g}^o_{NO} + \overline{g}^o_{O} - \overline{g}^o_{N} - \overline{g}^o_{O_2}, \tag{7.194}$$

$$= -1.58757 \times 10^{13} - 9.77148 \times 10^{12} + 7.04286 \times 10^{12} + 1.65653 \times 10^{13}, \tag{7.195}$$

$$= -2.03897 \times 10^{12}\ \frac{erg}{mole}. \tag{7.196}$$

[8] R. J. Kee, et al., 2000, "The Chemkin Thermodynamic Data Base," part of the Chemkin Collection Release 3.6, Reaction Design, San Diego, CA.

At 6000 K, we find the equilibrium constants for the $J = 2$ reactions are

$$\begin{aligned} K_{c,1} &= \exp\left(\frac{-\Delta G_1^o}{\overline{R}T}\right), && (7.197)\\ &= \exp\left(\frac{2.37351 \times 10^{12}}{(8.314 \times 10^7)(6000)}\right), && (7.198)\\ &= 116.52, && (7.199)\\ K_{c,2} &= \exp\left(\frac{-\Delta G_2^o}{\overline{R}T}\right), && (7.200)\\ &= \exp\left(\frac{2.03897 \times 10^{12}}{(8.314 \times 10^7)(6000)}\right), && (7.201)\\ &= 59.5861. && (7.202) \end{aligned}$$

Again, omitting details, we find the two differential equations governing the evolution of the free variables are

$$\frac{d\overline{\rho}_{NO}}{dt} = 0.723 + 2.22 \times 10^7 \overline{\rho}_N + 1.15 \times 10^{13} \overline{\rho}_N^2 - 9.44 \times 10^5 \overline{\rho}_{NO} - 3.20 \times 10^{13} \overline{\rho}_N \overline{\rho}_{NO}, \quad (7.203)$$

$$\frac{d\overline{\rho}_N}{dt} = 0.723 - 2.33 \times 10^7 \overline{\rho}_N - 1.13 \times 10^{13} \overline{\rho}_N^2 + 5.82 \times 10^5 \overline{\rho}_{NO} - 1.00 \times 10^{13} \overline{\rho}_N \overline{\rho}_{NO}. \quad (7.204)$$

Solving numerically, we obtain a solution shown in Fig. 7.8. The numerics show a relaxation to final concentrations of

$$\begin{aligned} \lim_{t\to\infty} \overline{\rho}_{NO} &= 7.336 \times 10^{-7} \ \frac{mole}{cm^3}, && (7.205)\\ \lim_{t\to\infty} \overline{\rho}_N &= 3.708 \times 10^{-8} \ \frac{mole}{cm^3}. && (7.206) \end{aligned}$$

Equations (7.203-7.204) are of the form

$$\begin{aligned} \frac{d\overline{\rho}_{NO}}{dt} &= f_{NO}(\overline{\rho}_{NO}, \overline{\rho}_N), && (7.207)\\ \frac{d\overline{\rho}_N}{dt} &= f_N(\overline{\rho}_{NO}, \overline{\rho}_N). && (7.208) \end{aligned}$$

At equilibrium, we must have

$$\begin{aligned} f_{NO}(\overline{\rho}_{NO}, \overline{\rho}_N) &= 0, && (7.209)\\ f_N(\overline{\rho}_{NO}, \overline{\rho}_N) &= 0. && (7.210) \end{aligned}$$

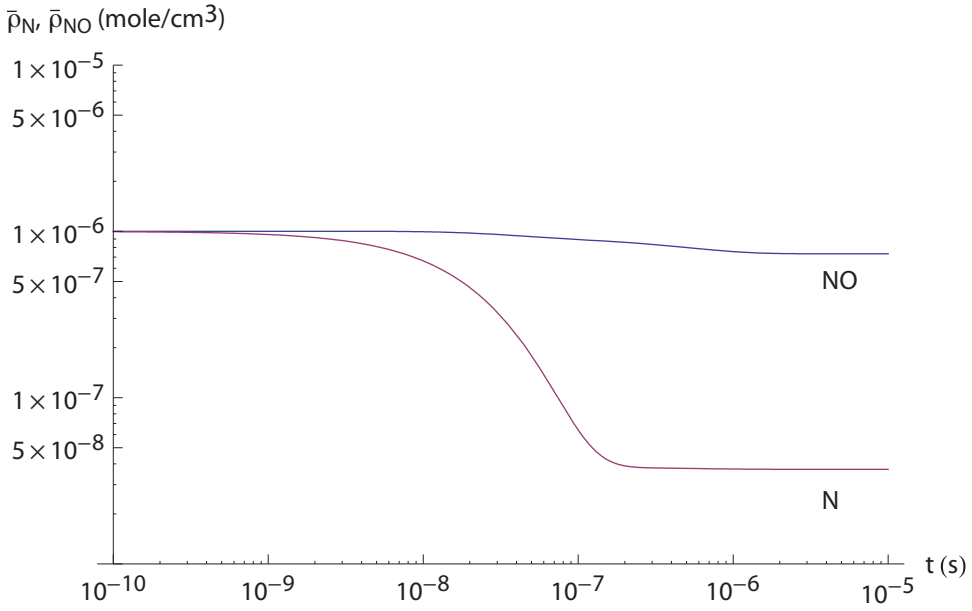

Figure 7.8: NO and N concentrations versus time for $T = 6000\ K$, $P = 2.4942 \times 10^6\ dyne/cm^2$ Zel'dovich mechanism.

We find three finite roots to this problem:

$$1 \ : \ (\overline{\rho}_{NO}, \overline{\rho}_N) = (-1.605 \times 10^{-6}, -3.060 \times 10^{-8}) \ \frac{mole}{cm^3}, \qquad \text{non-physical,} \quad (7.211)$$

$$2 \ : \ (\overline{\rho}_{NO}, \overline{\rho}_N) = (-5.173 \times 10^{-8}, -2.048 \times 10^{-6}) \ \frac{mole}{cm^3}, \qquad \text{non-physical,} \quad (7.212)$$

$$3 \ : \ (\overline{\rho}_{NO}, \overline{\rho}_N) = (7.336 \times 10^{-7}, 3.708 \times 10^{-8}) \ \frac{mole}{cm^3}, \qquad \text{physical.} \quad (7.213)$$

Obviously, because of negative concentrations, roots 1 and 2 are non-physical. Root 3 however is physical; moreover, it agrees with the equilibrium we found by direct numerical integration of the full non-linear equations.

We can use local linear analysis in the neighborhood of each equilibria to rigorously ascertain the stability of each root. Taylor series expansion of Eqs. (7.207-7.208) in the neighborhood of an equilibrium point yields

$$\frac{d}{dt}\left(\overline{\rho}_{NO} - \overline{\rho}^e_{NO}\right) = \underbrace{f_{NO}|_e}_{=0} + \left.\frac{\partial f_{NO}}{\partial \overline{\rho}_{NO}}\right|_e \left(\overline{\rho}_{NO} - \overline{\rho}^e_{NO}\right) + \left.\frac{\partial f_{NO}}{\partial \overline{\rho}_N}\right|_e \left(\overline{\rho}_N - \overline{\rho}^e_N\right) + \ldots, \quad (7.214)$$

$$\frac{d}{dt}\left(\overline{\rho}_N - \overline{\rho}^e_N\right) = \underbrace{f_N|_e}_{=0} + \left.\frac{\partial f_N}{\partial \overline{\rho}_{NO}}\right|_e \left(\overline{\rho}_{NO} - \overline{\rho}^e_{NO}\right) + \left.\frac{\partial f_N}{\partial \overline{\rho}_N}\right|_e \left(\overline{\rho}_N - \overline{\rho}^e_N\right) + \ldots. \quad (7.215)$$

Evaluation of Eqs. (7.214-7.215) near the physical root, root 3, yields the system

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_{NO}-7.336\times10^{-7}\\ \overline{\rho}_{N}-3.708\times10^{-8}\end{pmatrix}=\underbrace{\begin{pmatrix}-2.129\times10^{6} & -4.155\times10^{5}\\ 2.111\times10^{5} & -3.144\times10^{7}\end{pmatrix}}_{=\mathbf{J}=\frac{\partial\mathbf{f}}{\partial\overline{\boldsymbol{\rho}}}\Big|_e}\begin{pmatrix}\overline{\rho}_{NO}-7.336\times10^{-7}\\ \overline{\rho}_{N}-3.708\times10^{-8}\end{pmatrix}. \tag{7.216}$$

This is of the form

$$\frac{d}{dt}\left(\overline{\boldsymbol{\rho}}-\overline{\boldsymbol{\rho}}^{e}\right)=\left.\frac{\partial\mathbf{f}}{\partial\overline{\boldsymbol{\rho}}}\right|_{e}\cdot\left(\overline{\boldsymbol{\rho}}-\overline{\boldsymbol{\rho}}^{e}\right)=\mathbf{J}\cdot\left(\overline{\boldsymbol{\rho}}-\overline{\boldsymbol{\rho}}^{e}\right). \tag{7.217}$$

It is the eigenvalues of the Jacobian[9] matrix $\mathbf{J}$ that give the time scales of evolution of the concentrations as well as determine the stability of the local equilibrium point. Recall that we can usually decompose square matrices via the diagonalization

$$\mathbf{J}=\mathbf{S}\cdot\boldsymbol{\Lambda}\cdot\mathbf{S}^{-1}. \tag{7.218}$$

Here, $\mathbf{S}$ is the matrix whose columns are composed of the right eigenvectors of $\mathbf{J}$, and $\boldsymbol{\Lambda}$ is the diagonal matrix whose diagonal is populated by the eigenvalues of $\mathbf{J}$. For some matrices (typically not those encountered after our removal of linear dependencies), diagonalization is not possible, and one must resort to the so-called near-diagonal Jordan form. This will not be relevant to our discussion, but could be easily handled if necessary. We also recall the eigenvector matrix and eigenvalue matrix are defined by the standard eigenvalue problem

$$\mathbf{J}\cdot\mathbf{S}=\mathbf{S}\cdot\boldsymbol{\Lambda}. \tag{7.219}$$

We also recall that the components λ of $\boldsymbol{\Lambda}$ are found by solving the characteristic polynomial which arises from the equation

$$\det\left(\mathbf{J}-\lambda\mathbf{I}\right)=0, \tag{7.220}$$

where $\mathbf{I}$ is the identity matrix. Defining $\mathbf{z}$ such that

$$\mathbf{S}\cdot\mathbf{z}\equiv\overline{\boldsymbol{\rho}}-\overline{\boldsymbol{\rho}}^{e}, \tag{7.221}$$

and using the decomposition Eq. (7.218), Eq. (7.217) can be rewritten to form

$$\frac{d}{dt}(\mathbf{S}\cdot\mathbf{z}) = \underbrace{\mathbf{S}\cdot\boldsymbol{\Lambda}\cdot\mathbf{S}^{-1}}_{\mathbf{J}}\cdot\underbrace{(\mathbf{S}\cdot\mathbf{z})}_{\overline{\boldsymbol{\rho}}-\overline{\boldsymbol{\rho}}^{e}}, \tag{7.222}$$

$$\mathbf{S}\cdot\frac{d\mathbf{z}}{dt} = \mathbf{S}\cdot\boldsymbol{\Lambda}\cdot\mathbf{z}, \tag{7.223}$$

$$\mathbf{S}^{-1}\cdot\mathbf{S}\cdot\frac{d\mathbf{z}}{dt} = \mathbf{S}^{-1}\cdot\mathbf{S}\cdot\boldsymbol{\Lambda}\cdot\mathbf{z}, \tag{7.224}$$

$$\frac{d\mathbf{z}}{dt} = \boldsymbol{\Lambda}\cdot\mathbf{z}. \tag{7.225}$$

[9] after Carl Gustav Jacob Jacobi, 1804-1851, German mathematician.

Eq. (7.225) reduces to the diagonal form

$$\frac{d\mathbf{z}}{dt} = \mathbf{\Lambda} \cdot \mathbf{z}. \tag{7.226}$$

This has solution for each component of $\mathbf{z}$ of

$$\begin{aligned} z_1 &= C_1 \exp(\lambda_1 t), && (7.227)\\ z_2 &= C_2 \exp(\lambda_2 t), && (7.228)\\ &\vdots && (7.229) \end{aligned}$$

Here, our matrix $\mathbf{J}$, see Eq. (7.216), has two real, negative eigenvalues in the neighborhood of the physical root 3:

$$\begin{aligned} \lambda_1 &= -3.143 \times 10^7 \ \frac{1}{s}, && (7.230)\\ \lambda_2 &= -2.132 \times 10^6 \ \frac{1}{s}. && (7.231) \end{aligned}$$

Thus we can conclude that the physical equilibrium is linearly stable. The local time constants near equilibrium are given by the reciprocal of the magnitude of the eigenvalues. These are

$$\begin{aligned} \tau_1 &= 1/|\lambda_1| = 3.181 \times 10^{-8} \ s, && (7.232)\\ \tau_2 &= 1/|\lambda_2| = 4.691 \times 10^{-7} \ s. && (7.233) \end{aligned}$$

Evolution on these two time scales is predicted in Fig. 7.8. This in fact a multiscale problem. One of the major difficulties in the numerical simulation of combustion problems comes in the effort to capture the effects at all relevant scales. The problem is made more difficult as the breadth of the scales expands. In this problem, the breadth of scales is not particularly challenging. Near equilibrium the ratio of the slowest to the fastest time scale, the *stiffness* ratio κ, is

$$\kappa = \frac{\tau_2}{\tau_1} = \frac{4.691 \times 10^{-7} \ s}{3.181 \times 10^{-8} \ s} = 14.75. \tag{7.234}$$

Many combustion problems can have stiffness ratios over 10^6. This is more prevalent at lower temperatures.

We can do a similar linearization near the initial state, find the local eigenvalues, and the the local time scales. At the initial state here, we find those local time scales are

$$\begin{aligned} \tau_1 &= 2.403 \times 10^{-8} \ s, && (7.235)\\ \tau_2 &= 2.123 \times 10^{-8} \ s. && (7.236) \end{aligned}$$

So initially the stiffness, $\kappa = (2.403 \times 10^{-8} \ s)/(2.123 \times 10^{-8} \ s) = 1.13$ is much less, but the time scale itself is small. It is seen from Fig. 7.8 that this initial time scale of $10^{-8} \ s$ well

predicts where significant evolution of species concentrations commences. For $t < 10^{-8}\ s$, the model predicts essentially no activity. This can be correlated with the mean time between molecular collisions–the theory on which estimates of the collision frequency factors a_j are obtained.

We briefly consider the non-physical roots, 1 and 2. A similar eigenvalue analysis of root 1 reveals that the eigenvalues of its local Jacobian matrix are

$$\lambda_1 = -1.193 \times 10^7 \ \frac{1}{s}, \tag{7.237}$$

$$\lambda_2 = 5.434 \times 10^6 \ \frac{1}{s}. \tag{7.238}$$

Thus root 1 is a saddle and is unstable.

For root 2, we find

$$\lambda_1 = 4.397 \times 10^7 + i7.997 \times 10^6 \ \frac{1}{s}, \tag{7.239}$$

$$\lambda_2 = 4.397 \times 10^7 - i7.997 \times 10^6 \ \frac{1}{s}. \tag{7.240}$$

The eigenvalues are complex with a positive real part. This indicates the root is an unstable spiral source.

A detailed phase portrait is shown in Fig. 7.9. Here we see all three roots. Their local character of sink, saddle, or spiral source is clearly displayed. We see that trajectories are attracted to a curve labeled SIM for "Slow Invariant Manifold." A part of the SIM is constructed by the trajectory which originates at root 1 and travels to root 3. The other part is constructed by connecting an equilibrium point at infinity into root 3. Details are omitted here.

7.1.2.2 Stiffness, time scales, and numerics

One of the key challenges in computational chemistry is accurately predicting species concentration evolution with time. The problem is made difficult because of the common presence of physical phenomena which evolve on a widely disparate set of time scales. Systems which evolve on a wide range of scales are known as stiff, recognizing a motivating example in mass-spring-damper systems with stiff springs. Here we will examine the effect of temperature and pressure on time scales and stiffness. We shall also look simplistically how different numerical approximation methods respond to stiffness.

7.1.2.2.1 Effect of temperature Let us see how the same Zel'dovich mechanism behaves at lower temperature, $T = 1500\ K$; all other parameters, including the initial species concentrations are the same as the previous high temperature example. The pressure however, lowers, and here is $P = 6.23550 \times 10^5\ dyne/cm^2$, which is close to atmospheric pressure. For this case, a plot of species concentrations versus time is given in Figure 7.10.

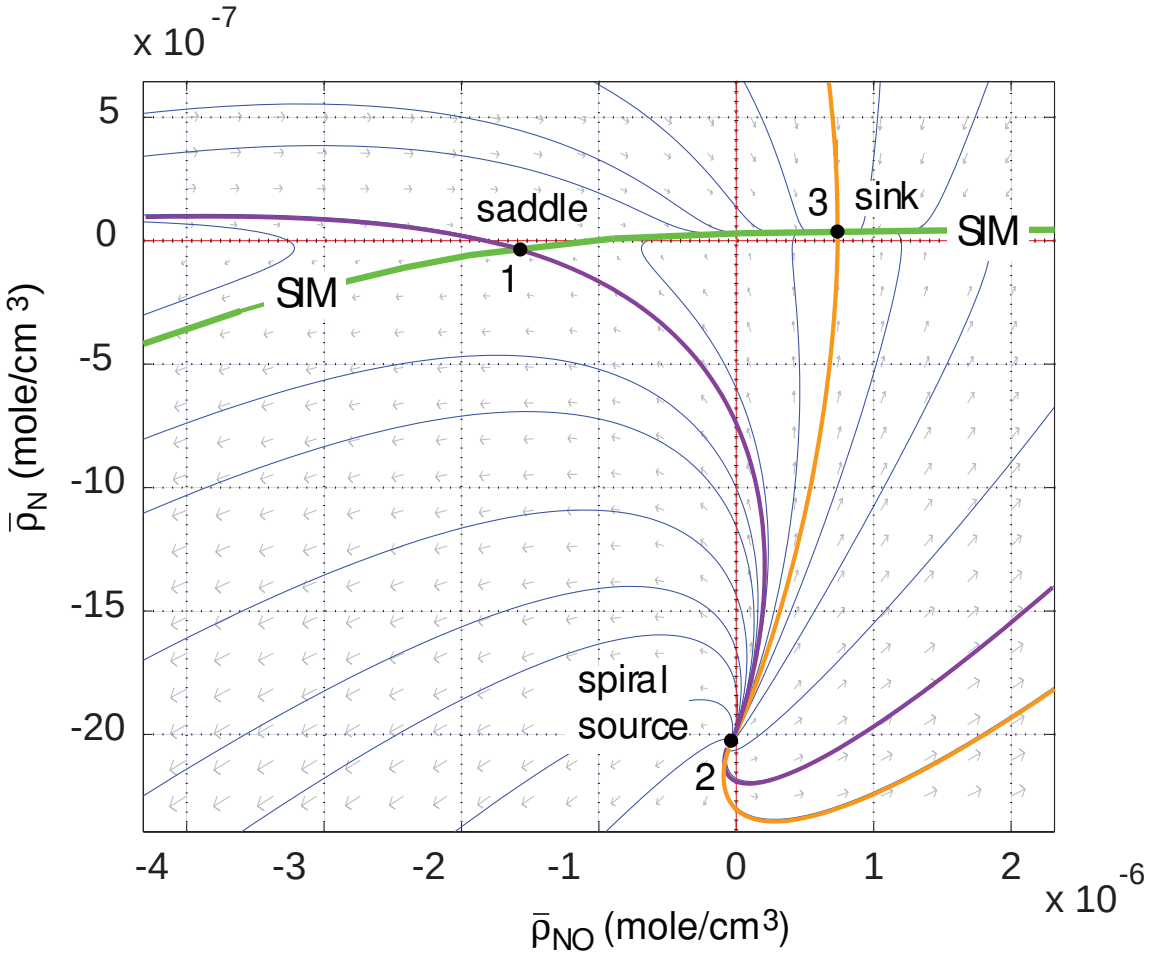

Figure 7.9: NO and N phase portraits for $T = 6000\ K$, $P = 2.4942 \times 10^6\ dyne/cm^2$ Zel'dovich mechanism.

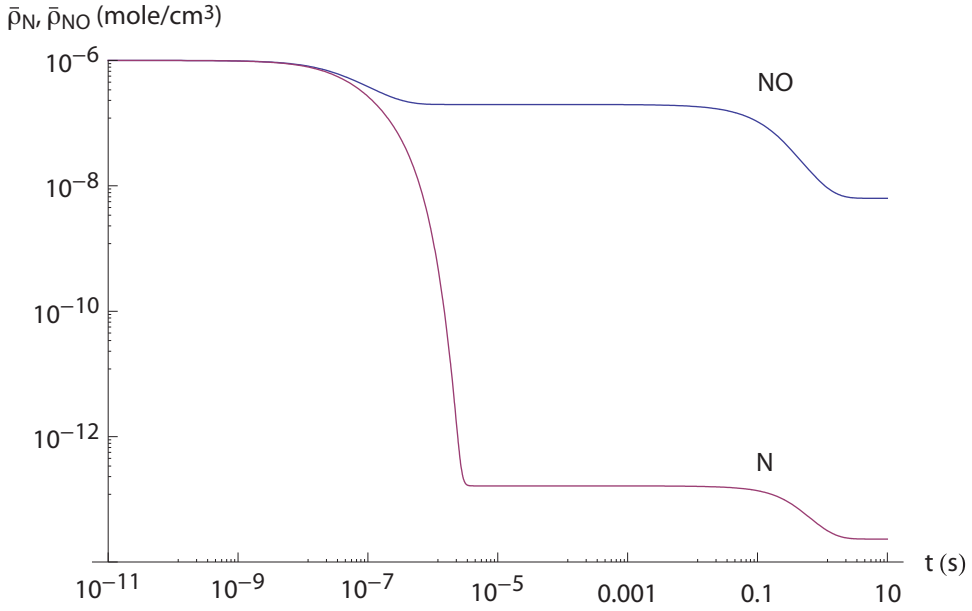

Figure 7.10: $\overline{\rho}_{NO}$ and $\overline{\rho}_N$ versus time for Zel'dovich mechanism at $T = 1500\ K$, $P = 6.23550 \times 10^5\ dyne/cm^2$.

At $T = 1500\ K$, we notice some dramatic differences relative to the earlier studied $T = 6000\ K$. First, we see the reaction commences in around the same time, $t \sim 10^{-8}\ s$. For $t \sim 10^{-6}\ s$, there is a temporary cessation of significant reaction. We notice a long plateau in which species concentrations do not change over several decades of time. This is actually a pseudo-equilibrium. Significant reaction recommences for $t \sim 0.1\ s$. Only around $t \sim 1\ s$ does the system approach final equilibrium. We can perform an eigenvalue analysis both at the initial state and at the equilibrium state to estimate the time scales of reaction. For this dynamical system which is two ordinary differential equations in two unknowns, we will always find two eigenvalues, and thus two time scales. Let us call them τ_1 and τ_2. Both these scales will evolve with t.

At the initial state, we find

$$\tau_1 = 2.37 \times 10^{-8}\ s, \tag{7.241}$$

$$\tau_2 = 4.25 \times 10^{-7}\ s. \tag{7.242}$$

The onset of significant reaction is consistent with the prediction given by τ_1 at the initial state. Moreover, initially, the reaction is not very stiff; the stiffness ratio is $\kappa = 17.9$.

At equilibrium, we find

$$\lim_{t\to\infty} \overline{\rho}_{NO} = 4.6 \times 10^{-9}\ \frac{mole}{cm^3}, \tag{7.243}$$

$$\lim_{t\to\infty} \overline{\rho}_{N} = 4.2 \times 10^{-14}\ \frac{mole}{cm^3}, \tag{7.244}$$

and

$$\tau_1 = 7.86 \times 10^{-7}\ s, \tag{7.245}$$
$$\tau_2 = 3.02 \times 10^{-1}\ s. \tag{7.246}$$

The slowest time scale near equilibrium is an excellent indicator of how long the system takes to relax to its final state. Note also that near equilibrium, the stiffness ratio is large, $\kappa = \tau_2/\tau_1 \sim 3.8 \times 10^5$. This is known as the *stiffness ratio*. When it is large, the scales in the problem are widely disparate and accurate numerical solution becomes challenging.

In summary, we find the effect of lowering temperature while leaving initial concentrations constant

- lowers the pressure somewhat, slightly slowing down the collision time, and slightly slowing the fastest time scales, and
- slows the slowest time scales many orders of magnitude, stiffening the system significantly, since collisions may not induce reaction with their lower collision speed.

7.1.2.2.2 Effect of initial pressure Let us maintain the initial temperature at $T = 1500\ K$, but drop the initial concentration of each species to

$$\widehat{\overline{\rho}}_{NO} = \widehat{\overline{\rho}}_{N} = \widehat{\overline{\rho}}_{N_2} = \widehat{\overline{\rho}}_{O_2} = \widehat{\overline{\rho}}_{O} = 10^{-8}\ \frac{mole}{cm^3}. \tag{7.247}$$

With this decrease in number of moles, the pressure now is

$$P = 6.23550 \times 10^3\ \frac{dyne}{cm^2}. \tag{7.248}$$

This pressure is two orders of magnitude lower than atmospheric. We solve for the species concentration profiles and show the results of numerical prediction in Figure 7.11 Relative to the high pressure $P = 6.2355 \times 10^5\ dyne/cm^2$, $T = 1500\ K$ case, we notice some similarities and dramatic differences. The overall shape of the time-profiles of concentration variation is similar. But, we see the reaction commences at a much later time, $t \sim 10^{-6}\ s$. For $t \sim 10^{-4}\ s$, there is a temporary cessation of significant reaction. We notice a long plateau in which species concentrations do not change over several decades of time. This is again actually a pseudo-equilibrium. Significant reaction recommences for $t \sim 10\ s$. Only around $t \sim 100\ s$ does the system approach final equilibrium. We can perform an eigenvalue analysis both at the initial state and at the equilibrium state to estimate the time scales of reaction.

At the initial state, we find

$$\tau_1 = 2.37 \times 10^{-6}\ s, \tag{7.249}$$
$$\tau_2 = 4.25 \times 10^{-5}\ s. \tag{7.250}$$

The onset of significant reaction is consistent with the prediction given by τ_1 at the initial state. Moreover, initially, the reaction is not very stiff; the stiffness ratio is $\kappa = 17.9$.

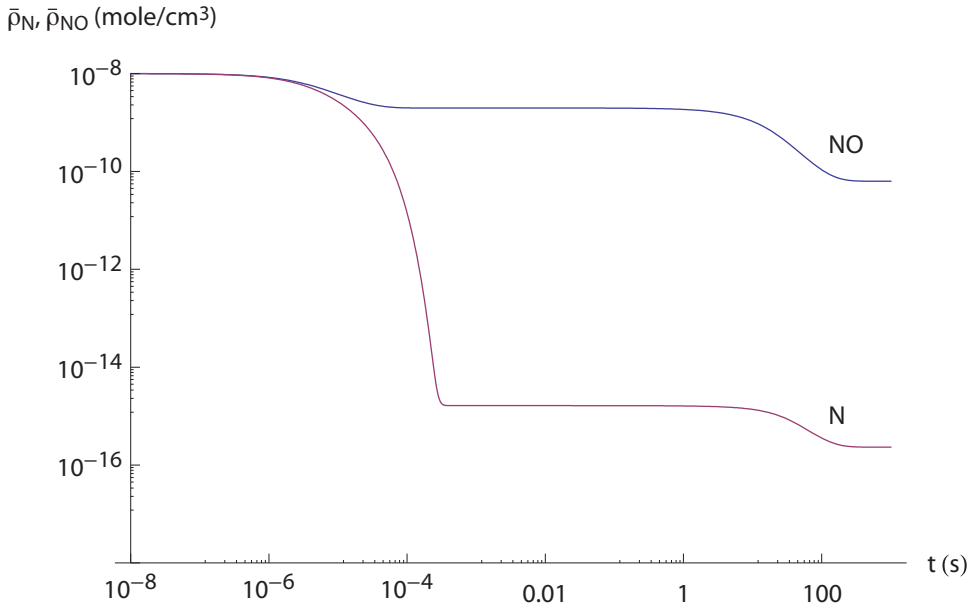

Figure 7.11: $\overline{\rho}_{NO}$ and $\overline{\rho}_N$ versus time for Zel'dovich mechanism at $T = 1500\ K$, $P = 6.2355 \times 10^3\ dyne/cm^2$.

Interestingly, by decreasing the initial pressure by a factor of 10^2, we increased the initial time scales by a complementary factor of 10^2; moreover, we did not alter the stiffness.

At equilibrium, we find

$$\lim_{t\to\infty} \overline{\rho}_{NO} = 4.6 \times 10^{-11}\ \frac{mole}{cm^3}, \tag{7.251}$$

$$\lim_{t\to\infty} \overline{\rho}_{N} = 4.2 \times 10^{-16}\ \frac{mole}{cm^3}, \tag{7.252}$$

$$\tag{7.253}$$

and

$$\tau_1 = 7.86 \times 10^{-5}\ s, \tag{7.254}$$

$$\tau_2 = 3.02 \times 10^{1}\ s. \tag{7.255}$$

By decreasing the initial pressure by a factor of 10^2, we decreased the equilibrium concentrations by a factor of 10^2 and increased the time scales by a factor of 10^2, leaving the stiffness ratio unchanged.

In summary, we find the effect of lowering the initial concentrations significantly while leaving temperature constant

- lowers the pressure significantly, proportionally slowing down the collision time, as well as the fastest and slowest time scales, and
- does not affect the stiffness of the system.

7.1.2.2.3 Stiffness and numerics The issue of how to simulate stiff systems of ordinary differential equations, such as presented by our Zel'dovich mechanism, is challenging. Here a brief summary of some of the issues will be presented. The interested reader should consult the numerical literature for a full discussion. See for example the excellent text of Iserles.[10]

We have seen throughout this section that there are two time scales at work, and they are often disparate. The species evolution is generally characterized by an initial fast transient, followed by a long plateau, then a final relaxation to equilibrium. We noted from the phase plane of Fig. 7.9 that the final relaxation to equilibrium (shown along the green line labeled "SIM") is an attracting manifold for a wide variety of initial conditions. The relaxation onto the SIM is fast, and the motion on the SIM to equilibrium is relatively slow.

Use of common numerical techniques can often mask or obscure the actual dynamics. Numerical methods to solve systems of ordinary differential equations can be broadly categorized as *explicit* or *implicit*. We give a brief synopsis of each class of method. We cast each as a method to solve a system of the form

$$\frac{d\overline{\boldsymbol{\rho}}}{dt} = \mathbf{f}(\overline{\boldsymbol{\rho}}). \tag{7.256}$$

- *Explicit:* The simplest of these, the forward Euler method, discretizes Eq. (7.256) as follows:

$$\frac{\overline{\boldsymbol{\rho}}_{n+1} - \overline{\boldsymbol{\rho}}_n}{\Delta t} = \mathbf{f}(\overline{\boldsymbol{\rho}}_n), \tag{7.257}$$

  so that

$$\overline{\boldsymbol{\rho}}_{n+1} = \overline{\boldsymbol{\rho}}_n + \Delta t\ \mathbf{f}(\overline{\boldsymbol{\rho}}_n). \tag{7.258}$$

  Explicit methods are summarized as

  - easy to program, since Eq. (7.258) can be solved explicitly to predict the new value $\overline{\boldsymbol{\rho}}_{n+1}$ in terms of the old values at step n.
  - need to have $\Delta t < \tau_{fastest}$ in order to remain numerically stable,
  - able to capture all physics and all time scales at great computational expense for stiff problems,
  - requiring much computational effort for little payoff in the SIM region of the phase plane, and thus
  - inefficient for some portions of stiff calculations.

- *Implicit:* The simplest of these methods, the backward Euler method, discretizes Eq. (7.256) as follows:

$$\frac{\overline{\boldsymbol{\rho}}_{n+1} - \overline{\boldsymbol{\rho}}_n}{\Delta t} = \mathbf{f}(\overline{\boldsymbol{\rho}}_{n+1}), \tag{7.259}$$

[10] A. Iserles, 2008, *A First Course in the Numerical Analysis of Differential Equations*, Cambridge University Press, Cambridge, UK.

so that

$$\overline{\boldsymbol{\rho}}_{n+1} = \overline{\boldsymbol{\rho}}_n + \Delta t \ \mathbf{f}(\overline{\boldsymbol{\rho}}_{n+1}). \tag{7.260}$$

Implicit methods are summarized as

- more difficult to program since a non-linear set of algebraic equations, Eq. (7.260), must be solved at every time step with no guarantee of solution,
- requiring potentially significant computational time to advance each time step,
- capable of using very large time steps and remaining numerically stable,
- suspect to missing physics that occur on small time scales $\tau < \Delta t$,
- in general better performers than explicit methods.

A wide variety of software tools exist to solve systems of ordinary differential equations. Most of them use more sophisticated techniques than simple forward and backward Euler methods. One of the most powerful techniques is the use of *error control*. Here the user specifies how far in time to advance and the error that is able to be tolerated. The algorithm, which is complicated, selects then internal time steps, for either explicit or implicit methods, to achieve a solution within the error tolerance at the specified output time. A well known public domain algorithm with error control is provided by `lsode.f`, which can be found in the `netlib` repository.[11]

Let us exercise the Zel'dovich mechanism under the conditions simulated in Fig. 7.11, $T = 1500\ K$, $P = 6.2355 \times 10^3\ dyne/cm^2$. Recall in this case the fastest time scale near equilibrium is $\tau_1 = 7.86 \times 10^{-5}\ s \sim 10^{-4}\ s$ at the initial state, and the slowest time scale is $\tau = 3.02 \times 10^1\ s$ at the final state. Let us solve for these conditions using `dlsode.f`, which uses internal time stepping for error control, in both an explicit and implicit mode. We specify a variety of values of Δt and report typical values of number of internal time steps selected by `dlsode.f`, and the corresponding effective time step Δt_{eff} used for the problem, for both explicit and implicit methods, as reported in Table 7.3.

Obviously if output is requested using $\Delta t > 10^{-4}\ s$, the early time dynamics near $t \sim 10^{-4}\ s$ will be missed. For physically stable systems, codes such as `dlsode.f` will still provide a correct solution at the later times. For physically unstable systems, such as might occur in turbulent flames, it is not clear that one can use large time steps and expect to have fidelity to the underlying equations. The reason is the physical instabilities may evolve on the same time scale as the fine scales which are overlooked by large Δt.

7.2 Adiabatic, isochoric kinetics

It is more practical to allow for temperature variation within a combustor. The best model for this is adiabatic kinetics. Here we will restrict our attention to isochoric problems.

[11] Hindmarsh, A. C., 1983,"ODEPACK, a Systematized Collection of ODE Solvers," *Scientific Computing*, edited by R. S. Stepleman, et al., North-Holland, Amsterdam, pp. 55-64. Source code at `http://www.netlib.org/alliant/ode/prog/lsode.f`

	Explicit	Explicit	Implicit	Implicit
$\Delta t\ (s)$	$N_{internal}$	$\Delta t_{eff}\ (s)$	$N_{internal}$	$\Delta t_{eff}\ (s)$
10^2	10^6	10^{-4}	10^0	10^2
10^1	10^5	10^{-4}	10^0	10^1
10^0	10^4	10^{-4}	10^0	10^0
10^{-1}	10^3	10^{-4}	10^0	10^{-1}
10^{-2}	10^2	10^{-4}	10^0	10^{-2}
10^{-3}	10^1	10^{-4}	10^0	10^{-3}
10^{-4}	10^0	10^{-4}	10^0	10^{-4}
10^{-5}	10^0	10^{-5}	10^0	10^{-5}
10^{-6}	10^0	10^{-6}	10^0	10^{-6}

Table 7.3: Results from computing Zel'dovich NO production using implicit and explicit methods with error control in `dlsode.f`.

7.2.1 Thermal explosion theory

There is a simple description known as *thermal explosion theory* which provides a good explanation for how initially slow exothermic reaction induces a sudden temperature rise accompanied by a final relaxation to equilibrium.

Let us consider a simple isomerization reaction in a closed volume

$$A \leftrightharpoons B. \tag{7.261}$$

Let us take A and B to both be calorically perfect ideal gases with identical molecular masses $M_A = M_B = M$ and identical specific heats, $\overline{c}_{vA} = \overline{c}_{vB} = c_v$; $\overline{c}_{PA} = \overline{c}_{PB} = \overline{c}_P$. We can consider A and B to be isomers of an identical molecular species. So we have $N = 2$ species reacting in $J = 1$ reactions. The number of elements L here is irrelevant.

7.2.1.1 One-step reversible kinetics

Let us insist our reaction process be isochoric and adiabatic, and commence with only A present. The reaction kinetics with $\beta = 0$ are

$$\frac{d\overline{\rho}_A}{dt} = -\underbrace{\underbrace{a \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{=k}\left(\overline{\rho}_A - \frac{1}{K_c}\overline{\rho}_B\right)}_{=r}, \tag{7.262}$$

$$\frac{d\overline{\rho}_B}{dt} = \underbrace{\underbrace{a \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)}_{=k}\left(\overline{\rho}_A - \frac{1}{K_c}\overline{\rho}_B\right)}_{=r}, \tag{7.263}$$

$$\overline{\rho}_A(0) = \widehat{\overline{\rho}}_A, \tag{7.264}$$

$$\overline{\rho}_B(0) = 0. \tag{7.265}$$

For our alternate compact linear algebra based form, we note that

$$r = a \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)\left(\overline{\rho}_A - \frac{1}{K_c}\overline{\rho}_B\right), \tag{7.266}$$

and that

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_A \\ \overline{\rho}_B\end{pmatrix} = \begin{pmatrix}-1 \\ 1\end{pmatrix}(r). \tag{7.267}$$

Performing the decomposition yields

$$\frac{d}{dt}\begin{pmatrix}\overline{\rho}_A \\ \overline{\rho}_A + \overline{\rho}_B\end{pmatrix} = \begin{pmatrix}-1 \\ 0\end{pmatrix}(r). \tag{7.268}$$

Expanded, this is

$$\begin{pmatrix}1 & 0 \\ 1 & 1\end{pmatrix}\frac{d}{dt}\begin{pmatrix}\overline{\rho}_A \\ \overline{\rho}_B\end{pmatrix} = \begin{pmatrix}-1 \\ 0\end{pmatrix}(r). \tag{7.269}$$

Combining Eqs. (7.262-7.263) and integrating yields

$$\begin{aligned}\frac{d}{dt}(\overline{\rho}_A + \overline{\rho}_B) &= 0, &(7.270)\\ \overline{\rho}_A + \overline{\rho}_B &= \widehat{\overline{\rho}}_A, &(7.271)\\ \overline{\rho}_B &= \widehat{\overline{\rho}}_A - \overline{\rho}_A. &(7.272)\end{aligned}$$

Thus, Eq. (7.262) reduces to

$$\frac{d\overline{\rho}_A}{dt} = -a \exp\left(\frac{-\overline{E}}{\overline{R}T}\right)\left(\overline{\rho}_A - \frac{1}{K_c}\left(\widehat{\overline{\rho}}_A - \overline{\rho}_A\right)\right). \tag{7.273}$$

Scaling, Eq. (7.273) can be rewritten as

$$\frac{d}{d(at)}\left(\frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}\right) = -\exp\left(-\frac{\overline{E}}{\overline{R}T_o}\frac{1}{T/T_o}\right)\left(\frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A} - \frac{1}{K_c}\left(1 - \frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}\right)\right). \tag{7.274}$$

7.2.1.2 First law of thermodynamics

Recall the first law of thermodynamics and neglecting potential and kinetic energy changes:

$$\frac{dU}{dt} = \dot{Q} - \dot{W}. \tag{7.275}$$

Here U is the total internal energy. Because we insist the problem is adiabatic $\dot{Q} = 0$. Because we insist the problem is isochoric, there is no work done, so $\dot{W} = 0$. Thus we have

$$\frac{dU}{dt} = 0. \tag{7.276}$$

Thus, we find

$$U = U_o. \tag{7.277}$$

Recall the total internal energy for a mixture of two calorically perfect ideal gases is

$$\begin{aligned}
U &= n_A\overline{u}_A + n_B\overline{u}_B, && (7.278)\\
&= V\left(\frac{n_A}{V}\overline{u}_A + \frac{n_B}{V}\overline{u}_B\right), && (7.279)\\
&= V\left(\overline{\rho}_A\overline{u}_A + \overline{\rho}_B\overline{u}_B\right), && (7.280)\\
&= V\left(\overline{\rho}_A\left(\overline{h}_A - \frac{P_A}{\overline{\rho}_A}\right) + \overline{\rho}_B\left(\overline{h}_B - \frac{P_B}{\overline{\rho}_B}\right)\right), && (7.281)\\
&= V\left(\overline{\rho}_A\left(\overline{h}_A - \overline{R}T\right) + \overline{\rho}_B\left(\overline{h}_B - \overline{R}T\right)\right), && (7.282)\\
&= V\left(\overline{\rho}_A\left(\overline{c}_P(T-T_o) + \overline{h}^o_{T_o,A} - \overline{R}T\right) + \overline{\rho}_B\left(\overline{c}_P(T-T_o) + \overline{h}^o_{T_o,B} - \overline{R}T\right)\right), && (7.283)\\
&= V\left((\overline{\rho}_A + \overline{\rho}_B)(\overline{c}_P(T-T_o) - \overline{R}T) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), && (7.284)\\
&= V\left((\overline{\rho}_A + \overline{\rho}_B)((\overline{c}_P - \overline{R})T - \overline{c}_P T_o) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), && (7.285)\\
&= V\left((\overline{\rho}_A + \overline{\rho}_B)((\overline{c}_P - \overline{R})T - (\overline{c}_P - \overline{R} + \overline{R})T_o) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), && (7.286)\\
&= V\left((\overline{\rho}_A + \overline{\rho}_B)(\overline{c}_v T - (\overline{c}_v + \overline{R})T_o) + \overline{\rho}_A\overline{h}^o_{T_o,A} + \overline{\rho}_B\overline{h}^o_{T_o,B}\right), && (7.287)\\
&= V\left((\overline{\rho}_A + \overline{\rho}_B)\overline{c}_v(T-T_o) + \overline{\rho}_A(\overline{h}^o_{T_o,A} - \overline{R}T_o) + \overline{\rho}_B(\overline{h}^o_{T_o,B} - \overline{R}T_o)\right), && (7.288)\\
&= V\left((\overline{\rho}_A + \overline{\rho}_B)\overline{c}_v(T-T_o) + \overline{\rho}_A\overline{u}^o_{T_o,A} + \overline{\rho}_B\overline{u}^o_{T_o,B}\right). && (7.289)
\end{aligned}$$

Now at the initial state, we have $T = T_o$, so

$$U_o = V\left(\widehat{\overline{\rho}}_A\overline{u}^o_{T_o,A} + \widehat{\overline{\rho}}_B\overline{u}^o_{T_o,B}\right). \tag{7.290}$$

So, we can say our caloric equation of state is

$$\begin{aligned}
U - U_o &= V\left((\overline{\rho}_A + \overline{\rho}_B)\overline{c}_v(T-T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{u}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{u}^o_{T_o,B}\right), && (7.291)\\
&= V\left((\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B)\overline{c}_v(T-T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{u}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{u}^o_{T_o,B}\right). && (7.292)
\end{aligned}$$

As an aside, on a molar basis, we scale Eq. (7.292) to get

$$\overline{u} - \overline{u}_o = \overline{c}_v(T-T_o) + (y_A - y_{Ao})\overline{u}^o_{T_o,A} + (y_B - y_{Bo})\overline{u}^o_{T_o,B}. \tag{7.293}$$

And because we have assumed the molecular masses are the same, $M_A = M_B$, the mole fractions are the mass fractions, and we can write on a mass basis

$$u - u_o = c_v(T-T_o) + (c_A - c_{Ao})u^o_{T_o,A} + (c_B - c_{Bo})u^o_{T_o,B}. \tag{7.294}$$

Returning to Eq. (7.292), our energy conservation relation, Eq. (7.277), becomes

$$0 = V\left((\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B)\overline{c}_v(T - T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{u}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{u}^o_{T_o,B}\right). \quad (7.295)$$

Now we solve for T

$$0 = (\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B)\overline{c}_v(T - T_o) + (\overline{\rho}_A - \widehat{\overline{\rho}}_A)\overline{u}^o_{T_o,A} + (\overline{\rho}_B - \widehat{\overline{\rho}}_B)\overline{u}^o_{T_o,B}, \quad (7.296)$$

$$0 = \overline{c}_v(T - T_o) + \frac{\overline{\rho}_A - \widehat{\overline{\rho}}_A}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\overline{u}^o_{T_o,A} + \frac{\overline{\rho}_B - \widehat{\overline{\rho}}_B}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\overline{u}^o_{T_o,B}, \quad (7.297)$$

$$T = T_o + \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\frac{\overline{u}^o_{T_o,A}}{\overline{c}_v} + \frac{\widehat{\overline{\rho}}_B - \overline{\rho}_B}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}\frac{\overline{u}^o_{T_o,B}}{\overline{c}_v}. \quad (7.298)$$

Now we impose our assumption that $\widehat{\overline{\rho}}_B = 0$, giving also $\overline{\rho}_B = \widehat{\overline{\rho}}_A - \overline{\rho}_A$,

$$T = T_o + \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A}\frac{\overline{u}^o_{T_o,A}}{\overline{c}_v} - \frac{\overline{\rho}_B}{\widehat{\overline{\rho}}_A}\frac{\overline{u}^o_{T_o,B}}{\overline{c}_v}, \quad (7.299)$$

$$= T_o + \frac{\widehat{\overline{\rho}}_A - \overline{\rho}_A}{\widehat{\overline{\rho}}_A}\frac{\overline{u}^o_{T_o,A} - \overline{u}^o_{T_o,B}}{\overline{c}_v}. \quad (7.300)$$

In summary, realizing that $\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B} = \overline{u}^o_{T_o,A} - \overline{u}^o_{T_o,B}$ we can write T as a function of $\overline{\rho}_A$:

$$T = T_o + \frac{(\widehat{\overline{\rho}}_A - \overline{\rho}_A)}{\widehat{\overline{\rho}}_A\overline{c}_v}(\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}). \quad (7.301)$$

We see then that if $\overline{h}^o_{T_o,A} > \overline{h}^o_{T_o,B}$, that as $\overline{\rho}_A$ decreases from its initial value of $\widehat{\overline{\rho}}_A$ that T will increase. We can scale Eq. (7.301) to form

$$\left(\frac{T}{T_o}\right) = 1 + \left(1 - \frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}\right)\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}{\overline{c}_v T_o}\right). \quad (7.302)$$

We also note that our caloric state equation, Eq. (7.293) can, for $y_{Ao} = 1$, $y_{Bo} = 0$ as

$$\overline{u} - \overline{u}_o = \overline{c}_v(T - T_o) + (y_A - 1)\overline{u}^o_{T_o,A} + y_B\overline{u}^o_{T_o,B}, \quad (7.303)$$

$$= \overline{c}_v(T - T_o) + ((1 - y_B) - 1)\overline{u}^o_{T_o,A} + y_B\overline{u}^o_{T_o,B}, \quad (7.304)$$

$$= \overline{c}_v(T - T_o) - y_B(\overline{u}^o_{T_o,A} - \overline{u}^o_{T_o,B}). \quad (7.305)$$

Similarly, on a mass basis, we can say,

$$u - u_o = c_v(T - T_o) - c_B(u^o_{T_o,A} - u^o_{T_o,B}). \quad (7.306)$$

For this problem, we also have

$$K_c = \exp\left(\frac{-\Delta G^o}{\overline{R}T}\right), \quad (7.307)$$

with

$$\begin{aligned}
\Delta G^o &= \overline{g}^o_B - \overline{g}^o_A, && (7.308)\\
&= \overline{h}^o_B - T\overline{s}^o_B - (\overline{h}^o_A - T\overline{s}^o_A), && (7.309)\\
&= (\overline{h}^o_B - \overline{h}^o_A) - T(\overline{s}^o_B - \overline{s}^o_A), && (7.310)\\
&= (\overline{h}^o_{T_o,B} - \overline{h}^o_{T_o,A}) - T(\overline{s}^o_{T_o,B} - \overline{s}^o_{T_o,A}). && (7.311)
\end{aligned}$$

So

$$\begin{aligned}
K_c &= \exp\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B} - T(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{R}T}\right), && (7.312)\\
&= \exp\left(\frac{\overline{c}_v T_o}{\overline{R}T}\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B} - T(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{c}_v T_o}\right)\right), && (7.313)\\
&= \exp\left(\frac{1}{k-1}\frac{1}{\frac{T}{T_o}}\left(\frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}{\overline{c}_v T_o} - \frac{T}{T_o}\frac{(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{c}_v}\right)\right). && (7.314)
\end{aligned}$$

Here we have used the definition of the ratio of specific heats, $k = \overline{c}_P/\overline{c}_v$ along with $\overline{R} = \overline{c}_P - \overline{c}_v$. So we can solve Eq. (7.273) by first using Eq. (7.314) to eliminate K_c and then Eq. (7.301) to eliminate T.

7.2.1.3 Dimensionless form

Let us try writing dimensionless variables so that our system can be written in a compact dimensionless form. First lets take dimensionless time τ to be

$$\tau = at. \tag{7.315}$$

Let us take dimensionless species concentration to be z with

$$z = \frac{\overline{\rho}_A}{\widehat{\overline{\rho}}_A}. \tag{7.316}$$

Let us take dimensionless temperature to be θ with

$$\theta = \frac{T}{T_o}. \tag{7.317}$$

Let us take dimensionless heat release to be q with

$$q = \frac{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}{\overline{c}_v T_o}. \tag{7.318}$$

Let us take dimensionless activation energy to be Θ with

$$\Theta = \frac{\overline{E}}{\overline{R}T_o}. \tag{7.319}$$

And let us take the dimensionless entropy change to be σ with

$$\sigma = \frac{(\overline{s}^o_{T_o,A} - \overline{s}^o_{T_o,B})}{\overline{c}_v}. \tag{7.320}$$

So our equations become

$$\frac{dz}{d\tau} = -\exp\left(-\frac{\Theta}{\theta}\right)\left(z - \frac{1}{K_c}(1-z)\right), \tag{7.321}$$

$$\theta = 1 + (1-z)q, \tag{7.322}$$

$$K_c = \exp\left(\frac{1}{k-1}\frac{1}{\theta}\left(q - \theta\sigma\right)\right). \tag{7.323}$$

It is more common to consider the products. Let us define for general problems

$$\lambda = \frac{\overline{\rho}_B}{\overline{\rho}_A + \overline{\rho}_B} = \frac{\overline{\rho}_B}{\widehat{\overline{\rho}}_A + \widehat{\overline{\rho}}_B}. \tag{7.324}$$

Thus λ is the mass fraction of product. For our problem, $\widehat{\overline{\rho}}_B = 0$ so

$$\lambda = \frac{\overline{\rho}_B}{\widehat{\overline{\rho}}_A} = \frac{\widehat{\overline{\rho}_A} - \overline{\rho}_A}{\widehat{\overline{\rho}}_A}. \tag{7.325}$$

Thus,

$$\lambda = 1 - z. \tag{7.326}$$

We can think of λ as a reaction progress variable as well. When $\lambda = 0$, we have $\tau = 0$, and the reaction has not begun. Thus, we get

$$\frac{d\lambda}{d\tau} = \exp\left(-\frac{\Theta}{\theta}\right)\left((1-\lambda) - \frac{1}{K_c}\lambda\right), \tag{7.327}$$

$$\theta = 1 + q\lambda, \tag{7.328}$$

$$K_c = \exp\left(\frac{1}{k-1}\frac{1}{\theta}\left(q - \theta\sigma\right)\right). \tag{7.329}$$

7.2.1.4 Example calculation

Let us choose some values for the dimensionless parameters:

$$\Theta = 20, \quad \sigma = 0, \quad q = 10, \quad k = \frac{7}{5}. \tag{7.330}$$

With these choices, our kinetics equations reduce to

$$\frac{d\lambda}{d\tau} = \exp\left(\frac{-20}{1+10\lambda}\right)\left((1-\lambda) - \lambda\exp\left(\frac{-25}{1+10\lambda}\right)\right), \qquad \lambda(0) = 0. \tag{7.331}$$

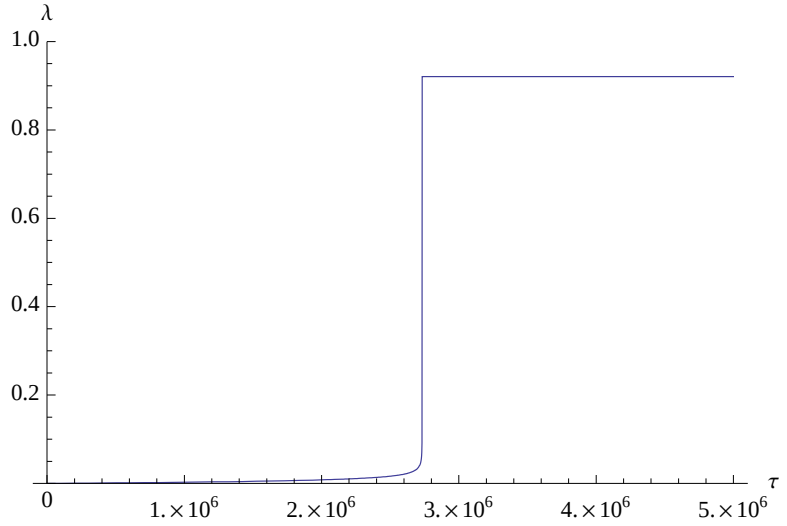

Figure 7.12: Dimensionless plot of reaction product concentration λ versus time τ for adiabatic isochoric combustion with simple reversible kinetics.

The right side of Eq. (7.331) is at equilibrium for values of λ which drive it to zero. Numerical root finding methods show this to occur at $\lambda \sim 0.920539$. Near this root, Taylor series expansion shows the dynamics are approximated by

$$\frac{d}{d\tau}(\lambda - 0.920539) = -0.17993(\lambda - 0.920539) + \dots \tag{7.332}$$

Thus the local behavior near equilibrium is given by

$$\lambda = 0.920539 + C \exp\left(-0.17993\ \tau\right). \tag{7.333}$$

Here C is some arbitrary constant. Clearly the equilibrium is stable, with a time constant of $1/0.17993 = 5.55773$.

Numerical solution shows the full behavior of the dimensionless species concentration $\lambda(\tau)$; see Figure 7.12. Clearly the product concentration λ is small for some long period of time. At a critical time near $\tau = 2.7 \times 10^6$, there is a so-called thermal explosion with a rapid increase in λ. *Note that the estimate of the time constant near equilibrium is orders of magnitude less than the explosion time,* $5.55773 << 2.7 \times 10^6$. *Thus, linear analysis here is a poor tool to estimate an important physical quantity, the ignition time.* Once the ignition period is over, there is a rapid equilibration to the final state. The dimensionless temperature plot is shown in Figure 7.13. The temperature plot is similar in behavior to the species concentration plot. At early time, the temperature is cool. At a critical time, the thermal explosion time, the temperature rapidly rises. This rapid rise, coupled with the exponential sensitivity of reaction rate to temperature, accelerates the formation of product. This process continues until the reverse reaction is activated to the extent it prevents further creation of product.

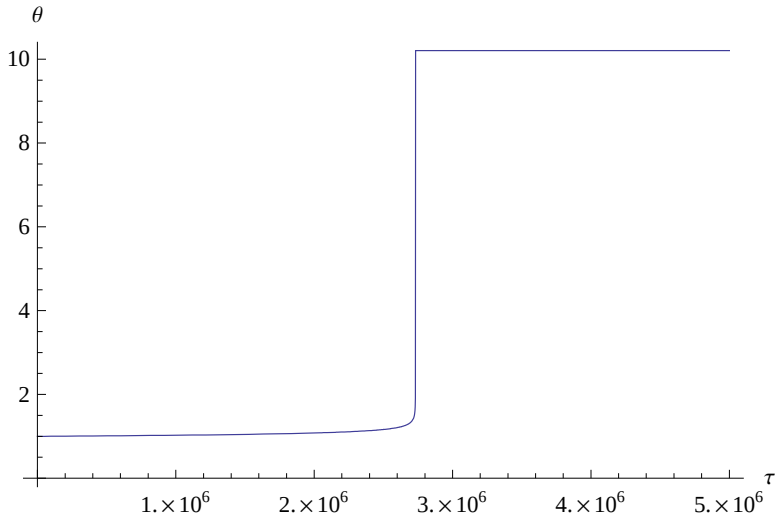

Figure 7.13: Dimensionless plot of temperature θ versus time τ for adiabatic, isochoric combustion with simple reversible kinetics.

7.2.1.5 High activation energy asymptotics

Let us see if we can get an *analytic* prediction of the thermal explosion time, $\tau \sim 2.7 \times 10^6$. Such a prediction would be valuable to see how long a slowing reacting material might take to ignite. Our analysis is similar to that given by Buckmaster and Ludford in their Chapter 1.[12]

For convenience let us restrict ourselves to $\sigma = 0$. In this limit, Eqs. (7.327-7.329) reduce to

$$\frac{d\lambda}{d\tau} = \exp\left(-\frac{\Theta}{1+q\lambda}\right)\left((1-\lambda) - \lambda \exp\left(\frac{-q}{(k-1)(1+q\lambda)}\right)\right), \tag{7.334}$$

with $\lambda(0) = 0$. The key trouble in getting an analytic solution to Eq. (7.334) is the presence of λ in the denominator of an exponential term. We need to find a way to move it to the numerator. Asymptotic methods provide one such way.

Now we recall for early time $\lambda << 1$. Let us assume λ takes the form

$$\lambda = \epsilon\lambda_1 + \epsilon^2\lambda_2 + \epsilon^3\lambda_3 + \ldots \tag{7.335}$$

Here we will assume $0 < \epsilon << 1$ and that $\lambda_1(\tau) \sim \mathcal{O}(1)$, $\lambda_2(\tau) \sim \mathcal{O}(1)$, $\ldots$, and will define ϵ in terms of physical parameters shortly. Now with this assumption, we have

$$\frac{1}{1+q\lambda} = \frac{1}{1+\epsilon q\lambda_1 + \epsilon^2 q\lambda_2 + \epsilon^3 q\lambda_3 + \ldots}. \tag{7.336}$$

[12] J. D. Buckmaster and G. S. S. Ludford, 1983, *Lectures on Mathematical Combustion*, SIAM, Philadelphia.

Long division of the term on the right side yields the approximation

$$\frac{1}{1+q\lambda} = = 1 - \epsilon q\lambda_1 + \epsilon^2(q^2\lambda_1^2 - q\lambda_2) + \dots, \tag{7.337}$$

$$= 1 - \epsilon q\lambda_1 + \mathcal{O}(\epsilon^2). \tag{7.338}$$

So

$$\exp\left(-\frac{\Theta}{1+q\lambda}\right) \sim \exp\left(-\Theta(1 - \epsilon q\lambda_1 + \mathcal{O}(\epsilon^2))\right), \tag{7.339}$$

$$\sim e^{-\Theta}\exp\left(\epsilon q\Theta\lambda_1 + \mathcal{O}(\epsilon^2)\right), \tag{7.340}$$

We have moved λ from the denominator to the numerator of the most important exponential term.

Now, let us take the *limit of high activation energy* by defining ϵ to be

$$\epsilon \equiv \frac{1}{\Theta}. \tag{7.341}$$

Let us let the assume the remaining parameters, q and k are both $\mathcal{O}(1)$ constants. When Θ is large, ϵ will be small. With this definition, Eq. (7.340) becomes

$$\exp\left(-\frac{\Theta}{1+q\lambda}\right) \sim e^{-1/\epsilon}\exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right). \tag{7.342}$$

With these assumptions and approximations, Eq. (7.334) can be written as

$$\frac{d}{d\tau}(\epsilon\lambda_1 + \dots) = e^{-1/\epsilon}\exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right) \times \left((1 - \epsilon\lambda_1 - \dots) - (\epsilon\lambda_1 + \dots)\exp\left(\frac{-q}{(k-1)(1+q\epsilon\lambda_1 + \dots)}\right)\right). \tag{7.343}$$

Now let us rescale time via

$$\tau_* = \frac{1}{\epsilon}e^{-1/\epsilon}\tau. \tag{7.344}$$

With this transformation, the chain rule shows how derivatives transform:

$$\frac{d}{d\tau} = \frac{d\tau_*}{d\tau}\frac{d}{d\tau_*} = \frac{1}{\epsilon e^{1/\epsilon}}\frac{d}{d\tau_*}. \tag{7.345}$$

With this transformation, Eq. (7.343) becomes

$$\frac{1}{\epsilon e^{1/\epsilon}}\frac{d}{d\tau_*}(\epsilon\lambda_1 + \dots) = \frac{1}{e^{1/\epsilon}}\exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right) \times \left((1 - \epsilon\lambda_1 - \dots) - (\epsilon\lambda_1 + \dots)\exp\left(\frac{-q}{(k-1)(1+q\epsilon\lambda_1 + \dots)}\right)\right). \tag{7.346}$$

This simplifies to

$$\frac{d}{d\tau_*}\left(\lambda_1 + \dots\right) = \exp\left(q\lambda_1 + \mathcal{O}(\epsilon^2)\right) \times \left(\left(1 - \epsilon\lambda_1 - \dots\right) - \left(\epsilon\lambda_1 + \dots\right)\exp\left(\frac{-q}{(k-1)(1+q\epsilon\lambda_1 + \dots)}\right)\right). \tag{7.347}$$

Retaining only $\mathcal{O}(1)$ terms in Eq. (7.347), we get

$$\frac{d\lambda_1}{d\tau_*} = \exp\left(q\lambda_1\right). \tag{7.348}$$

This is supplemented by the initial condition $\lambda_1(0) = 0$. Separating variables and solving, we get

$$\exp(-q\lambda_1)d\lambda_1 = d\tau_*, \tag{7.349}$$

$$-\frac{1}{q}\exp(-q\lambda_1) = \tau_* + C. \tag{7.350}$$

Applying the initial condition gives

$$-\frac{1}{q}\exp(-q(0)) = C, \tag{7.351}$$

$$-\frac{1}{q} = C. \tag{7.352}$$

So

$$-\frac{1}{q}\exp(-q\lambda_1) = \tau_* - \frac{1}{q}, \tag{7.353}$$

$$\exp(-q\lambda_1) = -q\tau_* + 1, \tag{7.354}$$

$$\exp(-q\lambda_1) = -q\left(\tau_* - \frac{1}{q}\right), \tag{7.355}$$

$$-q\lambda_1 = \ln\left(-q\left(\tau_* - \frac{1}{q}\right)\right), \tag{7.356}$$

$$\lambda_1 = -\frac{1}{q}\ln\left(-q\left(\tau_* - \frac{1}{q}\right)\right). \tag{7.357}$$

For $q = 10$, a plot of $\lambda_1(\tau_*)$ is shown in Fig. 7.14. We note at a finite τ_* that λ_1 begins to exhibit unbounded growth. In fact, it is obvious from Eq. (7.348) that as

$$\tau_* \to \frac{1}{q},$$

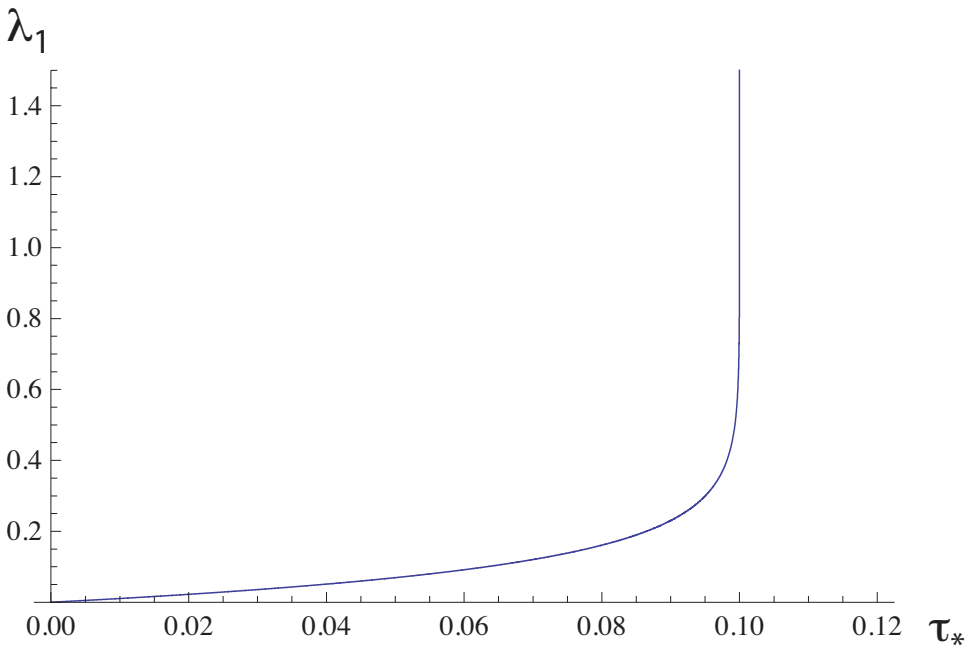

Figure 7.14: λ_1 versus τ_* for ignition problem.

that

$$\lambda_1 \to \infty.$$

That is there exists a finite time for which λ_1 violates the assumptions of our asymptotic theory which assumes $\lambda_1 = \mathcal{O}(1)$. We associate this time with the ignition time, τ_{*i}:

$$\tau_{*i} = \frac{1}{q}. \tag{7.358}$$

Let us return this to more primitive variables:

$$\frac{1}{\epsilon} \exp\left(\frac{-1}{\epsilon}\right) \tau_i = \frac{1}{q}, \tag{7.359}$$

$$\tau_i = \frac{\epsilon \exp\left(\frac{1}{\epsilon}\right)}{q}, \tag{7.360}$$

$$\tau_i = \frac{\exp \Theta}{\Theta q}. \tag{7.361}$$

For our system with $\Theta = 20$ and $q = 10$, we estimate the dimensionless ignition time as

$$\tau_i = \frac{\exp 20}{(20)(10)} = 2.42583 \times 10^6. \tag{7.362}$$

This is a surprisingly good estimate, given the complexity of the problem. Recall the numerical solution showed ignition for $\tau \sim 2.7 \times 10^6$.

In terms of dimensional time, ignition time prediction becomes

$$t_i = \frac{\exp\Theta}{a\Theta q}, \tag{7.363}$$

$$= \frac{1}{a}\left(\frac{\overline{R}T_o}{\overline{E}}\right)\left(\frac{\overline{c}_v T_o}{\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B}}\right)\exp\left(\frac{\overline{E}}{\overline{R}T_o}\right). \tag{7.364}$$

Note the ignition is suppressed if the ignition time is lengthened, which happens when

- he activation energy $\overline{E}$ is increased, since the exponential sensitivity is stronger than the algebraic sensitivity,
- the energy of combustion $(\overline{h}^o_{T_o,A} - \overline{h}^o_{T_o,B})$ is decreased because it takes longer to react to drive the temperature to a critical value to induce ignition, and
- the collision frequency factor a is decreased, which suppresses reaction.

7.2.2 Detailed $H_2 - O_2 - N_2$ kinetics

Here is an example which uses multiple reactions for an adiabatic isothermal system is given. Consider the full time-dependency of a problem similar to the thermal explosion problem just considered.

A closed, fixed, adiabatic volume, $V = 0.3061251\ cm^3$, contains at $t = 0\ s$ a stoichiometric hydrogen-air mixture of $2 \times 10^{-5}\ mole$ of H_2, $1 \times 10^{-5}\ mole$ of O_2, and $3.76 \times 10^{-5}\ mole$ of N_2 at $P_o = 2.83230 \times 10^6\ Pa$ and $T_o = 1542.7\ K$.[13] Thus the initial molar concentrations are

$$\overline{\rho}_{H_2} = 6.533 \times 10^{-5}\ mole/cm^3,$$

$$\overline{\rho}_{O_2} = 3.267 \times 10^{-5}\ mole/cm^3,$$

$$\overline{\rho}_{H_2} = 1.228 \times 10^{-4}\ mole/cm^3.$$

The initial mass fractions are calculated via $c_i = M_i\overline{\rho}_i/\rho$. They are

$$c_{H_2} = 0.0285,$$

$$c_{O_2} = 0.226,$$

$$c_{N_2} = 0.745.$$

To avoid issues associated with numerical roundoff errors at very early time for species with very small compositions, the minor species were initialized at a small non-zero value near machine precision; each was assigned a value of $10^{-15}\ mole$. The minor species all have $\overline{\rho}_i = 1.803 \times 10^{-16}\ mole/cm^3$. They have correspondingly small initial mass fractions.

[13] This temperature and pressure correspond to that of the same ambient mixture of H_2, O_2 and N_2 which was shocked from $1.01325 \times 10^5\ Pa$, $298\ K$, to a value associated with a freely propagating detonation.

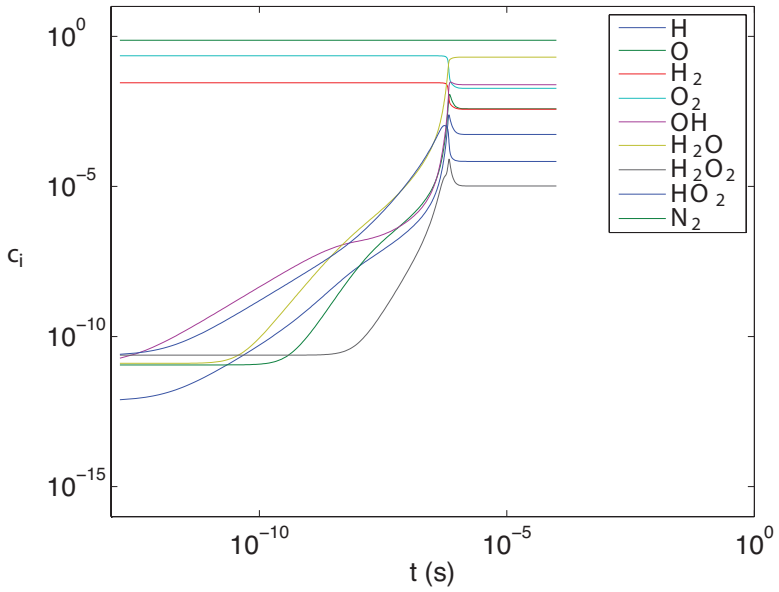

Figure 7.15: Plot of $c_{H_2}(t)$, $c_H(t)$, $c_O(t)$, $c_{O_2}(t)$, $c_{OH}(t)$, $c_{H_2O}(t)$, $c_{HO_2}(t)$, $c_{H_2O_2}(t)$, $c_{N_2}(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2+O_2+3.76N_2$ initially at $T_o = 1542.7\ K$, $P_o = 2.8323 \times 10^6\ Pa$.

We seek the reaction dynamics as the system proceeds from its initial state to its final state. We use the reversible detailed kinetics mechanism of Table 7.2. This problem requires a detailed numerical solution. Such a solution was performed by solving the appropriate equations for a mixture of nine interacting species: H_2, H, O, O_2, OH, H_2O, HO_2, H_2O_2, and N_2. The dynamics of the reaction process are reflected in Figs. 7.15-7.17.

At early time, $t < 10^{-7}\ s$, the pressure, temperature, and major reactant species concentrations (H_2, O_2, N_2) are nearly constant. However, the minor species, e.g. OH, HO_2, and the major product, H_2O, are undergoing very rapid growth, albeit with math fractions whose value remains small. In this period, the material is in what is known as the *induction period*.

After a certain critical mass of minor species has accumulated, exothermic recombination of these minor species to form the major product H_2O induces the temperature to rise, which accelerates further the reaction rates. This is manifested in a *thermal explosion*. A common definition of the end of the induction period is the *induction time*, $t = t_{ind}$, the time when dT/dt goes through a maximum. Here one finds

$$t_{ind} = 6.6 \times 10^{-7}\ s. \tag{7.365}$$

A close-up view of the species concentration profiles is given in Fig. 7.18.

At the end of the induction zone, there is a final relaxation to equilibrium. The equilib-

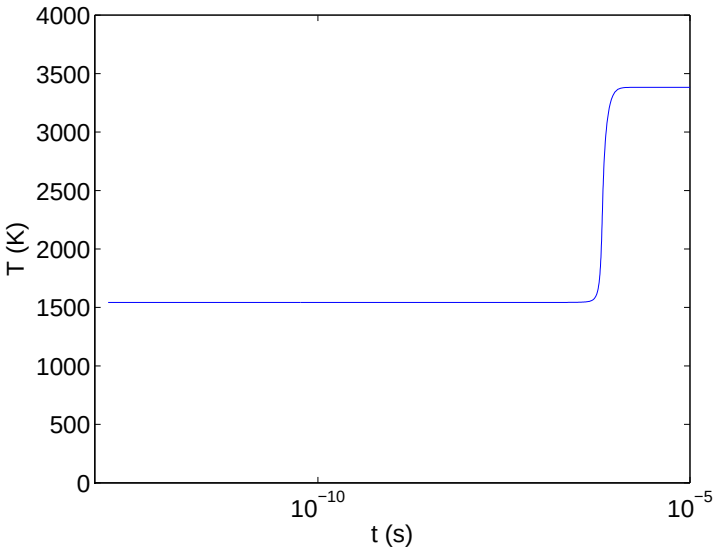

Figure 7.16: Plot of $T(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2$+O_2+$3.76N_2$ initially at $T_o = 1542.7\ K$, $P_o = 2.8323 \times 10^6\ Pa$.

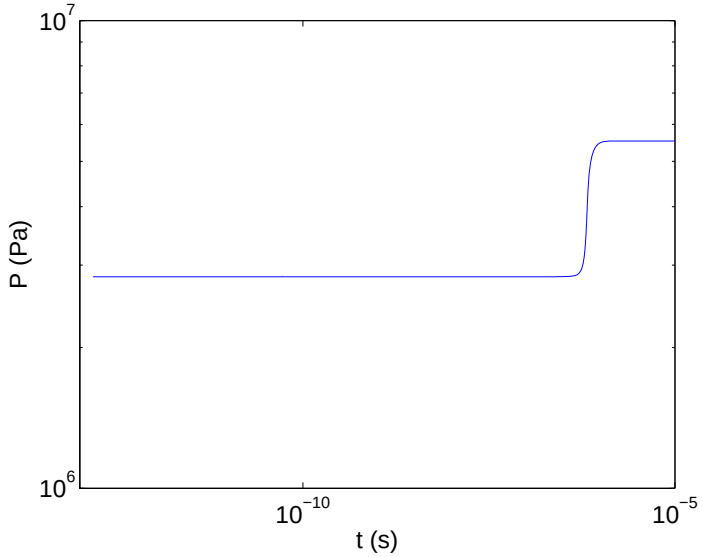

Figure 7.17: Plot of $P(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2 + O_2 + 3.76N_2$ initially at $T_o = 1542.7\ K$, $P_o = 2.8323 \times 10^6\ Pa$.

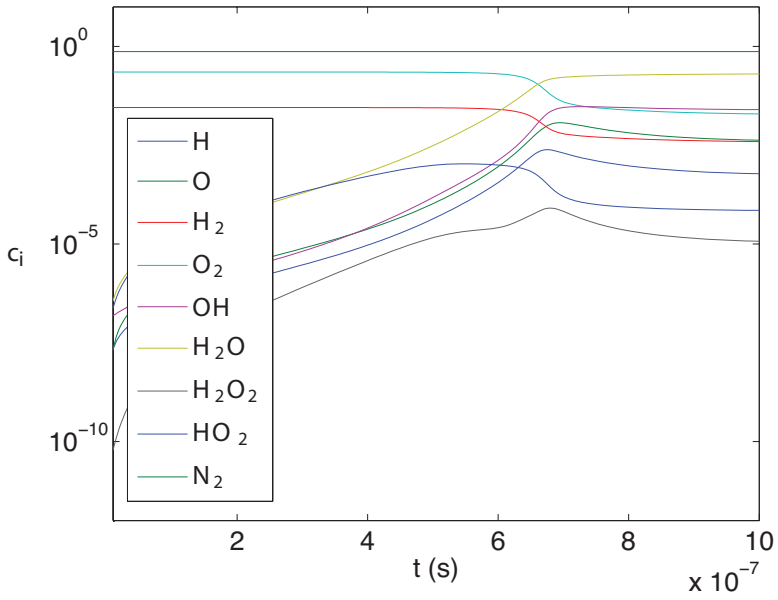

Figure 7.18: Plot near thermal explosion time of $c_{H_2}(t)$, $c_H(t)$, $c_O(t)$, $c_{O_2}(t)$, $c_{OH}(t)$, $c_{H_2O}(t)$, $c_{HO_2}(t)$, $c_{H_2O_2}(t)$, $c_{N_2}(t)$, for adiabatic, isochoric combustion of a mixture of $2H_2+O_2+3.76N_2$ initially at at $T_o = 1542.7\ K$, $P_o = 2.8323 \times 10^6\ Pa$.

rium mass fractions of each species are

$$c_{O_2} = 1.85 \times 10^{-2}, \tag{7.366}$$
$$c_H = 5.41 \times 10^{-4}, \tag{7.367}$$
$$c_{OH} = 2.45 \times 10^{-2}, \tag{7.368}$$
$$c_O = 3.88 \times 10^{-3}, \tag{7.369}$$
$$c_{H_2} = 3.75 \times 10^{-3}, \tag{7.370}$$
$$c_{H_2O} = 2.04 \times 10^{-1}, \tag{7.371}$$
$$c_{HO_2} = 6.84 \times 10^{-5}, \tag{7.372}$$
$$c_{H_2O_2} = 1.04 \times 10^{-5}, \tag{7.373}$$
$$c_{N_2} = 7.45 \times 10^{-1}. \tag{7.374}$$

We note that because our model takes N_2 to be inert that its value remains unchanged. Other than N_2, the final products are dominated by H_2O. The equilibrium temperature is 3382.3 K and $5.53 \times 10^6\ Pa$.

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This is a good undergraduate book on thermodynamics from a physics perspective. It covers classical theory well in its first sections, then goes on to treat kinetic theory and statistical mechanics. It first appeared in 1964.

I. Müller and T. Ruggeri, 1998, *Rational Extended Thermodynamics*, Springer-Verlag, New York.

This modern, erudite monograph gives a rigorous treatment of some of the key issues at the frontier of modern continuum thermodynamics.

I. Müller and W. Weiss, 2005, *Entropy and Energy*, Springer-Verlag, New York.

This is a unique treatise on fundamental concepts in thermodynamics. The author provide mathematical rigor, historical perspective, and examples from a diverse set of scientific fields.

I. Müller, 2007, *A History of Thermodynamics: the Doctrine of Energy and Entropy*, Springer-Verlag, Berlin.

The author gives a readable text at an advanced undergraduate level which highlights some of the many controversies of thermodynamics, both ancient and modern.

I. Müller and W. H. Müller, 2009, *Fundamentals of Thermodynamics and Applications: with Historical Annotations and Many Citations from Avogadro to Zermelo*, Springer, Berlin.

The author presents an eclectic view of classical thermodynamics with much discussion of its history. The text is aimed at a curious undergraduate who is unsatisfied with industrial-strength yet narrow and intellectually vapid textbooks.

W. Nernst, 1969, *The New Heat Theorem: Its Foundation in Theory and Experiment*, Dover, New York.

This monograph gives the author's exposition of the development of the third law of thermodynamics. It first appeared in English translation in 1917 and was originally published in German.

W. Pauli, 2000, *Thermodynamics and the Kinetic Theory of Gases*, Dover, New York.

This is a monograph on statistical thermodynamics by the winner of the 1945 Nobel Prize in physics. It is actually derived from his lecture course notes given at ETH Zurich, as compiled by a student in his class, E. Jucker, published in 1952.

M. Planck, 1990, *Treatise on Thermodynamics*, Dover, New York.

This brief book, which originally appeared in German in 1897, gives many unique insights from the great scientist who was the winner of the 1918 Nobel Prize in physics. It is rigorous, but readable by an interested undergraduate student.

H. Poincaré, 1892, *Thermodynamique: Leçons Professèes Pendant le Premier Semestre 1888-89*, Georges Carré, Paris.

This text of classical undergraduate thermodynamics has been prepared by one of the premier mathematicians of the nineteenth century.

J. M. Powers, 2016, *Combustion Thermodynamics and Dynamics*, Cambridge, New York.

This is a graduate level text on combustion and its interplay with both thermodynamics and dynamics. It uses a large portion of the present course notes as a foundation for its discussion of thermodynamics of reacting mixtures.

I. Prigogine, 1967, *Introduction to Thermodynamics of Irreversible Processes*, Third Edition, Interscience, New York.

This is a famous book that summarizes the essence of the work of the Belgian school for which the author was awarded the 1977 Nobel Prize in chemistry. This book first appeared in 1955.

W. J. M. Rankine, 1908, *A Manual of the Steam Engine and Other Prime Movers*, Seventeenth Edition, Griffin, London.

This in an accessible undergraduate text for mechanical engineers of the nineteenth century. It first appeared in 1859. It contains much practical information on a variety of devices, including steam engines.

L. E. Reichl, 1998, *A Modern Course in Statistical Physics*, John Wiley, New York.

This full service graduate text has a good summary of key concepts of classical thermodynamics and a strong development of modern statistical thermodynamics.

O. Reynolds, 1903, *Papers on Mechanical and Physical Subjects, Volume III, The Sub-Mechanics of the Universe*, Cambridge, Cambridge.

This volume compiles various otherwise unpublished notes of Reynolds and includes his detailed derivations of general equations of conservation of mass, momentum, and energy employing his transport theorem.

W. C. Reynolds, 1968, *Thermodynamics*, Second Edition, McGraw-Hill, New York.

This is an unusually good undergraduate text written for mechanical engineers. The author has wonderful qualitative problems in addition to the usual topics in such texts. A good introduction to statistical mechanics is included as well. This particular edition is highly recommended; the first edition appeared in 1965.

S. I. Sandler, 1998, *Chemical and Engineering Thermodynamics*, Third Edition, John Wiley, New York.

This is an advanced undergraduate text in thermodynamics from a chemical engineering perspective with a good mathematical treatment. It first appeared in 1977.

E. Schrödinger, 1989, *Statistical Thermodynamics*, Dover, New York.

This is a short monograph written by the one of the pioneers of quantum physics, the co-winner of the 1933 Nobel Prize in Physics. It is based on a set of lectures delivered to the Dublin Institute for Advanced Studies in 1944, and was first published in 1946.

A. H. Shapiro, 1953, *The Dynamics and Thermodynamics of Compressible Fluid Flow*, Vols. I and II, John Wiley, New York.

This classic two volume set has a comprehensive treatment of the subject of its title. It has numerous worked example problems, and is written from a careful engineer's perspective.

J. M. Smith, H. C. van Ness, and M. Abbott, 2004, *Introduction to Chemical Engineering Thermodynamics*, Seventh Edition, McGraw-Hill, New York.

This is probably the most common undergraduate text in thermodynamics in chemical engineering. It first appeared in 1959. It is rigorous and has went through many revisions.

A. Sommerfeld, 1956, *Thermodynamics and Statistical Mechanics*, Lectures on Theoretical Physics, Vol. V, Academic Press, New York.

This is a compilation of the author's lecture notes on this subject. The book reflects the author's stature of a leader of theoretical physics of the twentieth century who trained a generation of students (e.g. Nobel laureates Heisenberg, Pauli, Debye and Bethe). The book gives a fine description of classical thermodynamics with a seamless transition into quantum and statistical mechanics.

J. W. Tester and M. Modell, 1997, *Thermodynamics and Its Applications*, Third Edition, Prentice Hall, Upper Saddle River, New Jersey.

First appearing in 1974, this entry level graduate text in thermodynamics is written from a chemical engineer's perspective. It has a strong mathematical development for both classical and statistical thermodynamics.

C. A. Truesdell, 1980, *The Tragicomic History of Thermodynamics, 1822-1854*, Springer Verlag, New York.

This idiosyncratic monograph has a lucid description of the history of nineteenth century thermal science. It is written in an erudite fashion, and the reader who is willing to dive into a difficult subject will be rewarded for diligence by gain of many new insights.

C. A. Truesdell, 1984, *Rational Thermodynamics*, Second Edition, Springer-Verlag, New York.

This is an update on the evolution of classical thermodynamics in the twentieth century. The book itself first appeared in 1969. The second edition includes additional contributions by some contemporaneous leaders of the field.

S. R. Turns, 2000, *An Introduction to Combustion*, Second Edition, McGraw-Hill, Boston.

This is a senior-level undergraduate text on combustion which uses many notions from thermodynamics of mixtures. It first appeared in 1996.

H. C. van Ness, 1983, *Understanding Thermodynamics*, Dover, New York.

This is a short readable monograph from a chemical engineering perspective. It first appeared in 1969.

W. G. Vincenti and C. H. Kruger, 1976, *Introduction to Physical Gas Dynamics*, Krieger, Malabar, Florida.

This graduate text on high speed non-equilibrium flows contains a good description of the interplay of classical and statistical mechanics. There is an emphasis on aerospace science and fundamental engineering applications. It first appeared in 1965.

F. M. White, 2010, *Fluid Mechanics*, Seventh Edition, McGraw-Hill, Boston.

This standard undergraduate fluid text draws on thermodynamics in its presentation of the first law and in its treatment of compressible flows. It first appeared in 1979.

B. Woodcraft, 1851, *The Pneumatics of Hero of Alexandria*, London, Taylor Walton and Maberly.

This is a translation and compilation from the ancient Greek of the work of Hero (10 A.D.-70 A.D.). The discussion contains descriptions of the engineering of a variety of technological devices including a primitive steam engine. Other devices which convert heat into work are described as well.

L. C. Woods, 1975, *The Thermodynamics of Fluid Systems*, Clarendon, Oxford.

This graduate text gives a good, detailed survey of the thermodynamics of irreversible processes, especially related to fluid systems in which convection and diffusion play important roles.