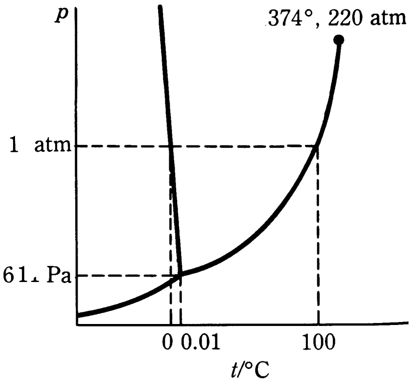
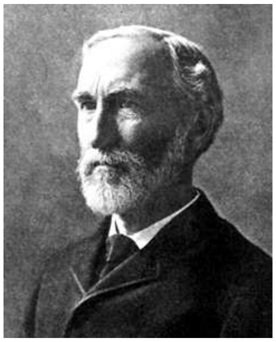
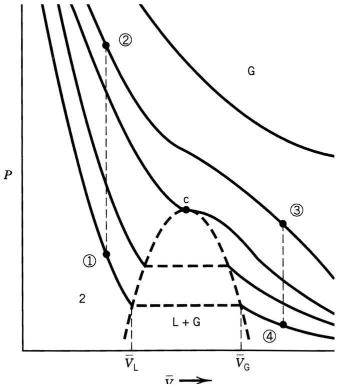




Chemistry 243 : Introductory Physical Chemistry II

David Ronis
McGill University



Chemistry 243

Introductory Physical Chemistry II

David Ronis

McGill University

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CHEMISTRY 243: Introductory Physical Chemistry II.

1. General Information

Lectures: Monday & Wednesday 10:30 - 11:30 A.M.
Burnside Hall, 1B 23
Course Web Site: http://ronispc.chem.mcgill.ca/ronis/chem243
(Username: chem243; Password: Gibbs)

Professor: David Ronis
Office: Otto Maass Room 426
E-mail: David.Ronis@McGill.CA

Texts

Thomas Engel and Philip Reid, *Thermodynamics, Statistical Thermodynamics, and Kinetics, 2nd edition* (Pearson Education, Inc., 2006)

J.R. Barrante, *Applied Mathematics for Physical Chemistry, 3rd edition* (Pearson Education, Inc., 2004)

Supplementary Texts

1. G. W. Castellan, *Physical Chemistry* 3rd edition (Benjamin Cummings Pub. Co., 1983)(Out of print but excellent).
2. R.J. Silbey, R.A. Alberty and M.G. Bawendi, *Physical Chemistry, 4th edition* (John Wiley & Sons, Inc., 2005).
3. Gordon M. Barrow, *Physical Chemistry*.
4. R. Kubo, *Thermodynamics* (Physics orientation, advanced)

Grades

There will be approximately one problem set every 3-4 lectures, one midterm and a final exam. The midterm will be given at 18:00 on:

Thursday, February 18, 2010 in Otto Maass 112 and 217 (a seating plan will be posted).

Completion of the homework is mandatory. Most of the problems will not be graded, although one or two problems may be chosen at random and graded. Solutions to the problem sets will be posted on the course web page. You are strongly encouraged to do the homework. The problems will cover many details not done in class and will prepare you for the exams. **The exams will involve extensive problem-solving and, in part, may contain problems from the homework!** The course grading scheme is:

Grade Distribution	
Problems	10%
Midterm	40%
Final	50%

CHEMISTRY 243: TENTATIVE OUTLINE

Date	Topic	Text Chapter Reid	 Castellan
Lecture 1.	Heterogeneous Equilibrium: The phase rule	8	12
Lecture 2.	Phase diagrams of Simple systems: Clapeyron and Clausius-Clapeyron equations	8	12
Lecture 3.	Ideal Solutions	9	13
Lecture 4.	Colligative properties	9	13
Lecture 5.	Colligative properties (continued)	9	13
Lecture 6.	Solutions of volatile components	9	14
Lecture 7.	Lever-principle and fractional distillation	9	14
Lecture 8.	Henry’s Law and solubility.	9	14
Lecture 9.	Solubility calculations	9	14
Lecture 10.	Electrolyte solutions	10	17
Lecture 11.	Activities & Debye-Huckel Theory	10	17
Lecture 12.	Electrochemistry: Electrochemical cells	11	17
Lecture 13.	Nernst equation and applications	11	17
Lecture 14.	Surface Phenomena: Surface Tension, Wetting, Properties of Small Particles, & Nucleation		
Lecture 15.	Surface Adsorption: Langmuir and BET		
Lecture 16.	Diffusion Controlled Reactions	18	33
Lecture 17.	Chemical Kinetics II: Detailed Balance & TST	18	33
Lecture 18.	Chemical Kinetics II: Ionic Effects	19	32, 34
Lecture 19.	Complex Mechanisms	19	32, 34
Lecture 20.	” (continued)	19	32, 34
Lecture 21.	Marcus Theory: Electron Transfer	19	32, 34

Note:

McGill University values academic integrity. Therefore all students must understand the meaning and consequences of cheating, plagiarism and other academic offenses under the code of student conduct and disciplinary procedures (see www.mcgill.ca/integrity for more information).

In accord with McGill University’s Charter of Students’ Rights, students in this course have the right to submit in English or in French any written work that is to be graded.

In the event of extraordinary circumstances beyond the University’s control, the content and/or evaluation scheme in this course is subject to change.

2. Phase Equilibrium

An important class of equilibria involves the different equilibria established between different states of matter, e.g., solids, liquids, and gases. As we shall now show, such equilibria are governed by very simple principles, essentially the same as those we worked out for chemical equilibria.

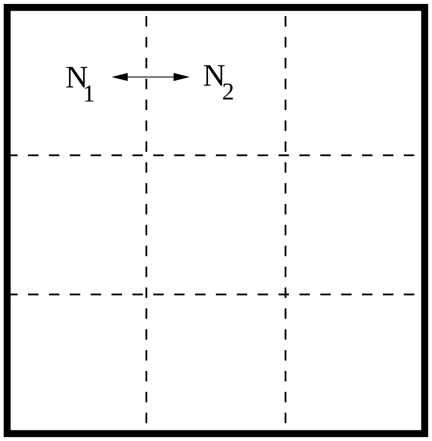


Figure 1

Consider a system containing an arbitrary number of non-reacting components placed in a constant pressure and temperature container (the space enclosed by the heavy lines in the figure). When equilibrium is attained, each part of the system will have a certain number of moles in each part. For example, if we divide the system up according to the dashed lines the figure, there will be N_1 moles of one component in the first part, N_2 in the second, etc.

Since the entire system is at constant T, P, and number of moles of each component, the Gibbs free energy, G, must be at a minimum at equilibrium. If so, consider what would happen if we changed the number of moles in the first two compartments by letting $N_1 \rightarrow N_1 + dN$ and $N_2 \rightarrow N_2 - dN$. Clearly, we have not changed the total number of moles. However,

$$dG = (\mu_{Compartment\ 1} - \mu_{Compartment\ 2})dN \tag{1}$$

which will be nonzero (and hence G cannot be a minimum) unless

$$\mu_{Compartment\ 1} = \mu_{Compartment\ 2}, \tag{2}$$

or, since the division into compartments was completely arbitrary, unless the chemical potential of each component is the same in each part of the system. Note, that this is just a special example of our criterion for chemical equilibrium for the trivial "chemical" reaction:

$$N_{Compartment\ 1} \rightleftarrows N_{Compartment\ 2}. \tag{3}$$

Since, our preceding discussion only depended on the ability to have matter exchanged between different parts of the system (but not on transfers to and from the surroundings), it will also hold for systems in which phase separation has occured, for example if there was a liquid-vapor interface in our system, or if there was a precipitate at the bottom of the container. Would it hold if there was a semipermiable membrane separating different parts of our container?

In order to study some of the general consequences of these equilibrium conditions, consider a system containing C components that have phase separated into P phases. Applying Eq. (2) to each component we see that

$$\begin{array}{ccccccc} \mu_1^{(1)} & = & \mu_1^{(2)} & = & \cdot & = & \mu_1^{(P)} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ \mu_C^{(1)} & = & \mu_C^{(2)} & = & \cdot & = & \mu_C^{(P)}, \end{array} \tag{4}$$

where $\mu_i^{(j)}$ is the chemical potential of component i in phase j. It is easy to see that there are $(P-1)C$ conditions. Each chemical potential depends on T and P (the same throughout the system, WHY?) and on the composition of the phase in question (e.g., as we saw for dilute gases). Since, we aren't currently interested in extensive properties, we can characterize the composition of each phase by the mole fractions, x_i, of which there are $C-1$ independent ones in each phase, or $P(C-1)$ in total. Thus, including temperature and pressure, there are a total of $P(C-1)+2$ unknowns to be determined by the $(P-1)C$ equations given in (4), and in general the system of equations will be either over- or under-determined. The extent to which this happens is obtained by looking at the number of degrees of freedom, f, the difference between the number of unknowns and equations; i.e.,

$$f = P(C-1)+2-C(P-1) = 2+C-P. \tag{5}$$

This simple result is known as the Gibbs Phase Rule.

As an example, suppose we have a one component system (C=1). According to Eq. (5), if there is only a single phase, $f=2$; i.e., we can pick T and P arbitrarily. If there are two phases in equilibrium, then $f=1$; i.e., we can pick at most either$T$ or P, but not both. Finally, f vanishes if there are three phases in equilibrium, which implies that we can't pick anything at the so-called triple point. For pure water, the triple point occurs at 0.01C and 611 Pa. Finally, note that while our simple counting arguments rule out over-determined solutions, they don't always guarantee the existence of solutions, e.g., as is found above the critical temperature in one-component systems.

We next turn to a more quantitative analysis of the equilibrium between phases. Suppose we have a one component system containing two phases (for concreteness, a liquid and its vapor). According to Eq. (5) we can pick one intensive quantity, e.g., the temperature, T, and the pressure at coexistence will be determined. How does the coexistence pressure change if we change the temperature? Since,

$$\mu_{liquid} = \mu_{vapor} \tag{6}$$

both before and after the change in temperature,

$$d\mu_{liquid} = d\mu_{vapor}. \tag{7}$$

However, since for a one component system, $\mu = G/N$,

$$d\mu_i = -\bar{S}_i dT + \bar{V}_i dP, \tag{8}$$

where $\bar{S}_i$ and $\bar{V}_i$ are the molar entropy and volume, respectively in phase i. By substituting Eq. (8) into (7) and rearranging the result, it follows that

$$\left(\frac{dP}{dT}\right)_{Coexistence} = \frac{\bar{S}_1 - \bar{S}_2}{\bar{V}_1 - \bar{V}_2} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}, \tag{9}$$

where the last equality follows by noting that $\Delta\bar{H} = T\Delta\bar{S}$ at equilibrium. Of course holds for any two-phase, one-component equilibrium, and is known as the Clapeyron equation. For the liquid-vapor equilibrium example, $\Delta\bar{H}$ is just the heat of vaporization. What is it for solid-liquid equilibria?

There are several approximations that follow from Eq. (9). For example, if we can ignore the temperature dependences of $\Delta\bar{H}$ and $\Delta\bar{V}$, then we can integrate both sides of (9) and obtain

$$P_2 - P_1 \approx \frac{\Delta\bar{H}}{\Delta\bar{V}} \ln(T_2/T_1) \approx \frac{\Delta\bar{H}\Delta T}{T_1\Delta\bar{V}}, \tag{10}$$

where the last approximation follows if $\Delta T/T_1$ is small. This is a reasonable approximation for cases where both phases are solids and/or liquids (and hence, their molar volumes don't change much with temperature).

Another approximation is obtained if one of the phases is a dilute gas and the other a solid or liquid, then

$$\Delta\bar{V} = \bar{V}_{Vapor} - \bar{V}_2 \approx \bar{V}_{Vapor} \approx \frac{RT}{P}, \tag{10}$$

which allows us to rewrite Eq. (9) as

$$\left(\frac{d\ln(P)}{dT}\right)_{Coexistence} = \frac{\Delta\bar{H}}{RT^2}, \tag{11}$$

which is known as the Clausius-Clapeyron equation. Compare this with the expression we obtained for the temperature dependence of the equilibrium constant, K_P. They are the same, perhaps as expected since, we can view the process as a chemical reaction, e.g.,

$$\text{liquid} \rightleftarrows \text{vapor},$$

for which the equilibrium would be determined from $P(T) = K_p$.

Finally, With the further assumption that that $\Delta\bar{H}$ is independent of temperature, we can integrate the Clausius-Clapeyron equation and show that the equilibrium vapor pressure of a liquid or solid obeys (approximately)

$$P(T) = P(T_0)\exp\left[\frac{\Delta\bar{H}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right], \tag{12}$$

again consistent with the *chemical equilibrium* point of view. How would you use this result to determine the normal boiling point of the material?

3. Minimum and Maximum Boiling Azeotropes: The Gibbs-Konovalov Theorem

As we discussed in class, a system where the temperature-composition phase diagram has a minimum or maximum for some composition is called an azeotrope. Here we will show that the composition of the vapor and liquid phases of azeotropes must be the same. This result is called the Gibbs-Konovalov theorem, and is an sophisticated exercise in Maxwell relations, equilibrium conditions, and partial molar quantities.

For what follow, we will call the two components 1 and 2. Quantities pertaining to the two phases will be distinguished by having a prime in the case of the vapor. Finally, the mole fraction of 1 in the liquid and vapor phases are x_1 and y_1, respectively.

The phase rule tells us that a two-phase, binary mixture has $F = 2 + 2 - 2 = 2$ degrees of freedom. One will be taken to be the pressure, which is held fixed. The other will be some convenient concentration variable. In general, the chemical potentials in either phase can be viewed as functions of T,P, and a mole fraction (e.g., x_1 or y_1). Hence, for arbitrary changes of state:

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,x_1} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_i}{\partial x_1}\right)_{P,T} dx_1. \tag{1}$$

The first two partial derivatives may be rewritten by using Maxwell relations obtained from the Gibbs free energy (recall, $dG = -SdT + VdP + \sum \mu_i dN_i$). Thus,

$$d\mu_i = -\bar{S}_i dT + \bar{V}_i dP + \left(\frac{\partial \mu_i}{\partial x_1}\right)_{P,T} dx_1, \tag{2}$$

where

$$\bar{S}_i \equiv \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_{j\neq i}},$$

and

$$\bar{V}_i \equiv \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

are the partial molar entropies and volumes, respectively.

Equation (2) must hold for either component in either phase (in the vapor phase, just add primes to all quantities and change x_1 to y_1). Moreover, for changes in state along the coexistence curve,

$$d\mu_i = d\mu_i' \quad i = 1, 2. \tag{3}$$

If we use Eq. (2) in (3), two equations relating changes in T, P, x_1 and y_1 are obtained. In addition, for the case at hand $dP = 0$, and thus, we find that

$$-(\bar{S}_i - \bar{S}_i')dT + \left(\frac{\partial \mu_i}{\partial x_1}\right)_{T,P} dx_1 = \left(\frac{\partial \mu_i'}{\partial y_1}\right)_{T,P} dy_{1,} \quad i = 1, 2. \tag{4}$$

Next, we divide through by dx_1, multiply the equation for component 1 by x_1, the equation for component 2 by x_2 and add the results. This gives

$$\begin{aligned}
&-[x_1(\bar{S}_1 - \bar{S}_1') + x_2(\bar{S}_2 - \bar{S}_2')]\left(\frac{\partial T}{\partial x_1}\right)_{P,coex} + x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \mu_2}{\partial x_1}\right)_{T,P} \\
&\qquad = \left[x_1\left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P} + x_2\left(\frac{\partial \mu_2'}{\partial y_1}\right)_{T,P}\right]\left(\frac{\partial y_1}{\partial x_1}\right)_{P,coex}.
\end{aligned} \tag{5}$$

The changes in the chemical potentials at constant T and P are not independent, but are related through the Gibbs-Duhem equations,

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{6a}$$

and

$$y_1 d\mu_1' + y_2 d\mu_2' = 0. \tag{6b}$$

Dividing Eqs. (6a) and (6b) by dx_1 and dy_2, respectively, and using the results in Eq. (5) shows that

$$-[x_1(\bar{S}_1 - \bar{S}_1') + x_2(\bar{S}_2 - \bar{S}_2')]\left(\frac{\partial T}{\partial x_1}\right)_{P,coex} = \left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P}\left(\frac{\partial y_1}{\partial x_1}\right)_{coex}\left[x_1 - \frac{x_2 y_1}{y_2}\right] \tag{7}$$

$$= \left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P}\left(\frac{\partial y_1}{\partial x_1}\right)_{coex}\frac{(x_1 - y_1)}{y_2}, \tag{8}$$

where the last equality is obtained by noting that the sum of the mole fractions in either phase is unity.

The left hand side of the equation vanishes at a minimum or maximum of the T-X phase diagram; hence, one of the factors on the right hand side must be zero. Thermodynamic stability requirements (i.e., G is a minimum) can be used to show that

$$\left(\frac{\partial \mu_1'}{\partial x_1}\right)_{T,P} > 0.$$

It is also easy to show, using the definitions of the mole fractions and the fact that the total number of moles of each type is constant, that

$$\left(\frac{\partial y_1}{\partial x_1}\right)_{coex} \neq 0.$$

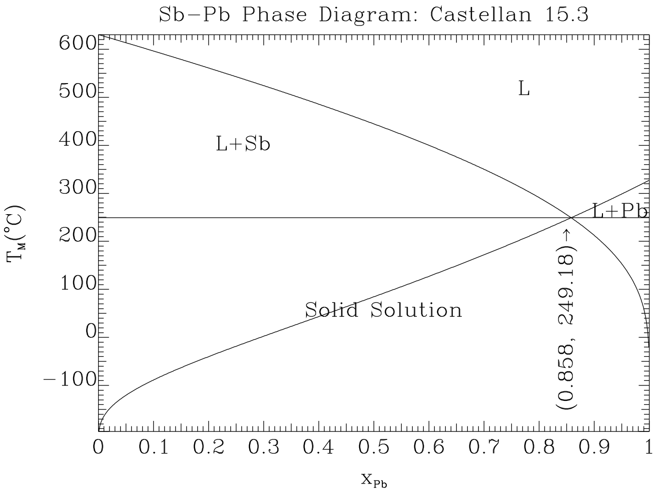
Hence, at an azeotropic point, $x_1 = y_1$; i.e., the compositions of the liquid and vapor phases are the same. This is called the Gibbs-Konovalov theorem. Note that the derivation did not require any specific properties of liquids or gases and our result will hold for any two-phase coexistence in binary mixtures.

Finally, note that essentially the same manipulations can be used to show that

$$\left(\frac{\partial P}{\partial x_1}\right)_{T,coex} = \frac{\left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P} \left(\frac{\partial y_1}{\partial x_1}\right)_{coex} (x_1 - y_1)}{y_2[x_1(\bar{V}_1 - \bar{V}_1') + x_2(\bar{V}_2 - \bar{V}_2')]} .$$

Hence, the P-X phase diagram will also have a minimum or maximum at the azeotropic composition.

4. Ideal Eutectic Phase Diagrams



The ideal lead-antimony eutectic phase diagram is shown in the figure, and was calculated assuming that the solids are completely immiscible and that the solution was ideal. The liquid-solid coexistence lines are computed from the equilibrium conditions:

$$\mu_i^{(0)}(\text{solid}, T) = \mu_i^{(0)}(\text{liquid}, T) + RT\ln(x_i), \quad i = A, B. \tag{1}$$

or using the fact that $\Delta\bar{G}_{fus}^{(0)}(i) \equiv \mu_i^{(0)}(\text{liquid}, T) - \mu_i^{(0)}(\text{solid}, T) = 0$ at the normal melting point, $T = T_{MP}^{(i)}$, of material i, we can rewrite Eq. (1) as

$$\ln(x_i) = \int_{T_{MP}^{(i)}}^{T} \frac{\Delta\bar{H}_{fus}^{(i)}}{RT^2} \approx \frac{\Delta\bar{H}_{fus}^{(i)}}{R}\left[\frac{1}{T_{MP}^{(i)}} - \frac{1}{T}\right], \tag{2}$$

where the last approximation follows by assuming the the heat of fusion is independent of temperature.

The point where the two curves cross is called the Eutectic point. The question is what happens below the eutectic temperature? From the point of view of the phase rule, or the equilibrium conditions given in Eqs. (1) or (2), we could still have L+A, L+B, or A+B (i.e., a mixture of the solid phases). Indeed, it is the last possibility which happens; WHY?

In order to answer this question, we must go back a few steps and remember that under constant T,P,N conditions, the equilibrium state is the one with the *lowest* Gibbs free energy; specifically if there are multiple local minima in G, it is the one that is lowest that should be observed at equilibrium. This is what happens below the eutectic temperature. To see this, consider the total free energy for the system (again for ideal solutions and immiscible solids):

$$G = n_A^{(s)}\mu_A^{(0)}(\text{solid}, T) + n_B^{(s)}\mu_B^{(0)}(\text{solid}, T)$$

$$+ n_A^{(l)}[\mu_A^{(0)}(\text{liquid}, T) + RT\ln(x_A)] + n_B^{(l)}[\mu_B^{(0)}(\text{liquid}, T) + RT\ln(x_B)] \tag{3a}$$

$$= N_A \mu_A^{(0)}(\text{solid}, T) + N_B \mu_B^{(0)}(\text{solid}, T)$$

$$+ n_A^{(l)}[\Delta \bar{G}_{fus}^{(0)}(A, T) + RT \ln(x_A)] + n_B^{(l)}[\Delta \bar{G}_{fus}^{(0)}(B, T) + RT \ln(x_B)], \tag{3b}$$

where $n_i^{(s)}$, $n_i^{(l)}$, and N_i are the number of moles of i in the solid, liquid, and total, respectively. Remembering that the total number of moles of each material remains constant, the equilibrium states must be local minima of G, and these are found by taking derivatives of Eq. (3b) with respect to $n_A^{(l)}$ or $n_b^{(l)}$ and setting the result to zero. It is straightforward to show that this results in Eq. (1).

As was discussed above, when deciding between different possibilities, it is necessary to go back to Eq. (3) and find the local minimum with the lowest free energy. For our example, consider the following two possibilities L+A or A+B. The latter obeys the liquid-solid equilibrium condition for A, cf. Eq. (1) and hence, from Eq. (3b) we see that the states have free energies:

$$G_{A+B} = N_A \mu_A^{(0)}(\text{solid}, T) + N_B \mu_B^{(0)}(\text{solid}, T) \tag{4a}$$

and

$$G_{L+A} = N_A \mu_A^{(0)}(\text{solid}, T) + N_B \mu_B^{(0)}(\text{solid}, T) + N_B[\Delta \bar{G}_{fus}^{(0)}(B, T) + RT \ln(x_B)], \tag{4b}$$

where we have set $n_A^{(l)} = n_B^{(l)} = 0$ for the A+B state and $n_B^{(l)} = N_B$ for the L+A state. Thus, L+A state will be the equilibrium one as long as

$$\frac{\Delta \bar{G}_{fus}^{(0)}(B, T)}{RT} + \ln(x_B) < 0 \tag{5}$$

or, approximately, as long as

$$\ln(x_B) < \frac{\Delta \bar{H}_{fus}}{R} \left(\frac{1}{T_{MP}^{(B)}} - \frac{1}{T} \right), \tag{6}$$

which, cf. Eq. (2), breaks down below the L+B coexistence line. Thus, since all points on the L+A coexistence line are below the L+B coexistence line below the eutectic temperature, there the L+A state has a higher free energy than A+B state. Clearly, there is nothing special about the notation for A, and hence, exactly the same conclusion can be drawn for B. Thus we see that the solid mixture is the minimum free energy solution below the eutectic temperature. Finally, while we have used ideal solutions in this example, you can show that the same argument still holds for a nonideal solution*.

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*To do this consider how Eqs. (1) and (3b) would have to be modified for the nonideal case, and what are the signs of the various terms in different parts of the phase diagram.

5. Electrolyte Solutions: Activity Coefficients and Debye-Huckel Theory

To understand the thermodynamics of electrolyte solutions, we have to understand how nature tries to keep systems electrically neutral. (WHY?). In particular, this leads to some additional definitions for the chemical potentials and activities. Consider the electrolyte dissociation

$$A^{z_+}_{\nu_+}B^{z_-}_{\nu_-} \rightarrow \nu_+ A^{z_+} + \nu_- B^{z_-}, \tag{1}$$

where ν_i is the stochiometric coefficient of the ith ion which has charge ez_i, $i = + \; or \; -$, where e is the magnitude of the charge on an electron.

There is some ambiguity in how to think about the solution, i.e., as comprised of dissociated ions or of undissociated molecules. Of course, in reality an equilibrium for Eq. (1) will be established, and thus,

$$\mu_{A_{\nu_+}B_{\nu_-}} = \nu_+ \mu_{A^{z_+}} + \nu_- \mu_{B^{z_-}}. \tag{2}$$

We've seen that chemical potentials can be written in terms of activities as $\mu_i = \mu_i^o + RT\ \ln(a_i)$, which in our case gives

$$\mu_{A_{\nu_+}B_{\nu_-}} = \mu^o_{A_{\nu_+}B_{\nu_-}} + RT\ \ln(a_{A_{\nu_+}B_{\nu_-}}), \tag{3a}$$

$$\mu_{A_{\nu_+}} = \mu^o_{A_{\nu_+}} + RT\ \ln(a_{A_{\nu_+}}), \tag{3b}$$

and

$$\mu_{B_{\nu_-}} = \mu^o_{B_{\nu_-}} + RT\ \ln(a_{B_{\nu_-}}). \tag{3c}$$

It turns out that the activities of the positive and negative ions always appear together, e.g., as in the equation for the dissociation equilibrium:

$$\frac{a^{\nu_+}_{A_{\nu_-}} a^{\nu_-}_{B_{\nu_-}}}{a_{A_{\nu_+}B_{\nu_-}}} = K,$$

cf. Eqs. (2) and (3). Because of this it is convenient to define mean ionic activities as:

$$\mu_{\pm} \equiv \frac{\nu_+ \mu_{A_{\nu_+}} + \nu_- \mu_{B_{\nu_-}}}{\nu} \equiv \mu^o_{\pm} + RT \ln a_{\pm}, \tag{4a}$$

with

$$\nu \equiv \nu_+ + \nu_-, \tag{4b}$$

$$\nu \mu^o_{\pm} \equiv \nu_+ \mu^o_{A_{\nu_+}} + \nu_- \mu^o_{B_{\nu_-}}, \tag{4c}$$

and

$$a_{\pm}^{\nu} \equiv a_{A_{\nu_+}}^{\nu_+} a_{B_{\nu_-}}^{\nu_-}. \tag{4d}$$

Hence, the dissociation equilibrium becomes:

$$\frac{a_{\pm}^{\nu}}{a_{A_{\nu_+}B_{\nu_-}}} = K.$$

Finally, if we define a mean mole fraction as $x_{\pm}^{\nu} \equiv x_{+}^{\nu_+} x_{-}^{\nu_-}$ it follows from Eq. (4d) that the mean activity coefficient is given by $\gamma_{\pm}^{\nu} \equiv \gamma_{+}^{\nu_+}\gamma_{-}^{\nu_-}$.

We next consider a model for the activities of dilute electrolyte solutions. Since the undissociated molecule is neutral, $\nu_+ z_+ + \nu_- z_- = 0$. If ρ_i is the concentration of the ith ion, then the fact that we start with a electrically neutral compound implies that

$$\sum_i \rho_i e z_i = 0. \tag{5}$$

Does electro-neutrality hold locally; i.e., very near to one of the ions? Consider a statistical model for the local charge density. Based on our work on the kinetic theory of gases, we know that

$$Probability \propto \exp(-Energy/k_B T), \tag{6}$$

and for electrical problems it is reasonable to assume that

$$Energy = e z_i \phi(r) \tag{7}$$

where $\phi(r)$ is the electrical potential around one of the ions in the solution, here assumed to be at the origin of our coordinate system. Using these probabilities to moderate the local density, we see that local charge density, $\sigma(r)$ is

$$\sigma(r) = \sum_i \rho_i e z_i \exp(-e z_i \phi(r)/k_B T) \tag{8}$$

For a positive ion at the origin, we expect that $\phi(r) > 0$ and hence, Eq. (8) predicts a net excess negative charge density in the local vicinity of our ion. This is the physical basis of the phenomena of screening. If the electrostatic energies are small compared with thermal energies, i.e., $e\phi(r) \ll k_B T$, we can use the well known approximation for the exponential,

$$e^x \approx 1 + x + \frac{x^2}{2} + \cdots, \tag{9}$$

in Eq. (8) to show that

$$\sigma(r) \approx -\frac{2Ie^2}{k_B T}\phi(r) + \cdots, \tag{10}$$

where

$$I \equiv \frac{1}{2}\sum_i \rho_i z_i^2 \tag{11}$$

is called the ionic strength and has units of concentration (indeed, for 1-1 electrolytes it is simply the concentration in molecules per unit volume). In obtaining Eq. (10) overall electro-neutrality, cf. Eq. (5), was used to eliminate the leading order terms.

How much charge will be induced by having an ion (with charge Q) at the origin? Gauss's law strongly suggests that the induced charge, cf. Eqs. (8) or (10), exactly balance the charge at the origin; i.e., local electro-neutrality will hold, and thus,

$$Q = -\int d\mathbf{r}\,\sigma(r) = -4\pi\int_0^\infty dr\, r^2\sigma(r) \approx \frac{2Ie^2}{k_BT}\int_0^\infty dr\, r^2\phi(r) \tag{12}$$

where the second to last equality follows by switching to polar coordinates, and the final one by using Eq. (10). In the absence of screening, the potential is simply Coulomb's law; namely,

$$\phi(r) = \frac{Q}{4\pi\varepsilon r}\,, \tag{13}$$

where ε is the electric permittivity of the solvent. How will this change if the charge is screened? To answer this requires some physics that is a bit beyond this course* and instead

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*Specifically, as you will see in PHYS 242, you need to know Poisson's equation for the electric potential due to a charge distribution in a dielectric medium; i.e.,

$$\nabla^2\phi(r) = -\sigma(r)/\varepsilon.$$

When Eq. (8) is used for the charge density, we obtain what is known as the nonlinear Poisson-Boltzmann equation, which cannot be solved analytically for all but 1-dimensional problems. When Eq. (10) is used the linearized Poisson-we’ll simply guess the form of the screened potential, i.e.,

$$\phi(r) = \frac{Q}{4\pi\varepsilon r}\, e^{-\kappa_D r}, \tag{14}$$

where the exponential accounts for the screening and κ_D is known as the Debye screening wave-vector. The screening sets in on a length scale of $\lambda_D = 1/\kappa_D$.

What is the screening length? To answer this we’ll impose local electro-neutrality, cf. the last equality in Eq. (12); hence,

$$Q = \frac{2Ie^2Q}{\varepsilon k_BT}\int_0^\infty dr\, re^{-\kappa_D r} = \frac{2Ie^2Q}{\varepsilon k_BT}\,\frac{1}{\kappa_D^2}\,. \tag{15}$$

Thus, by solving for κ_D, we see that

$$\kappa_D = \sqrt{\frac{2e^2I}{\varepsilon k_BT}} = \sqrt{\frac{2F^2I}{\varepsilon RT}}\,, \tag{16}$$

where the second equality is obtained when the ionic strength and electron charge are expressed as mol/m^3 and the Faraday, F, respectively. For a 1:1 electrolyte in water at 25C, this gives a screening length of

$$\lambda_D = \frac{1}{\kappa_D} = \frac{3.04}{c^{1/2}}\ \ (\text{in Å}),$$

where c is the molar salt concentration; hence, the counter-ion cloud around any given ion in a 0.01M salt solution is about 50 Å in radius ($\lambda_D = 30.4$Å, but the cloud extends beyond λ_D somewhat).

How much work was done on the system in placing the ion and the screening ions at the origin? Clearly,

$$W = \int d\mathbf{r}\,\phi(r)\sigma(r) = 4\pi\int_0^\infty dr\, r^2\phi(r)\sigma(r) = -\frac{8\pi Ie^2}{k_BT}\int_0^\infty dr\, r^2\phi^2(r) = -\frac{\kappa_D Q^2}{8\pi\varepsilon}\,, \tag{17}$$

where we’ve again switched to polar coordinates and used Eqs. (10), (14), and (16). Thus, for a mole of either of the ions, the work is just done is

$$-\frac{N_A\kappa_D e^2 z_i^2}{8\pi\varepsilon}\,.$$

Boltzmann or Debye-Huckel equation is obtained; this can be solved in closed form and gives the result presented in the text.

Of course, this is just another contribution to the non-PV work or chemical potential associated with dissolving the ith ionic species. Hence,

$$RT \ln \gamma_i = -\frac{N_A \kappa_D e^2 z_i^2}{8\pi\varepsilon} \tag{18a}$$

or

$$\ln \gamma_i = -\frac{\kappa_D e^2 z_i^2}{8\pi k_B T \varepsilon} = -\frac{\kappa_D F^2 z_i^2}{8\pi N_A RT \varepsilon}\,. \tag{18b}$$

This is known as the Debye-Huckel limiting law and is valid at low concentrations (typically, it breaks down in the 0.005 to 0.01 M range). Note that the sign of the ionic charge is irrelevant and that $\ln \gamma_i \propto I^{1/2}$.

With Eq. (18) it is easy to work out the mean activity coefficient; specifically,

$$\ln \gamma_\pm = -\frac{\kappa_D e^2}{8\pi k_B T \varepsilon} \frac{(\nu_+ z_+^2 + \nu_- z_-^2)}{\nu}\,, \tag{19a}$$

$$= \frac{\kappa_D e^2}{8\pi k_B T \varepsilon} z_+ z_-, \tag{19b}$$

where the second relation follows by noting that the undissociated molecule is neutral.

6. Capillary Rise and Depression

Consider a two phase system with a flat interface as shown in Fig. 1.

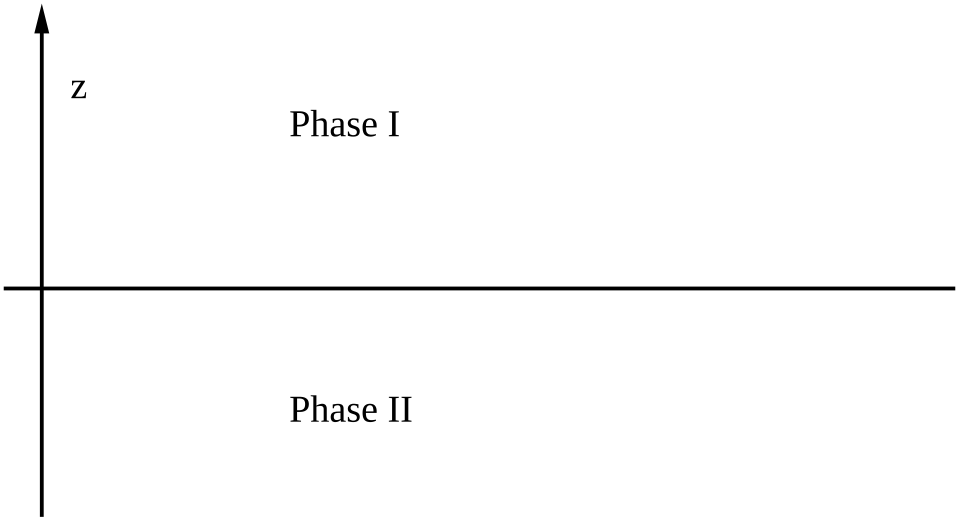

FIG. 1

Since the two phases are in equilibrium in the presence of a gravity field, the pressure varies with height, z; namely,

$$p_1(z) = p_1(0) - \rho_1 g z \tag{1}$$

in phase 1, and

$$p_2(z) = p_2(0) - \rho_2 g z \tag{2}$$

in phase 2, where $\rho_{1(2)}$ is the density in phase 1(2). Of course, at the interface (here assumed flat) the pressures must be equal and

$$p_1(0) = p_2(0) \equiv p_0. \tag{3}$$

Now put a capillary tube into the system as shown in Fig. 2.

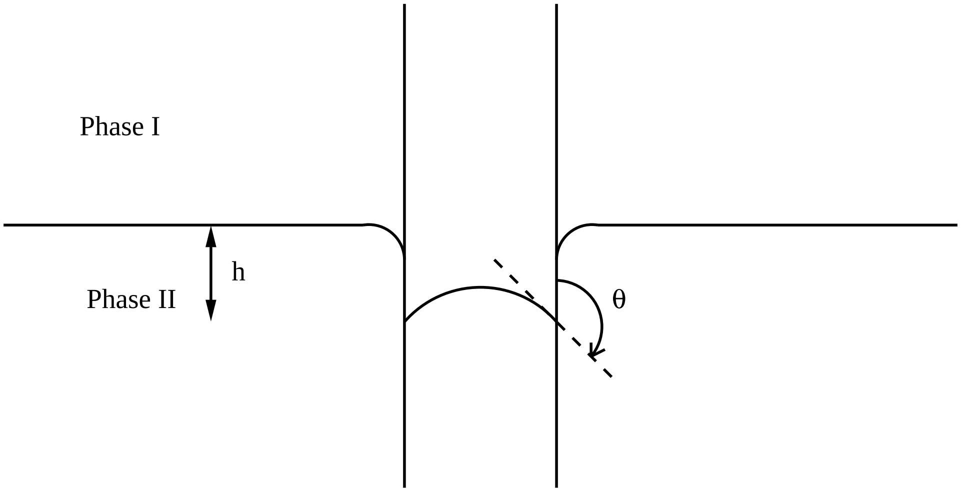

FIG. 2

The surface tension, γ, between phase 1 and phase 2 wants the pressures between the two phases to be unequal at the curved interface (why?). Specifically, for the convex surface shown in Fig. 2, we know that

$$p_2(-h) - p_1(-h) = \frac{2\gamma}{R}\ . \tag{4}$$

The only way in which the pressure difference can be achieved is by moving the curved interface to a new position in the fluid. (Changing the pressure in the gas or liquid from that of the surrounding material at the same height would cause material to flow from the high to low pressure regions until the pressures were equal at all points at the same height). Thus, by using our expressions for the pressure dependence in the phases at any given heights [Eqs. (1), (2), and (3)] in Eq. (4) we find that

$$p_0 + \rho_2 gh - (p_0 + \rho_1 gh) = \frac{2\gamma}{R} \tag{5}$$

or

$$h = \frac{2\gamma}{Rg(\rho_2 - \rho_1)} \approx \frac{2\gamma}{Rg\rho_2} \text{ for } \rho_2 \gg \rho_1, \tag{6}$$

where the approximate expression is useful for liquid-vapor interfaces. (If the interface is concave then the pressures in Eq. (4) must be switched and the sign of h changes.)

Finally, if we write R, the radius of curvature of the interface, in terms of d, the radius of the tube and the contact angle θ, it follows that

$$h = -\frac{2\gamma\cos(\theta)}{dg(\rho_2 - \rho_1)}$$

For a 45^o contact angle in a capillary tube with a $1mm$ radius containing water ($\gamma = 72.75 dynes/cm$ the capillary *rise* will be $1.05cm$

7. Problem Sets

Note that the due dates are last year's. This year's will be announced in class and on the web site.

7.1. Problem Set 1

DUE: Wednesday, January 20, 2010

1. Engel and Reid, Problem P8.6

2. Engel and Reid, Problem P8.8

3. Engel and Reid, Problem P8.24

4. (Castellan, Problem 13.5) A stream of air is bubbled slowly through liquid benzene in a flask at 20.0C against an ambient pressure of 100.56 kPa. After the passage of 4.80L of air, measured at 20.0C and 100.56 kPa before it contains benzene vapor, it is found that 1.705 g of benzene have been evaporated. Assuming that the air is saturated with benzene, calculate the equilibrium vapor pressure of benzene at 20.0C.

5. (Castellan, Problem 13.9) Ethylene glycol, $C_2H_4(OH)_2$ is commonly used as a permanent antifreeze; assume that the mixture with water is ideal. Plot the freezing point of the mixture as a function of the volume percent of glycol in the mixture mixture. The densities are: H_2O 1.00 g/cm^3, glycol, 1.11 g/cm^3, and $\Delta\bar{H}_{fus}(H_2O) = 6009.5 J/mol$.

7.2. Problem Set 2

DUE: Wednesday, February 3, 2010

1. Engel and Reid, Problem P9.7

2. Engel and Reid, Problem P9.11

3. Engel and Reid, Problem P9.26

4. (Castellan, Problem 14.20) The distribution coefficient of iodine between CCl_4 and H_2O is $c_{CCl_4}/c_{H_2O} \equiv K = 85$, where c_i is the molar concentration of I_2 in the i'th phase.

a) If 90% of the iodine in 100 cm^3 of aqueous solution is to be extracted in one step, what volume of CCl_4 is required?

b) What volume of CCl_4 is required if two extractions, using equal volumes, are permitted?

c) If β is the fraction of I_2 that is to remain in the water layer after n extractions using equal volumes of CCl_4, show that the limiting total volume of CCl_4 needed as $n \to \infty$ is $K^{-1} \ln(1/\beta)$ per unit volume of the aqueous layer.

5. (Castellan, Problem 15.4) From the melting points of the mixtures of Al and Cu, sketch the melting point curve.

Mass % Cu	0	20	40	60	80	100
T (C)	660	600	540	610	930	1083

b) For copper, $T_m = 1356\,K$ and $\Delta H^o_{fus}(Cu) = 13.05\,kJ/mol$; for aluminum $T_m = 933\,K$ and $\Delta H^o_{fus}(Al) = 10.75\,kJ/mol$. Sketch the ideal solubility curves and compare with the experimental curve in (a).

7.3. Problem Set 3

DUE: Monday, February 15, 2010

1. Engel and Reid, Problem P10.3
2. Engel and Reid, Problem P10.7
3. Engel and Reid, Problem P9.16
4. Engel and Reid, Problem P9.38
5. Castellan, Problem 16.5. A regular binary solution is defined by the equation

$$\mu_i = \mu_i^o + RT \ln x_i + w(1 - x_i)^2$$

where w is a constant.

a) What is the significance of μ_i^o?

b) Calculate the activity coefficients, γ_i (defined in terms of mole fractions).

c) At 25C, $w = 324 J/mol$ for mixtures of benzene and CCl_4. Plot γ_{CCl_4} for $0 \le x_{CCl_4} \le 1$.

7.4. Problem Set 4

DUE: Wednesday, March 10, 2010

1. (Castellan, Problem 17.8) Consider the cell

$$Pt(s)|H_2(g, 1\ atm), H^+(aq, 1M)||Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s),$$

given that $\Delta\varepsilon^o = 0.771V$ for

$$Fe^{3+} + e^- \rightarrow Fe^{2+}.$$

a) If the measured potential of the cell is 0.712 V, what is the ratio of concentrations of Fe^{2+} to Fe^{3+}? (Assume that the solutions are ideal.)

b) What is the ratio if the potential of the cell was 0.830V?

c) Plot the fraction of total iron present as Fe^{3+} over the voltage range 0.65 V to 0.9 V.

2. (Castellan, problem 17.4) The Edison storage cell is symbolized as

$$Fe(s)|FeO(s)|KOH(aq, a)|Ni_2O_3(s)|NiO(s)|Ni(s).$$

The half-cell reactions are

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-, \qquad \Delta\varepsilon^o = 0.4V,$$

$$FeO(s) + H_2O(l) + 2e^- \rightarrow Fe(s) + 2OH^-, \qquad \Delta\varepsilon^o = -0.87V.$$

a) What is the cell reaction?

b) How does the cell potential depend on the activity of KOH?

c) How much electrical energy can be obtained per kilogram of the active materials in the cell?

3. (Castellan, problem 17.11) A 0.1 mol/L solution of NaCl is titrated with $AgNO_3$. The titration if followed potentiometrically, using a silver wire as the indicating electrode and a suitable reference electrode. Calculate the potential of the silver wire when the amount of $AgNO_3$ added is 50%, 90%, 99%, 99.9%, 100%, 100.1%, 101%, 110% and 150% of the stochiometric requirement (assume that the solution is ideal and ignore the change in the volume of the solution). Note that

$$\Delta\varepsilon^o_{Cl^-|AgCl|Ag} = 0.222V, \qquad \Delta\varepsilon^o_{Ag^+|Ag} = 0.799V,$$

and that $K_{sp} = 1.7 \times 10^{-10}$ for $AgCl$.

4. (Castellan, problem 18.15) Assuming that crystals form as tiny cubes having edge length δ, calculate the freezing point of ice consisting of small crystals relative to the freezing point of

infinitely large crystals; $T_0 = 273.15K$. Assume that the inter-facial tension is $25mN/m$, $\Delta H^o_{fus} = 6.0kJ/mol$; $\bar{V}_s = 20cm^3/mol$. Calculate for $\delta = 10\mu m$, $1\mu m$, $0.1\mu m$ $0.01\mu m$, and $0.001\mu m$.

7.5. Problem Set 5

DUE: Friday, Monday, March 29, 2010

1. Engel and Reid, Problem 18.24
2. Engel and Reid, Problem 18.26
3. Engel and Reid, Problem 18.36
4. Engel and Reid, Problem 18.40
5. Engel and Reid, Problem 18.37

8. Past Exams

8.1. 2010 Midterm Exam

8.1.1. INSTRUCTIONS

1. No books or notes are permitted.
2. Calculators are permitted.
3. Answer all questions and show all work clearly.
4. There are 4 questions and each is of equal value.
5. Be sure to indicate the total number of exam books handed in on your exam book and on the log sheet.
6. You may need the following data:

Useful Constants

Constant	Value
Gas Constant, R	$8.31442\ J\ K^{-1}\ mole^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Speed of Light in Vacuum	$2.998 \times 10^{8} m/sec$
Faraday, F	96,484.6 Coul/mole
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
Permittivity of vacuum	$8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$
Elementary charge, e,	$1.602 \times 10^{-19} C$
1 cal	4.184 J

7. You may need the following results from calculus:

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

8. Good Luck.

1. (25%) Derive the Gibbs Phase rule. What is the maximum number of phases that coexist in a two component system?

2. (25%) Assume that Raoult's law holds for both components of a two component solution. Show how this leads to the forms of the chemical potentials of each component in the solution. What happens if the solute obeys Henry's Law over some limited range of concentration? **Be sure to explain what the symbols mean!**

3. (25%)

a) Derive the expression for the depression of the freezing point in an ideal solution. How is your expression modified if the solute is soluble in the solid phase?

b) 10g of an unknown compound is found to lower the freezing point of 100g of water ($T_{melt} = 273.15K,\ \Delta\bar{H}_{fus} = 6.01kJ/mol,\ MW = 18.01528g/mol$) by 5.0K. What is the molecular weight of the compound? Would your answer be wrong if the compound were ionic and fully ionized?

4. (25%)

a) Show how the ideal P-X phase diagram arises. In particular, show how the total pressure can be expressed in terms of the solution composition or vapor composition.

b) Sketch the P-T phase diagram, label the various regions, and use it to show how fractional distillation works.

c) What is an azeotrope and why does it limit the utility of fractional distillation?

8.2. 2010 Final Exam

8.2.1. INSTRUCTIONS

1. No books or notes are permitted. Translation dictionaries and calculators are permitted.
2. Answer all questions in the exam book and show all work clearly.
3. There are 3 pages (including this one) and 5 questions, each of equal value.
4. Be sure to indicate the total number of exam books handed in on book 1.
5. **You may keep the exam.**
6.

Useful Constants

Constant	Value
Gas Constant, R	$8.31442\ J\ K^{-1}\ mol^{-1}$
Boltzmann's Constant, k_B	$1.381 \times 10^{-23} J/K$
Standard Atmosphere	$1.01325 \times 10^{5} Pa$
Avogadro's Number	6.0225×10^{23}
Faraday Constant, F	$9.6485309 \times 10^{4}\ coul/mol$

7. You may need the following results from calculus:

$$\int_{-\infty}^{\infty} e^{-ax^2/2} dx = \sqrt{2\pi/a}, \qquad \int_A^B x\, e^{-ax^2/2} dx = \frac{1}{a}\left(e^{-aA^2/2} - e^{-aB^2/2}\right),$$

$$\int_A^B x^3 e^{-ax^2/2} dx = \frac{(aA^2+2)e^{-aA^2/2} - (aB^2+2)e^{-aB^2/2}}{a^2},$$

$$\int_A^B \frac{dx}{x} = \ln(B/A), \qquad \int_A^B \frac{dx}{x^2} = \frac{1}{A} - \frac{1}{B},$$

$$\ln(1+x) \approx x, \text{ and } \frac{1}{1-x} \approx 1 + x + x^2 + \cdots \text{ for } |x| \ll 1.$$

8. Good Luck.

1. (20%) The Lindemann mechanism for unimolecular reactions of the form

$$A \rightarrow Products$$

proposes:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^* + M$$

$$A^* \xrightarrow{k_2} Products$$

Determine the general form of the rate law and show under what circumstances it reduces to first order kinetics.

2. (20%)

a) Briefly discuss the assumptions behind Eyring rate theory, also known as Activated Complex or Transition State theory, and show how they lead to the form of an elementary rate constant.

b) For an elementary bimolecular gas phase reaction, show how to express the Arrhenius activation energy in terms of the parameters appearing in the activated complex theory.

c) Show what the activated complex theory predicts for the pressure dependence of a rate constant.

d) Use Debye-Huckel theory to predict the dependence of the bimolecular rate constant on charge and ionic strength.

e) Finally, show how detailed balance arises in the Eyring approach.

3. (20%, FROM THE HOMEWORK) (Castellan, problem 18.15) Assuming that crystals form as tiny cubes having edge length δ, calculate the freezing point of ice consisting of small crystals relative to the freezing point of infinitely large crystals; $T_0 = 273.15K$. Assume that the inter-facial tension is $25mN/m$, $\Delta H^o_{fus} = 6.0kJ/mol$; $\bar{V}_s = 20cm^3/mol$. Calculate the freezing point for $\delta = 0.001\mu m$.

4. (20%)

a) Derive the form for the diffusion limited rate constant. **HINT:** note that for spherically symmetric functions, i.e., $f(x, y, z) = f(r)$ in polar coordinates,

$$\nabla^2 f \equiv \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

$$= \frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r}$$

b) (**FROM THE HOMEWORK:** Reid and Engel, Problem P18.36) In enzyme catalysis, the first step involves the binding of a reactant molecule (referred to as a substrate) to a binding site on the enzyme. If this binding is extremely efficient (that is the equilibrium strongly favors the enzyme-complex over separate enzyme and substrate) and the formation of product is rapid, then the rate of reaction could be diffusion limited. Estimate the expected rate constant for a diffusion controlled reaction using typical values for an enzyme ($D = 10^{-7}\ cm^2/s$, and $R = 40\overset{o}{A}$) and a small molecule substrate ($D = 10^{-5} cm^2/s$ and $r = 5\overset{o}{A}$).

5. (20%)

a) What are Langmuir and BET theories for absorption?

b) In particular, for a surface with q_s binding sites per unit area, derive expressions in the two theories for the number of adsorbed molecules per unit area as a function of the pressure of the gas next to the surface .