

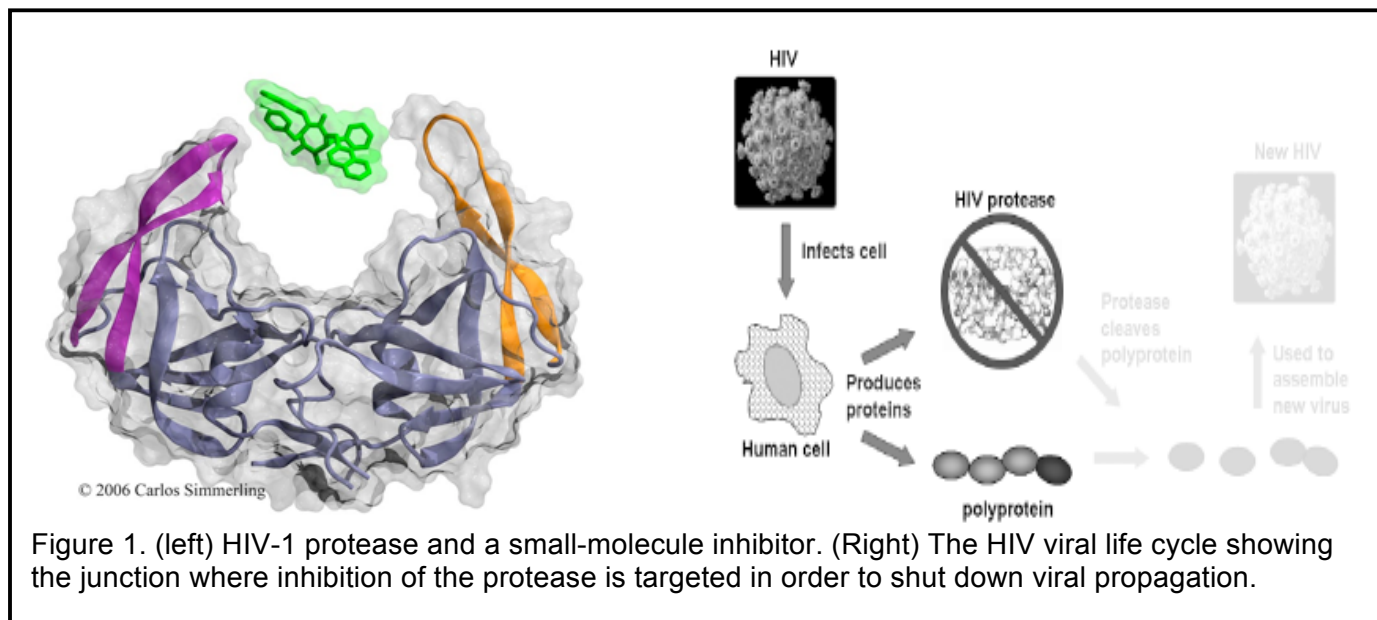
Directions: Please answer each question to the best of your ability. Make sure your response is **legible, precise, includes relevant dimensional units (where appropriate), logically presented (include non-mathematical language if necessary to convey your intent clearly and transparently), and correct/accurate.** You are free to use your Equations Handbook, Calculator, blunt/sharp writing instrument, and brain (your choice). If you have any doubt(s) about the meaning/intent of a question(s), please ask immediately so you do not wander off on an incorrect path! **Please leave all responses to be graded on the exam sheet. Work on scratch paper will not be considered.** For all questions (excluding multiple choice, fill in the blank, and true/false), even when ostensibly simple, single-value numerical values are requested, responses showing **no work** involved in the determination of final answers will be given **no credit**.

Problem	Points
1	/10
2	/10
3	/10
4	/10
5	/20
6	/15
7	/10
8	/10
9	/5
Extra Credit	/5
Total	/100

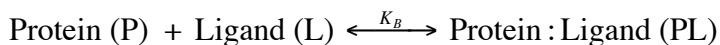
**1 (10 Points)** Matching / Fill-In. Provide the proper response from the right column in the blanks provided in the left column. *Keep in mind that some blanks in the left column may require multiple selections from the choices in the right column.*

1. Examples of colligative properties include freezing point depression and critical opalescence, true or false? <u>          <b>H</b>          </u>	<b>A</b> a
2. At the azeotropic condition for a two-phase (alpha and beta) binary (species A and B) system, what condition pertaining to phase compositions holds? <u>          <b>I</b>          </u>	<b>B</b> $\left(\frac{\partial F}{\partial P}\right)_U = \left(\frac{\partial V}{\partial G}\right)_H$
3. For a dilute solute in a binary solution (i.e. dissolved oxygen in water), the solute fugacity is expressed as $\hat{f}_i^{\text{liquid solution}}(T, P, \{x\}) = x_i K_i^{HL}(T, P)$ True or False? <u>   <b>G</b>   </u>	<b>C</b> Gibbs-Duhem equation
4. The formation of an ideal liquid solution entails what changes in total enthalpy and total volume? <u>          <b>S</b>          </u>	<b>D</b> less than zero
5. For a 3-phase, two-component system in equilibrium, how many intensive degrees of freedom are available? For this question, one chemical component is able to partition into all 3 phases, while the second component equilibrates between only two of the three phases. <u>   <b>M</b>   </u>	<b>E</b> greater than zero
6. The Third Law of Thermodynamics arises from the observation that as absolute temperature approaches zero, the <u>          <b>L</b>          </u> of a pure fluid also must approach zero to ensure that we can obtain a non-singular value of entropy at T = 0 Kelvin.	<b>F</b> $x_A = y_A; x_B = (1-x_B)$
7. In the Van der Waals equation of state, the <u>   <b>A</b>   </u> parameter relates to the attractive interactions between particles.	<b>G</b> true
8. Defining the equilibrium constant in terms of reactant and product molar concentrations is the most general formulation of this thermodynamic quantity. True or False? <u>          <b>H</b>          </u>	<b>H</b> false
9. In multi-component systems, the <u>   <b>C</b>   </u> relates individual species activities to one another.	<b>I</b> $x_A = y_A; x_B = (1-x_A)$
10. Consider the solidification of liquid water introduced into an environment at T= -10 Celsius ; the entropy change of the water is negative. What can we say about the entropy change of the environment? <u>   <b>E</b>   </u>	<b>J.</b> $\mu_i^A(T, P) = \mu_i^B(T, P)$
	<b>K</b> $\Delta H = 0; \Delta V = RT \ln(P)$
	<b>L</b> heat capacity
	<b>M</b> one
	<b>N</b> enthalpy
	<b>O</b> $\Delta H=RT \ln(x); \Delta V = RT \ln(P)$
	<b>P</b> zero
	<b>Q</b> $T^A=T^B$ (T=temperature)
	<b>R</b> Helmholtz Free Energy
	<b>S.</b> $\Delta H = 0; \Delta V = 0$

**2. (10 Points)** Much effort has been directed toward finding drugs to combat the AIDS syndrome caused by HIV. Thermodynamics makes a contribution to that effort by facilitating interpretation of experimental calorimetric titration data. *Isothermal titration calorimetry* (ITC) provides information about the energetics of the interactions between physiologically important macromolecules and small substrates (i.e. low-molecular weight drugs non-covalently interacting with, i.e. *binding* to, protein receptor targets). An example is the inhibitor drug Ritonavir binding to a polypeptide cleaving site of HIV-1 protease (a protease is a protein that cleaves peptide bonds) shown in *Figure 1*. (The binding of the drug in the binding site prevents the cleavage of the viral polypeptide chain into functionally active proteins the virus needs to propagate, *Figure 1, right panel*).



The ITC method is based on measuring the incremental amounts of heat requiring removal from or addition to a solution of the macromolecule as small amounts of the ligand (i.e., the small molecule) are added over time. In the simplest practical scenario, the reversible binding “reaction” is pictured as:



By assuming that there is a single binding site, one can derive relationships between the enthalpy of binding at standard conditions ( $\Delta H^\circ$ ), the binding constant,  $K_B$ , and the number of binding sites (in this case taken to be 1 binding site).

For the HIV-1 protease system, binding constants from ITC measurements at 25 Celsius are shown in Table 1. The enthalpies of binding, from the same set of experiments, are also shown. **Determine the associated changes in Gibbs free energy and entropy for the various drugs.**

	Ritonavir	Saquinavir	Nelfinavir	Indinavir
$\Delta H^\circ$ (kcal/mol)	-3.70	1.90	2.60	2.10
$K_B$	22.65	19.97	19.30	20.13
$\Delta G^\circ$ (kcal/mol)	-1.85	-1.78	-1.76	-1.78
$\Delta S^\circ$ (kcal/mol-K)	-0.0062	0.013	0.015	0.013

Binding enthalpy data from: Luque *et al.* PROTEINS: Structure, Function, Genetics. **49**:181-190. 2002.

Binding constant data from: Valezquez-Campoy *et al.* Archives of Biochemistry and Biophysics. **390**:169-175. 2001.

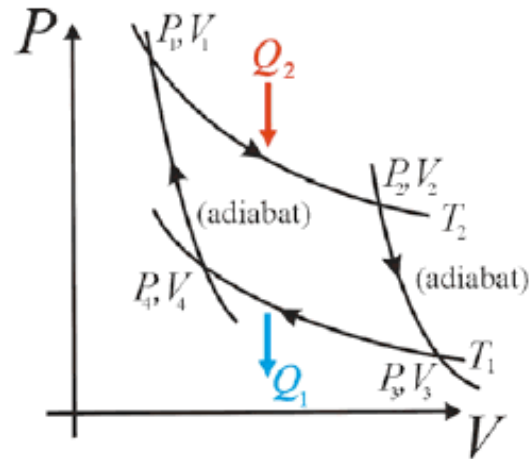
**Solution:**

$$\Delta G^\circ = -RT \ln(K_B) = -(0.00199 \frac{\text{kcal}}{\text{mol K}})(298\text{K}) \ln(22.65) = -1.85 \text{kcal/mol}$$

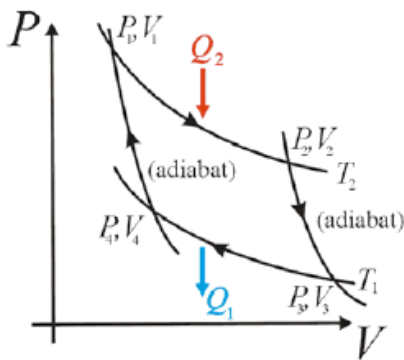
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-3.70 \text{kcal/mol} - (-1.85 \text{kcal/mol})}{298\text{K}} = -0.0062 \text{kcal/mol-K}$$

Repeat calculations for all drugs.

**3. (10 Points)** An ideal Carnot engine, with an efficiency  $\eta = 0.40$ , operates using 0.5 kilomoles of an ideal **diatomic gas** as the working substance. During the isothermal expansion stage, the pressure of the gas decreases to half of the maximum pressure on the cycle. At the end of the adiabatic expansion stage, the pressure of the gas is 9 atm and its volume is  $2 \text{ m}^3$ .



**A.** Calculate the heat absorbed from the high temperature reservoir during the isothermal expansion stage of the cycle.



We are given values of  $P$ ,  $V$  and  $n$  for one part of the low temperature isotherm (end of adiabatic expansion stage). We can use this info. to calculate  $T_1$ :

$$T_1 = \frac{P_3 V_3}{nR} = \frac{(9 \text{ atm}) \times (1.01 \times 10^5 \text{ Pa/atm}) \times (2 \text{ m}^3)}{0.5 \text{ kilomoles} \times 8314 \text{ J} \cdot \text{K}^{-1} \cdot \text{kilomoles}^{-1}} = 437 \text{ K},$$

where the subscripts refer to the figure (left). Now that we know  $T_1$ , we can calculate  $T_2$  from the efficiency (or we could calculate  $Q_1$ , then get  $Q_2$  from the efficiency).

$$\eta = 1 - \frac{T_1}{T_2} = 0.4 \quad \Rightarrow \quad \frac{T_1}{T_2} = 0.6, \quad \text{or} \quad T_2 = \frac{T_1}{0.6} = 729 \text{ K}.$$

On an isotherm,  $\Delta U = 0$ ,  $\Rightarrow \Delta Q = \Delta W$ , i.e.  $Q_2 = \int P dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT_2 \ln \frac{P_1}{P_2}$

$$\Rightarrow Q_2 = 0.5 \text{ kilomoles} \times 8314 \text{ J} \cdot \text{K}^{-1} \cdot \text{kilomole}^{-1} \times 729 \text{ K} \times \ln(2) = 2.10 \text{ MJ}.$$

B. Calculate the work done by the gas during each of the 4 stages of the cycle.

**(b) Calculate the work done by the gas during each of the four stages of the cycle.**

On the isotherms,  $dU = 0$  and  $dQ = dW$  ( $Q = W$ ). We already know  $Q_2 = W_{ie}$ , and we can calculate  $Q_1$  from the efficiency, i.e.  $Q_1 = -0.6 \times Q_2 = -1.26$  MJ. Thus,  $W_{ic} = -1.26$  MJ and  $W_{ie} = 2.10$  MJ, where the subscripts *ie* and *ic* stand for ‘isothermal compression’ and ‘isothermal expansion’, respectively.

On the adiabats,  $dQ = 0$ , so  $dU = -dW = nc_V \Delta T$ . For an ideal diatomic gas,  $c_V = 5R/2$ , and  $\Delta T = \pm(729 - 437)$  K =  $\pm 292$  K. Consequently,

$$W_{ae} = -nc_V (T_1 - T_2) = (0.5 \text{ kilomoles}) \times (2.5 \times 8314 \text{ J} \cdot \text{K}^{-1} \cdot \text{ kilomoles}^{-1}) \times (292 \text{ K}) = 3.03 \text{ MJ}.$$

$$W_{ac} = -W_{ae} = -3.03 \text{ MJ},$$

where the subscripts *ae* and *ac* stand for ‘adiabatic compression’ and ‘adiabatic expansion’, respectively.

C. Calculate the entropy changes for each of the 4 stages of the cycle.

**(c) Determine the change in entropy of the gas during each of the four stages of the cycle.**

The entropy is trivial. There is no change in entropy on the adiabats, because the Carnot cycle is reversible, i.e.  $\Delta S_{ae} = \Delta S_{ac} = 0$ .

For the isotherms, the entropy change is given simply by  $\Delta Q/T$ . Therefore,

$$\Delta S_{ie} = \frac{Q_2}{T_2} = \frac{2.1 \text{ MJ}}{729 \text{ K}} = 2880 \text{ J/K}$$

and

$$\Delta S_{ic} = \frac{Q_1}{T_1} = \frac{-1.26 \text{ MJ}}{437 \text{ K}} = -2880 \text{ J/K}$$

Since the Carnot cycle operates between two reversible adiabats, it should be no surprise that these answers are equal in magnitude and opposite in sign.

**4 (10 Points)** Consider a rubber band of length  $L$  maintained at a tension  $f$ . The total differential of the extensive internal energy of the rubber band comprised of  $n$  moles of material is:

$$dU = T dS + f dL + \mu dn$$

where  $U$  is the extensive internal energy,  $T$  is the temperature,  $S$  is the extensive entropy,  $f$  is the tension,  $L$  is the length,  $\mu$  is the chemical potential of the rubber band, and  $n$  is the number of moles of material. The

equation of state (EOS) of this system is  $U = \frac{\theta S^2 L}{n^2}$ . Derive the Gibbs-Duhem relation for this system. Recall that the Gibbs-Duhem relation is the total Legendre Transform of internal energy,  $U$ .

**Solution:**

$$dU = TdS + fdL + \mu dn$$

Thus

$$U = TS + fL + \mu n$$

The Gibbs-Duhem relation is the total Legendre Transform of  $U$ :

$$U - TS - fL - \mu n = 0$$

$$TdS + fdL + \mu dn - TdS - SdT - fdL - Ldf - \mu dn - nd\mu = 0$$

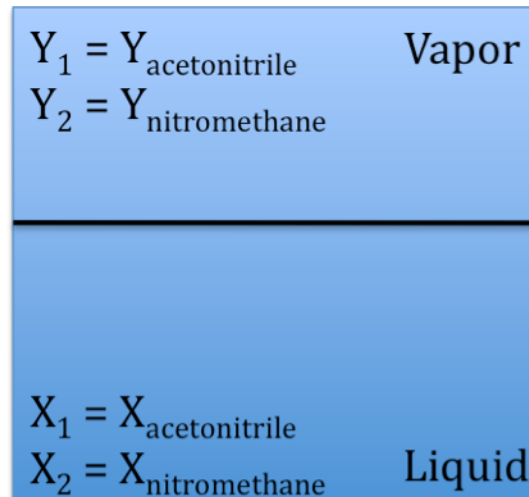
$$-SdT - Ldf - nd\mu = 0$$

or

$$SdT + Ldf + nd\mu = 0$$

The last two equations are expressions of the Gibbs-Duhem relation for this system

5. (20 Points) Consider the binary system composed of acetonitrile(1) and nitromethane(2). This system forms ideal vapor and liquid mixtures.



At thermodynamic conditions where the liquid mixture is in equilibrium with the gas mixture:

A. How many independent intensive variables (degrees of freedom) are available?

B. At a total pressure,  $P_{\text{Total}} = 70 \text{ kPa}$ , and liquid composition of  $x_1 = 0.5156$ , what are the **temperature** and **vapor phase composition**, again considering that vapor and liquid phases are in equilibrium. The following information may be helpful.

Temperature in Celsius and pressure in kilopascal (kPa) for the following equations.

$$\ln P_1^{\text{saturation}} = 14.2724 - \frac{2945.47}{T + 224.0}$$

$$\ln P_2^{\text{saturation}} = 14.2043 - \frac{2972.64}{T + 209.0}$$

**Solution:**

This question asks for the temperature at the given pressure and liquid-phase composition. This will be an iterative solution, since the temperature enters non-linearly into the analysis via the relations for the saturation pressures given above. Keep in mind that the vapor is an ideal gas mixture and the solution is ideal, thus following Raoult's expression.



$$P_{Total} = P_1 + P_2 = y_1 P_{Total} + y_2 P_{Total} = x_1 P_1^{saturation} + x_2 P_2^{saturation}$$

$$P_{Total} = P_2^{saturation} \left( x_1 \frac{P_1^{saturation}}{P_2^{saturation}} + x_2 \right) \quad (A)$$

Define,  $\alpha_{12}$

$$\alpha_{12} = \frac{P_1^{saturation}}{P_2^{saturation}} \Rightarrow \ln(\alpha_{12}) = 0.0681 - \frac{2945.47}{T + 224.0} + \frac{2972.64}{T + 209.0} \quad (B)$$

$$P_2^{saturation} = \frac{P_{Total}}{\left( x_1 \frac{P_1^{saturation}}{P_2^{saturation}} + x_2 \right)} = \frac{P_{Total}}{(x_1 \alpha_{12} + x_2)} \quad (C)$$

Iteration Procedure:

1. Pick initial temperature
2. Compute  $\alpha_{12}$  (equation B)
3. Compute  $P_2$ (saturation) (equation C)
4. Compute T using inverted saturation pressure relations
5. Compute new  $\alpha_{12}$  and  $P_2$  (saturation) using equations B and C
6. Iterate until convergence

Results of Iterations

Iteration #	Temp for step 2	Temp for step 4	Difference between Temp for steps 2 and 4
1	77.4065030730214	70.0000000000000	7.40650307302144
2	77.9577905146540	77.4065030730214	0.551287441632553
3	77.9970941220114	77.9577905146540	3.930360735745353E-002
4	77.9998874331253	77.9970941220114	2.793311113862273E-003
5	78.0000859095134	77.9998874331253	1.984763880500395E-004
6	78.0001000118627	78.0000859095134	1.410234932563981E-005

We achieve convergence within 6 iterations even with a bad guess of 70 Celsius in the initial step.

Vapor phase composition:

$$y_1 P_{Total} = x_1 P_1^{saturation}$$

$$y_1 = \frac{x_1 P_1^{saturation}}{P_{Total}} = \frac{(0.5156) \left( e^{14.2724 - \frac{2945.47}{78+224}} \right)}{70}$$

$$= (0.007366)(91.743)$$

$$= 0.6758$$

**6. (15 Points)** This problem addresses a simple model for the adsorption of particles in a gaseous phase onto a solid surface. This is one way to develop the Langmuir Adsorption Isotherm from a microscopic view of matter. Consider a surface having a total of 'A' binding sites. We are interested in 'N' particles adsorbing onto the surface (adsorption is non-covalent interaction of a particle with a surface binding site). For this problem, we will consider that the adsorbing particles do not interact with one another.

**A (10 Points)** Determine an expression for the entropy associated with 'N' particles adsorbed onto a surface having a total of 'A' binding sites. Consider that N is less than or equal to A. Cast your final expression for  $\frac{S}{Ak_B}$  in terms of fractional surface coverage,  $\theta = \frac{N}{A}$ . Also consider the thermodynamic limit

where  $N \rightarrow \infty$  and  $A \rightarrow \infty$ , with  $\theta = \frac{N}{A}$  still bound to finite values. Useful relations may be:

$$\frac{S}{k_B} = \ln(W); \quad \text{Binomial Coefficient, } W(n,k) = \frac{n!}{k!(n-k)!}, \quad 0 \leq k \leq n$$

*Stirling's Approximation :*

$$\ln(N!) = N \ln N - N$$

**Solution:**

$$S = k_B \ln(W)$$

$$\begin{aligned} \frac{S}{k_B} &= \ln(W) = \ln\left(\frac{A!}{N!(A-N)!}\right) = \ln(A!) - \ln(N!) - \ln((A-N)!) \\ &= \{A \ln(A) - A\} - \{N \ln(N) - N\} - \{(A-N) \ln(A-N) - (A-N)\} \\ &= A \ln(A) - N \ln(N) - (A-N) \ln(A-N) \\ &= A[\ln(A) - \ln(A-N)] - N[\ln(N) - \ln(A-N)] \end{aligned}$$

$$\frac{S}{Ak_B} = [\ln(A) - \ln(A-N)] - \left(\frac{N}{A}\right)[\ln(N) - \ln(A-N)] = \ln\left(\frac{A}{A-N}\right) - \left(\frac{N}{A}\right)\ln\left(\frac{N}{A-N}\right)$$

But  $N = \theta A$

$$\begin{aligned} \frac{S}{Ak_B} &= \ln\left(\frac{A}{A-\theta A}\right) - \left(\frac{N}{A}\right)\ln\left(\frac{A}{A-\theta A}\right) = \ln\left(\frac{1}{1-\theta}\right) - \theta \ln\left(\frac{\theta}{1-\theta}\right) \\ &= -\theta \ln(\theta) - (1-\theta)\ln(1-\theta) \end{aligned}$$

**B (5 Points)** What numerical value of  $\theta = \frac{N}{A}$  maximizes the surface entropy? Show all work necessary to arrive at your answer.

**Solution:**

$$\frac{dS}{d\theta} = 0 \quad \text{Maximizes entropy}$$

$$\frac{dS}{d\theta} = -\ln(\theta) - 1 + \ln(1-\theta) + 1 = 0$$

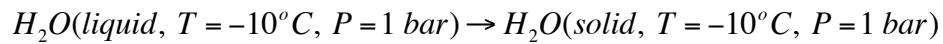
$$0 = \ln\left(\frac{1-\theta}{\theta}\right)$$

$$1 = \frac{1-\theta}{\theta}$$

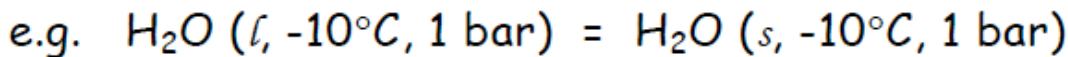
$$2\theta = 1$$

$$\theta = 0.5$$

7. (10 Points) For the following process at  $T = -10$  Celsius and  $P = 1$  bar (constant  $T$  and  $P$ ) in which water spontaneously and completely freezes, determine an expression for the entropy change for water. State any assumptions you make. For constant pressure or constant volume heat capacities used, please indicate what phase of the material the property is associated with. Also, please indicate the definition of any changes in thermodynamic properties you incorporate into your expression.

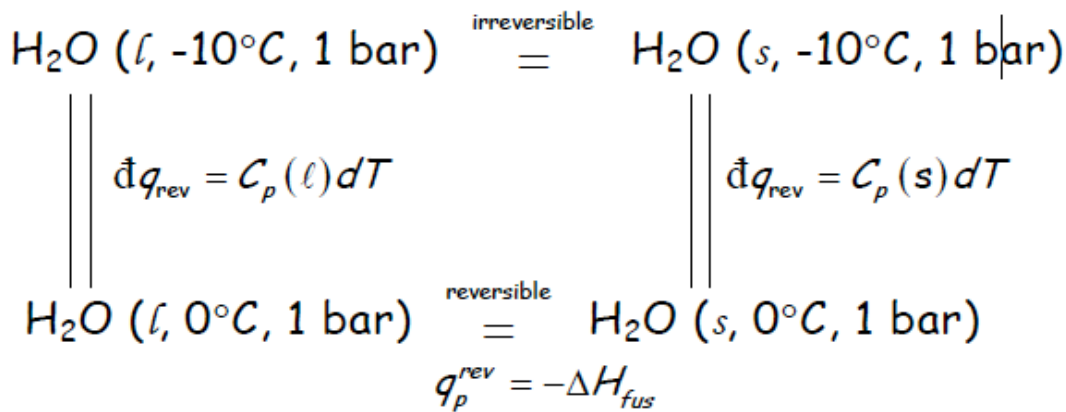


(d) Irreversible phase change at constant  $T$  and  $p$



This is spontaneous and irreversible.

$\therefore$  We need to find a reversible path between the two states to calculate  $\Delta S$ .

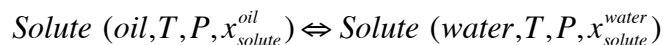


$$\begin{aligned}\Delta S &= \Delta S_{\text{heating}} + \Delta S_{\text{fus}} + \Delta S_{\text{cooling}} \\ &= \int_{T_1}^{T_{\text{fus}}} \frac{C_p(\ell) dT}{T} + \frac{-\Delta H_{\text{fus}}}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{T_1} \frac{C_p(s) dT}{T}\end{aligned}$$

$$\therefore \boxed{\Delta S = \frac{-\Delta H_{\text{fus}}}{T} + \int_{T_1}^{T_{\text{fus}}} [C_p(\ell) - C_p(s)] \frac{dT}{T}}$$

$$\Delta S = \frac{-\Delta H_{\text{fus}}}{T} + [C_p(\ell) - C_p(s)] \ln \frac{T_{\text{fus}}}{T_1} \quad \text{if } C_p \text{ values are } T\text{-independent}$$

**8 (10 Points)** A traditional property of medicinal compounds used to assess the ability of molecules to transfer between phases (i.e., aqueous to hydrophobic as involved in partitioning from outside to inside of cells) is the oil/water partition coefficient. This coefficient models the following equilibrium:



The partition coefficient is  $K_{\text{oil}}^{\text{water}}(T) = \frac{x_{\text{solute}}^{\text{water}}}{x_{\text{solute}}^{\text{oil}}}$ . We are given for a particular compound that at  $T=300\text{K}$ , the partitioning process between water and oil involves  $\Delta s^\circ = -50 \text{ cal (mol K)}^{-1}$  and  $\Delta h^\circ = 0$ .

**A.** What is  $\Delta\mu^\circ$  at  $T=300\text{K}$ ?

$$\Delta\mu^\circ = \Delta h^\circ - T\Delta s^\circ = 0 - (300\text{K})(-50\text{cal/mol K}) = 15\text{kcal/mol}$$

**B.** What is the partition coefficient at  $T=300\text{K}$ ?

$$\Delta\bar{G}^\circ = \Delta\mu^\circ = -RT \ln(K)$$

$$K = \exp\left(\frac{-\Delta\mu^\circ}{RT}\right) = \exp\left(\frac{-15\text{kcal/mol}}{(0.00199\text{kcal/mol K})(300\text{K})}\right) = 1.2 \times 10^{-11}$$

Since the entropy change for this molecule is so large and negative, the partition coefficient is very small. The free energy for partitioning is positive, thus driving the partition coefficient (equilibrium constant) to a small value.

**C.** Estimate the partition coefficient at  $T=320\text{K}$ ? State any assumptions you make.

$$\left(\frac{d \ln K}{dT}\right) = \frac{-\Delta h^\circ}{R} \frac{dT}{T^2} = 0$$

Assuming the enthalpy of partitioning is very weakly temperature dependent over this temperature range.

Thus,

$$K = 1.2 \times 10^{-11}$$

**9 (5 Points)** Find the molecular weight of a compound that has a weight concentration of 1.2 grams/L in solution and an osmotic pressure of 0.2 atm at T=300K.

$$\Pi = CRT$$

$$= \frac{n}{V} RT = \frac{w}{(V)(MW)} RT = \frac{1.2 \text{ gram}}{L} \frac{RT}{MW}$$

$$MW = \frac{1.2RT}{\Pi} = \frac{1.2(\text{gr} / L)(0.08206 L - \text{atm} / \text{molK})(300 K)}{0.2 \text{ atm}} = 147 \text{ gr} / \text{mol}$$

**Extra Credit (5 Points)** For a second order phase transition, the molar enthalpy, entropy, and volume for a pure fluid are **continuous** functions through the phase change. Thus, like the equality of chemical potentials of a pure fluid in the coexisting phases for a first-order transition, one can write the equality of the molar volume, enthalpy, and entropy of the two phases (denote them  $\alpha$  and  $\beta$ ) along the coexistence line for such fluids. Consider the equality of molar volume for this problem. Based on the above information, determine a relation analogous to the Clausius-Clapeyron equation that relates the slope along the coexistence line,  $\frac{dP}{dT}$  to the coefficient of thermal expansion and isothermal compressibility of the coexisting phases of the fluid. Recall that molar volume, a state function, can be expressed in terms of state variables such as temperature and pressure; that is,  $V_m = V_m(T,P)$ . Thus, its total differential can be expressed as:

$$dV_m(T,P) = \left( \frac{\partial V_m(T,P)}{\partial T} \right)_P dT + \left( \frac{\partial V_m(T,P)}{\partial P} \right)_T dP$$

$$V_m^\alpha = V_m^\beta$$

Moving along the coexistence line, the above equality leads to :

$$dV_m^\alpha = dV_m^\beta$$

Thus

$$\left( \frac{\partial V_m^\alpha(T,P)}{\partial T} \right)_P dT + \left( \frac{\partial V_m^\alpha(T,P)}{\partial P} \right)_T dP = \left( \frac{\partial V_m^\beta(T,P)}{\partial T} \right)_P dT + \left( \frac{\partial V_m^\beta(T,P)}{\partial P} \right)_T dP$$

But

$$V_m^\alpha \tau_V^\alpha dT - V_m^\alpha \kappa_V^\alpha dP = V_m^\beta \tau_V^\beta dT - V_m^\beta \kappa_V^\beta dP$$

where the coefficient of thermal expansion is  $\tau_V^\alpha = \frac{1}{V_m^\alpha} \left( \frac{\partial V_m^\alpha}{\partial T} \right)_P$  and the isothermal compressibility is

$$\kappa_V^\alpha = \frac{1}{V_m^\alpha} \left( \frac{\partial V_m^\alpha}{\partial P} \right)_T$$

Thus, since

$$V_m^\alpha = V_m^\beta$$

$$\tau_V^\alpha dT - \kappa_V^\alpha dP = \tau_V^\beta dT - \kappa_V^\beta dP$$

$$\frac{(\kappa_V^\alpha - \kappa_V^\beta) dP}{(\tau_V^\alpha - \tau_V^\beta) dT} = 1$$

$$\frac{dP}{dT} = \frac{(\tau_V^\alpha - \tau_V^\beta)}{(\kappa_V^\alpha - \kappa_V^\beta)}$$