Department of Chemistry
Cumulative Examinations
January 17, 2009

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% *would not* yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains ***five*** examinations.

On your examination booklet:

1) Print your student ID number.
2) Print the Exam Booklet number.
3) Print the question number you are answering.
4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, *you must use a separate examination booklet for each examination*.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.

PURDUE
UNIVERSITY

Analytical Cumulative Examination January 17, 2009

1. An analyte species, A, reacts with a reagent species, R, to give a product, P, with a rate constant of $k = 0.020\ M^{-1}s^{-1}$. Assuming the equilibrium constant to be very large, the reaction can be regarded as essentially irreversible, i.e.:

   $A + R \rightarrow P$

   Assume that the concentration of R, [R], can be held constant in answering the following questions.

   a.) How long will it take for 99% of the analyte to be converted to product if [R] = 0.5 M? [5 pts.]

   b.) Write the relationship for product concentration as a function of time, $[P]_t$. [5 pts]

   c.) If the initial concentration of A is determined by measuring the concentration of P at two distinct times to yield $\Delta[P]$, write the expression for sensitivity. Use the resulting relationship to justify whether greater sensitivity would be expected at long or short time differences between measurements of [P]. [10 pts.]

   d.) Write the relationship between the absolute random error associated with the initial analyte concentration, $s_{[A]0}$, and the absolute random error associated with the measurement of $\Delta[P]$, $s_{\Delta[P]}$. In other words, how does random error in the measurement of $\Delta[P]$ propagate to the error in [A]? [10 pts.]

   e.) If [R] is unknown and of interest and it is possible to measure [A] directly, indicate how [R] can be determined by measuring [A] at two or more times. (Provide the mathematical relationship you would use.) [10 pts.]

2. The titration of 49.50(±0.02) mL of a strong acid required 42.4(±0.2) mL of a 0.1017(±0.0002) M strong base to reach the equivalence point.

   a) What is the concentration of the strong acid? [5 pts.]

   b) What is the error associated with the value of the acid determined by this titration? (Show how you arrived at the result) [10 pts.]

3. An electrode potential responds to analyte concentration, [A], with the following relationship:

$E_{cell} = X + Y\ln[A]$

where X and Y are constants.

a) Draw the qualitative shape of the E_{cell} vs. [A] curve. [5 pts]

b) What is the relationship between [A] and sensitivity for this method? Write the appropriate relationship and draw the shape of the sensitivity versus concentration curve. [5 pts.]

c) Provide the relationship between random error and the resulting concentration error (i.e., indicate how the measurement error propagates to concentration error). Draw the shape of the curve expected for concentration error versus concentration when the measurement error is constant with concentration.

[10 pts.]

d) How does the relative concentration error depend upon concentration for this method? Draw the shape of the curve expected for relative concentration error versus concentration when the measurement error is constant with concentration. [10 pts.]

4. The behavior of an enzyme catalyzed reaction is often consistent with the generalized mechanism

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + E$$

where E is the enzyme, S is the substrate, ES is an enzyme-substrate complex, and P is the product. This mechanism was first proposed by (Leonor) Michaelis and (Maude) Menten. The relationship that gives the rate of product formation, v, (sometimes referred to as the velocity of the reaction) is given below:

$$v = \frac{k_2[S][E]_0}{K_M + [S]}$$

a) What are common terms used for K_M and k_2, what is the ratio k_2/K_M for a given enzyme/substrate combination often called, and what is K_M in terms of the rate constants indicated above and what are its units? [5 pts]

b) Draw a plot of initial rate versus substrate concentration and indicate the most appropriate regions of the plot for measuring substrate and enzyme concentrations, respectively. [10 pts]

Useful relationships:

$$\frac{de^u}{dx} = e^u \frac{du}{dx} \qquad \frac{d \ln u}{dx} = \frac{1}{u}\frac{du}{dx}$$

Biochemistry Cumulative Exam

Title: Transcription and Translation

January 17, 2009

1. (20 points). What are the functions of the following?

   (a) t-RNA Synthetase

   (b) Rho binding sites in RNA

   (c) σ-factor in prokaryotes

   (d) EF-G

2. (10 points) What are the start and termination points for the following biological phenomenon in prokaryotes? (a) Transcription (b) Translation.

3. (a) (5 marks) Why do Shine Dalgarno sequence occur in prokaryotes only?

   (b) (5 marks) Why prokaryotic mRNA is not modified post-transcriptionally?

4. (10 points) What is the function of an operon? Why do these occur in prokaryotic cells mainly?

5. (10 points) Provide any one example by which gene expression is controlled at (a) transcriptional level (b) translational level.

6. (20 points) Define the following terms in two to three sentences:

   (a) Intron (b) Attenuation in Trp operon (c) Ubiquitination (d) RNAi.

7. (10 points) What advantage wobble base pairing confers to a t-RNA?

8. (10 points) Which RNAs are transcribed by RNA Polymerase I and III?

Inorganic Chemistry Cumulative Exam

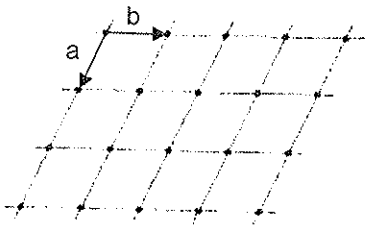
Purdue University

January 17, 2009

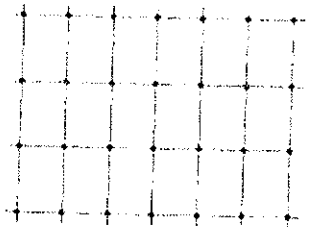
There are 100 possible points in this exam.

1. (30 points) A lattice is an infinite array of identical points (i.e. each one has exactly the same environment of other points) and the points are obtained one from another by translations only. This description is applicable, equally, in one-, two-, and three-dimensional space. A unit cell of a plane (2D) lattice is a parallelogram of two unit translations, a and b, with lattice points at the corners and is perfectly representative of the lattice. There are five 2D lattice types. They are:

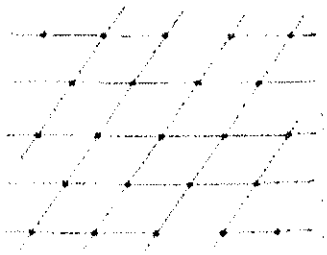
Oblique: $a \neq b$, $\gamma \neq 90°$



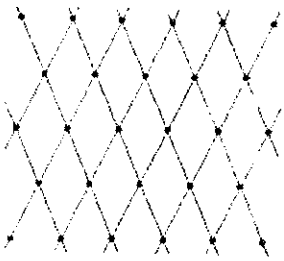
Rectangle: $a \neq b$, $\gamma = 90°$

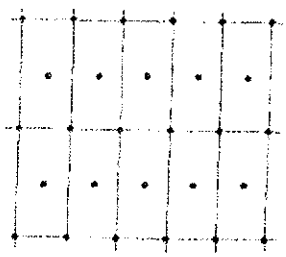


Hexagon: $a = b$, $\gamma = 120°$

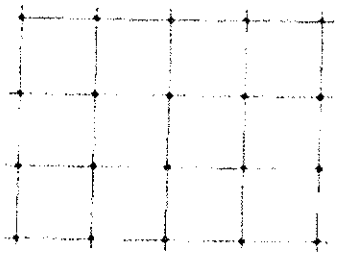


Rhombus (= centered rectangle): $a = b$, $\gamma \neq 90°$





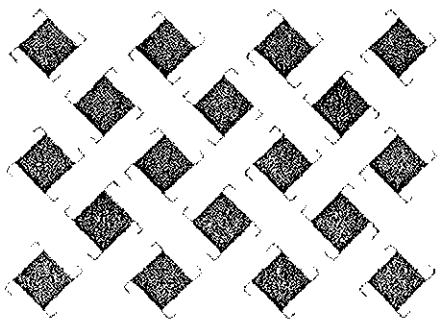
Square: $a = b$, $\gamma = 90°$



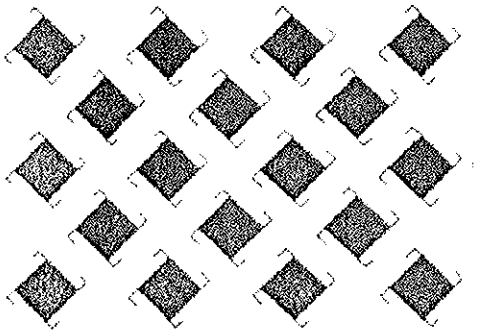
Draw a unit cell for the following 2D patterns (convention: choose the smallest repeat unit) and identify a lattice type. Do not forget to cut the patterns and attach them to your blue book. (A stapler is available at the podium).

----------cut here----------

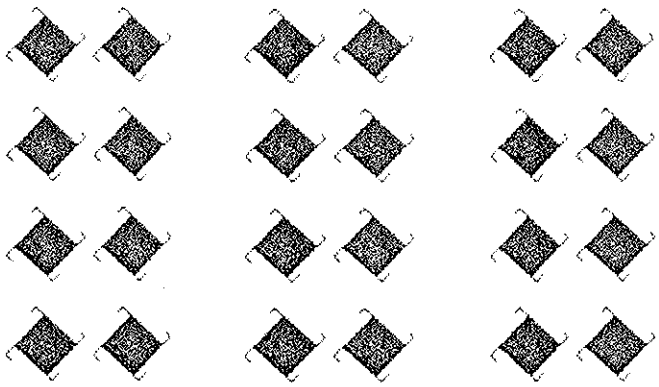
(a)



(b)



(c)



2. (20 ponits) Unit cells of the 14 Bravais lattices (3D lattices) are given below. Explain why the following lattice types do not exist.

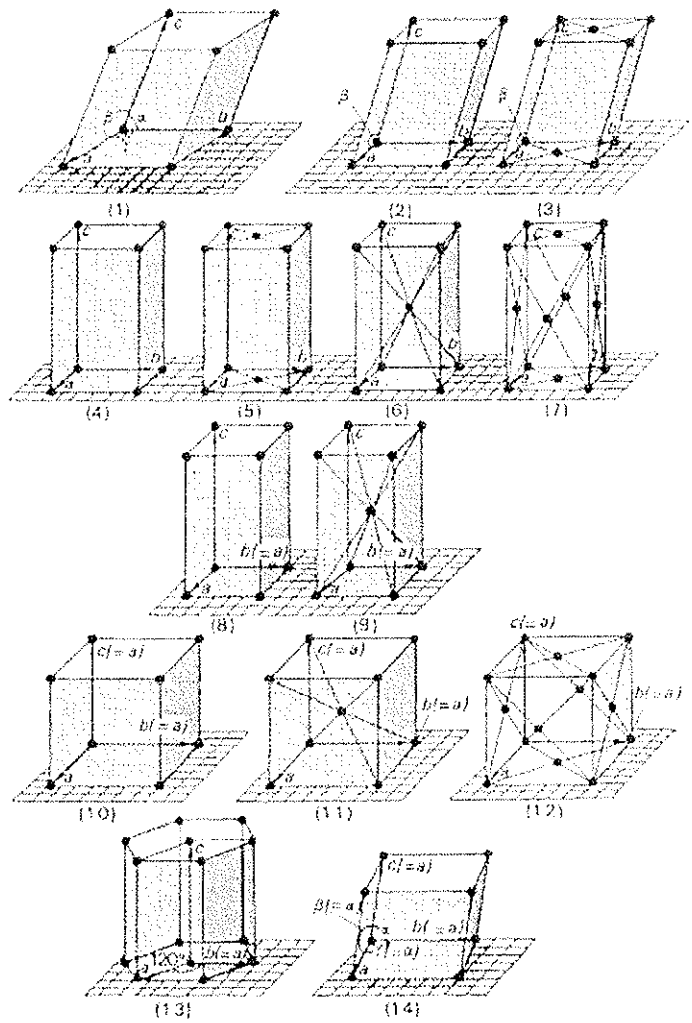
a) Cubic C
b) Tetragonal C
c) Tetragonal A
d) Tetragonal F

14 Bravais Lattices

(1) Triclinic P
(2) Monoclinic P
(3) Monoclinic C
(4) Orthorhombic P
(5) Orthorhombic C
(6) Orthorhombic I
(7) Orthorhombic F
(8) Tetragonal P
(9) Tetragonal I
(10) Cubic P
(11) Cubic I
(12) Cubic F
(13) Hexagonal P
(14) Trigonal R

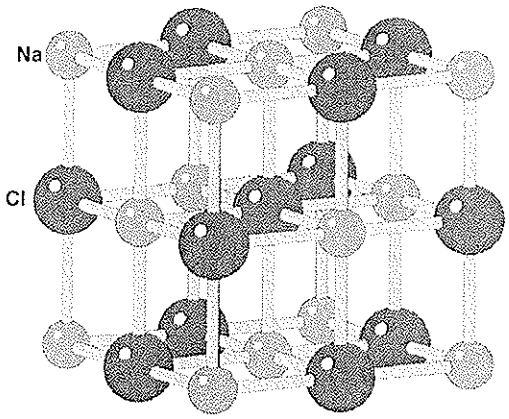
7 Crystal Systems

Triclinic ($a \neq b \neq c$, $\alpha \neq 90°$, $\beta \neq 90°$, $\gamma \neq 90°$)
Monoclinic ($a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$)
Orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$)
Tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$)
Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90°$)
Hexagonal ($a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$)
Trigonal ($a = b = c$, $\alpha = \beta = \gamma \neq 90°$, $< 120°$)

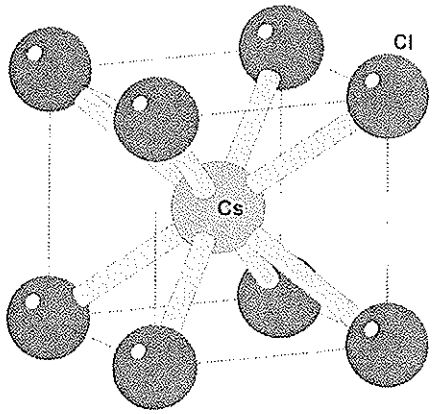


3. (15 points) Determine the Bravais lattice type for the following structures.

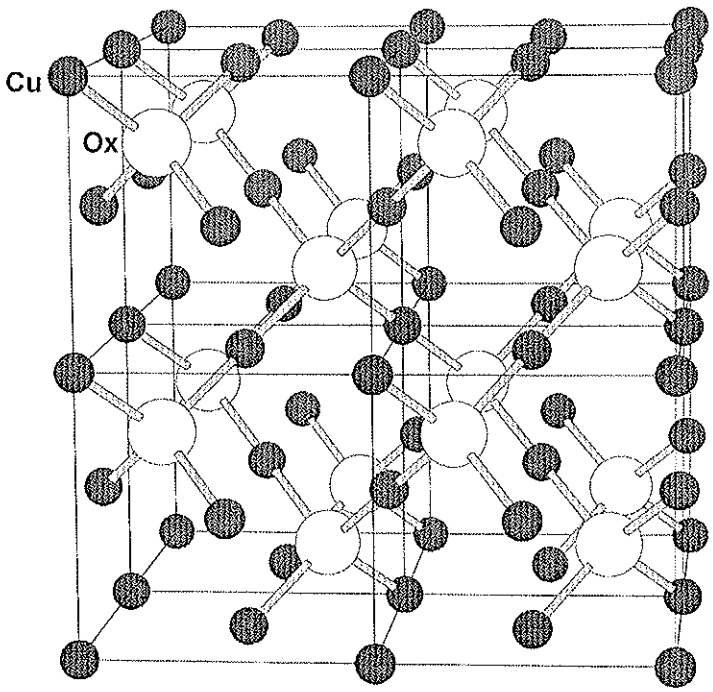
(a) NaCl
($a = b = c = 5.63$ Å, $\alpha = \beta = \gamma = 90°$)



(b) CsCl
($a = b = c = 4.02$ Å, $\alpha = \beta = \gamma = 90°$)



(c) Cu_2O ($a = b = c = 4.267$ Å, $\alpha = \beta = \gamma = 90°$)



4. (20 points) To which crystal system must each of the following space groups belong?

(a) I 4mm
(b) I mmm
(c) C m
(d) I m3m

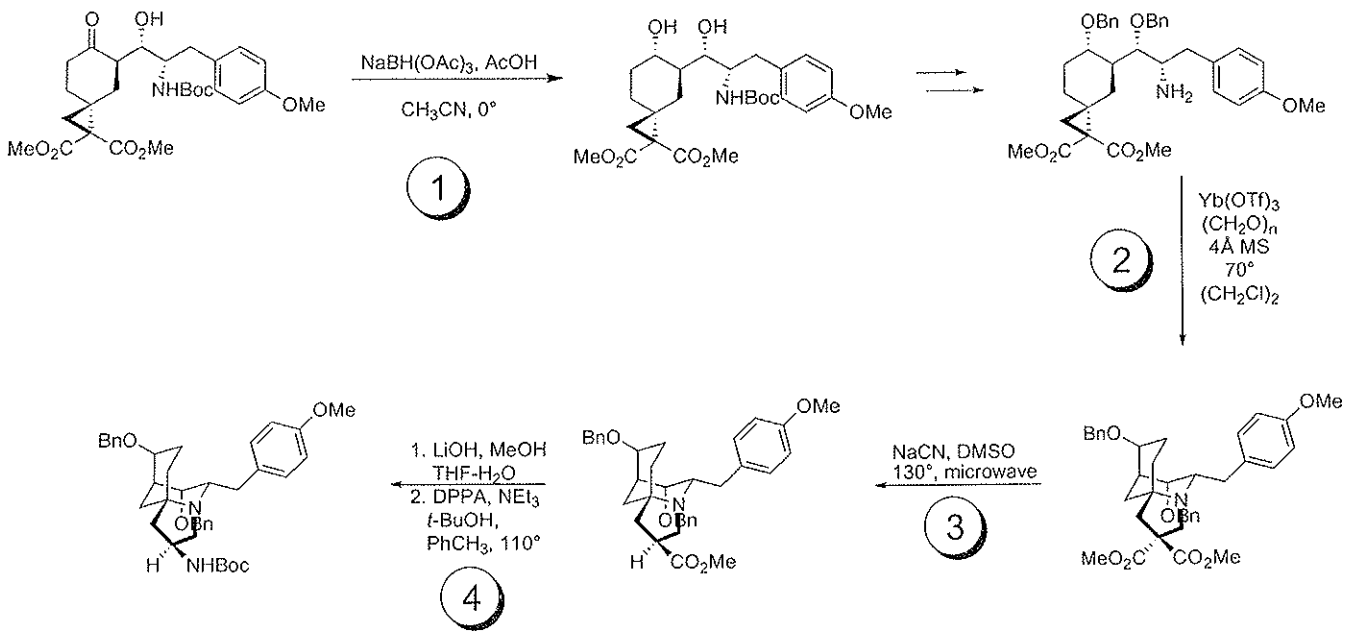
5. (15 points) Write a symmetry equivalent position(s) of a general position (x, y, z) generated by the following symmetry operations.

(a) body-centering
(b) 2 fold axis parallel to the y-axis
(c) 2_1 screw axis parallel to the y-axis
(d) a-glide plane perpendicular to the y-axis
(e) mirror plane perpendicular to the y-axis

Organic Cumulative Examination

January 17, 2009

Answer the questions on p. 2 concerning the scheme shown below:



Abbreviations:

Boc: *tert*-butyloxycarbonyl

DPPA: diphenylphosphoryl azide

1. (60 points) Provide mechanisms for the reactions involved in steps **1-4**. Use curved arrow formalism and show all likely intermediates. Assume an aqueous workup after each reaction.

2. (40 points) Provide <u>detailed</u> explanations for the stereoselectivities observed in steps **1** and **4**.

Physical Cumulative Exam
January 17, 2009

This cumulative exam deals with topics in chemical thermodynamics.

You will need the following information.

1. **Notation.**

An arbitrary extensive state function X for one mole of a pure substance is a function of only temperature T and pressure P, and will be denoted by $X_m(T,P)$. If P is the standard pressure $P^\circ \equiv 1\,\text{bar}$, $X_m(T,P)$ will be denoted concisely as $X_m^0(T) \equiv X_m\left(T, P = P^\circ\right)$. Of special interest is $X_m(T,P)$ at the *standard state* $T^0 \equiv 298.15\text{K}$ and P° which will be written as $X_m^0\left(T^0\right)$.

As an example, consider the Gibbs Free Energy $G(T,P,n)$. In our notation,

$$G(T,P = 1\text{bar}, n{=}1\text{mol}) = G_m^0(T). \tag{1}$$

Also recall that the chemical potential $\mu(T,P) = G_m(T,P)$. Thus from Eq. (1)

$$G(T,P = 1\text{bar}, n = 1\text{mol}) = G_m(T,P = 1\text{bar}) = \mu(T,P = 1\text{bar}) \equiv \mu^0(T). \tag{2}$$

2. **T,P Dependencies of μ**

Suppose μ is known numerically at a reference state T^*, P^*. Then it may be computed at an arbitrary state T,P from the following equation

$$\mu(T,P) = \mu\left(T^*,P^*\right) + \int_{P^*}^{P} V_m\left(T^*,P'\right)dP' - \int_{T^*}^{T} S_m\left(T',P\right)dT' \tag{3}$$

where V_m and S_m are the substance's molar volume and entropy.

If the reference state is the standard state ($T^* = T^0 = 298.15\text{K}$, $P^* = P^0 = 1\,\text{bar}$), Eq. (3) becomes

$$\mu(T,P) = \mu^0\left(T^0\right) + \int_{P^0}^{P} V_m\left(T^0,P'\right)dP' - \int_{T^0}^{T} S_m\left(T',P\right)dP'. \tag{4}$$

3. **Approximations for $\mu(T,P)$**

We will denote gases or vapors, liquids, and solids by, respectively, subscripts v, ℓ, and s. Thus, for example, for a vapor: $\mu(T,P) = \mu_v(T,P)$, $V_m(T,P) = V_{m,v}(T,P)$, and $S_m(T,P) = S_{m,v}(T,P)$.

To simplify Eqs. (4) we will assume the following.

(i) For *all* phases (v, ℓ, or s)

$$S_m(T,P) \cong S_m^0(T^0). \tag{5}$$

(ii) For a v phase

$$\int_{P^0}^{P} V_{m,v}(T^0,P')dP \cong RT_0 \ln\frac{P}{P^0}. \tag{6}$$

(iii) *For an ℓ or s phase the chemical potential is P independent.* Thus $\mu_{\ell \text{ or } s}(T,P) \cong \mu_{\ell \text{ or } s}^0(T)$.

From Eqs. (4) and (5), this implies

with these assumptions

$$\int_{P^0}^{P} V_{m,\ell \text{ or } s}(T^0,P') \cong 0. \tag{7}$$

With these assumptions, for a v phase, Eq. (4) reduces to

$$\mu_v(T,P) = \mu_v^0(T^0) + RT\ln\left(\frac{P}{P^0}\right) - S_v^0(T^0)(T-T^0). \tag{8a}$$

Correspondingly for an ℓ or s phase Eq. (4) reduces to

$$\mu_{\ell \text{ or } s}(T,P) = \mu_{\ell \text{ or } s}^0(T^0) - S_{v,\ell \text{ or } s}^0(T^0)(T-T^0). \tag{8b}$$

Eqs. (8) are our basic approximations to Eq. (4). Similar approximations to Eq. (3) are easily derived.

4. Equilibrium Conditions

The thermodynamic condition for equilibrium between two phases α and β is

$$\mu_\alpha(T,P) = \mu_\beta(T,P). \tag{9}$$

As an example of Eq. (9), for ℓ–v equilibrium (boiling) comparing Eqs. (8) and (9) yields

$$\mu_v^0(T^0) + RT\ln\left(\frac{P}{P^0}\right) - S_v^0(T^0)(T-T^0) = \mu_\ell^0(T^0) - S_\ell^0(T^0)(T-T^0). \tag{10}$$

When three phases α, β, and γ are in equilibrium, Eq. (9) generalizes to

$$\mu_\alpha(T,P) = \mu_\beta(T,P) \text{ and } \mu_\alpha(T,P) = \mu_\gamma(T,P). \tag{11}$$

5. Data for Water

This exam will deal solely with phase equilibria of water. Thus we will use v, ℓ, and s as abbreviations for $H_2O(v)$, $H_2O(\ell)$, and $H_2O(s)$.

For this problem you will need the following data for H_2O (assume the mass density of $H_2O[\ell]$ d_ℓ is T,P independent).

$$\begin{aligned} &\mu_v^0\left(T^0\right) = -228.57\text{kJmol}^{-1} \quad S_v^0\left(T^0\right) = 188.83\text{Jk}^{-1}\text{mol}^{-1} \\ &\mu_\ell^0\left(T^0\right) = -237.13\text{kJmol}^{-1} \quad S_\ell^0\left(T^0\right) = 69.91\text{Jk}^{-1}\text{mol}^{-1} \\ &d_\ell = 1.0\text{g cm}^{-3} \end{aligned} \tag{12}$$

6. Additional Information

You will also need the following.

$$\begin{aligned} &1\text{Lbar} = 100\text{J} = 0.1\text{kJ} \\ &R = 8.31447\text{Jk}^{-1}\text{mol}^{-1} \\ &1\text{L} = 1000\text{cm}^3. \end{aligned} \tag{13}$$

<u>Given this information solve the following two problems.</u>

Problem 1

a. From the standpoint of this problem, the validity of Eqs. (5)–(7) is only important in so far as it affects equilibrium behavior.

Assuming for simplicity that $T=T^0$, the *exact* ℓ–v equilibrium behavior is determined from Eqs. (4) and (9) as

$$\mu_v^0\left(T^0\right) + \int_{P^\circ}^{P} V_{m,v}\left(T^0,P'\right)dP = \mu_\ell^0\left(T\right) + \int_{P^\circ}^{P} V_{m,\ell}\left(T^0,V'\right)dP'. \tag{14}$$

The exact equilibrium condition for Eq. (4), for $T=T^0$, reduces to the approximate condition of Eq. (10) if:

$$V_{m,v}\left(T^0,P'\right) \gg V_{m,\ell}\left(T^0,P'\right) \tag{15}$$

and if

$$\int_{P_0}^{P} V_{m,v}\left(T^0,P'\right) = RT^0 \ln\left(\frac{P}{P^0}\right) \tag{16}$$

(i) Assuming that $P' = P^0$ and that the vapor is an ideal gas, show numerically that Eq. (15) is a valid approximation.

(ii) Assuming again that the vapor is an ideal gas, derive Eq. (16).

b. Explain why P in Eq. (10) is the vapor pressure of the liquid $P_{vap}(T)$ at temperature T.

c. From Eq. (10), numerically compute $P_{vap}(T^0)$ of $H_2O(\ell)$ in bars. Compare with the experimental value $P_{vap}(T^0) = 0.03168\text{bar}$.

Problem 2

Problem 2 concerns the triple point (tp) of water. The triple point is the state for which T and P have the values

$$T_{tp} = 273.16\text{K and } P_{tp} = 0.00611. \tag{17}$$

T_{tp} and P_{tp} may be computed by solving the following pair of simultaneous equations

$$\mu_\ell(T_{tp},P_{tp}) = \mu_v(T_{tp},P_{tp}) \text{ and } \mu_\ell(T_{tp},P_{tp}) = \mu_s(T_{tp},P_{tp}). \tag{18}$$

In this problem you will compute P_{tp} from an approximation to Eq. (18) and then compare your result with the experimental value given in Eq. (17).

This approximation is based on the fact that the standard melting temperature of water $T_{sf} = 273.15\text{K}$ (sf denotes standard fusion) is very close to $T_{tp} = 273.16\text{K}$. In fact the standard melting point of water is the state with the T,P values

$$T_{sf} = 273.15\text{K} \text{ and } P_{sf} = P^\circ. \tag{19}$$

a. Explain why Eq. (18) is the correct condition for determining T_{tp} and P_{tp}. (Hint: refer to Eq. [11].)

b. This part concerns determination of $\mu_\ell^0(T_{sf})$, $\mu_v^0(T_{sf})$, and $\mu_s^0(T_{sf})$.

(i) Compute in kJmol^{-1} $\mu_\ell^0(T_{sf})$. Box your result.

(ii) Compute kJmol^{-1} $\mu_v^0(T_{sf})$. Box your result.

(iii) Show numerically that

$$\mu_v^0(T_{sf}) > \mu_\ell^0(T_{sf}). \tag{20}$$

(iv) Explain why Eq. (20) proves that the v and ℓ phases are *not* in equilibrium for the standard melting state of Eq. (19).

(v) Explain why

$$\mu_s^0(T_{sf}) = \mu_\ell^0(T_{sf}) \tag{21}$$

c. This part concerns relating the μ's at T_{tp} to those at T_{sf}.

Because $T_{sf} = 273.15$ is so close to $T_{tp} = 273.15$K, we claim that to a very good approximation

$$\mu_\ell(T_{tp},P) = \mu_\ell(T_{sf},P) \tag{22a}$$

$$\mu_v(T_{tp},P) = \mu_v(T_{sf},P) \tag{22b}$$

and

$$\mu_s(T_{tp},P) = \mu_s(T_{tp},P). \tag{22c}$$

Numerically verify this claim for the case of Eq. (22a). That is, numerically compute the $\mu_\ell(T_{tp},P)$ and compare with your boxed result for $\mu_\ell(T_{sf},P)$.

(Recall we have assumed the μ_ℓ is pressure independent and so we can take $P=P^\circ$ when computing $\mu_\ell[T,P]$.)

d. Show that given Eqs (22) the triple point condition (18) reduces to

$$\mu_\ell^0(T_{sf}) = \mu_v(T_{sf},P_{tp}) \text{ and } \mu_\ell^0(T_{sf}) = \mu_s^0(T_{sf}). \tag{23}$$

e. The second relation in (23) is identical to Eq. (21) and thus is already obeyed. The first relation in (23) is an equation for P_{tp}.

(i) Solve the first relation in (23) to obtain a numerical result for P_{tp} in bar units. Box your result. (Hint: recall Eqs. [8] or Eq. [10].)

(ii) Compare your result to the experimental P_{tp} value given in Eq. (17). What is your opinion of the validity of the approximations we used?

Periodic Classification of the Elements

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	O
1 H 1.00797																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.903	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.9044	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac† (227)															

*Lanthanides	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
†Actinides	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lw (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)