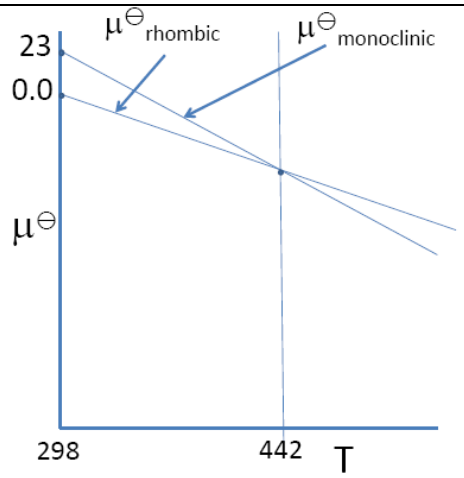
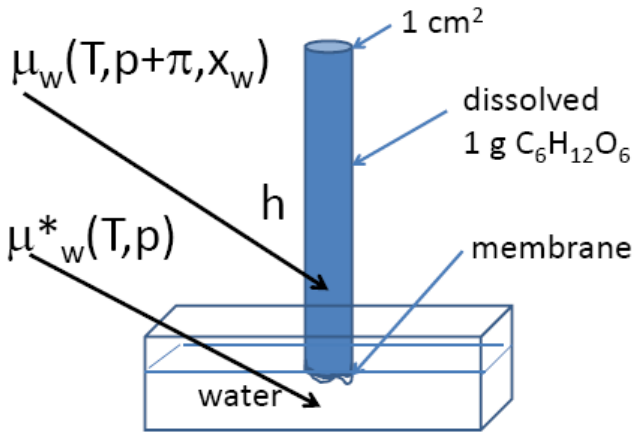
Solutions to Problem Set 7

1. (a) rhombic sulfur $\rightarrow$ monoclinic sulfur

Equation	Basis for the equation	Eq. #
$d\mathbf{G} = Vdp - \mathbf{S}dT$	one of the four fundamental equations of thermodynamics	1
$\int d\mathbf{G} = \int Vdp - \int \mathbf{S}dT$	integrate between (1 bar, 298 K) and (1 bar, T K)	2
$\mathbf{G}^{\ominus}_T - \mathbf{G}^{\ominus}_{298} = 0 - [T\mathbf{S}^{\ominus}_T - 298\ \mathbf{S}^{\ominus}_{298}]$		3
$\mathbf{G}^{\ominus}_T = \mathbf{G}^{\ominus}_{298} - [T\mathbf{S}^{\ominus}_T - 298\ \mathbf{S}^{\ominus}_{298}]$ $\mathbf{G}^{\ominus}_T = \mathbf{G}^{\ominus}_{298} - [T - 298\ ]\bullet\mathbf{S}^{\ominus}_{298}$	Assume that $\mathbf{S}^{\ominus}_T = \mathbf{S}^{\ominus}_{298}$ since given that the entropies vary only slightly with temperature for sulfur	4
$\mathbf{G}^{\ominus}_{T,r} = \mathbf{G}^{\ominus}_{298,r} - [T - 298\ ]\bullet\mathbf{S}^{\ominus}_{298,r}$ $\mathbf{G}^{\ominus}_{T,m} = \mathbf{G}^{\ominus}_{298,m} - [T - 298\ ]\bullet\mathbf{S}^{\ominus}_{298,m}$	Write this for rhombic and monoclinic sulfur	5
$\mathbf{G}^{\ominus}_{T,r} = \mathbf{G}^{\ominus}_{T,m}$	At temperature T rhombic and monoclinic sulfur are in equilibrium at 1 bar	6
$\mathbf{G}^{\ominus}_{298,r} - [T - 298\ ]\bullet\mathbf{S}^{\ominus}_{298,r} = \mathbf{G}^{\ominus}_{298,m} - [T - 298\ ]\bullet\mathbf{S}^{\ominus}_{298,m}$	Substituting Eq 5 into Eq 6	7
$0.0 - [T-298]\bullet 7.62 = 23 - [T - 298\ ]\bullet 7.78$	Substituting the numerical values into Eq. 7	8
T = 441.8 K **Answer**	Solving for T. At this temperature rhombic and monoclinic sulfur are in equilibrium at 1 bar	9
	Sketch $\mu^{\ominus}$ vs. T for rhombic and monoclinic sulfur. The slope of the $\mu^{\ominus}$(T) vs. T plot is $-\mathbf{S}^{\ominus}$ By the way, this problem is an example in lecture notes part 6.	10

1. (b) For equilibrium to be established (no more net influx of water from the water side through the membrane to the glucose solution side), the chemical potential of water should be the same on both sides of the membrane.
On the solution side of the membrane there is an additional pressure π arising from the column of solution. The osmotic pressure is the additional pressure that needs to be applied to the solution side to achieve equilibrium with the pure solvent at pressure p.



For the ideal solution, we can use mole fraction instead of activity

Equation	Basis for the equation	Eq. #
$\mu^*_{A,liquid} = \mu^*_{A,vapor}$	For pure liquid A in equilibrium with its own vapor at temperature T (* means pure)	1
$\mu_{A,\ liquid\ solution} = \mu_{A,vapor}$	For A in solution of A and B, in equilibrium with the vapor containing both A and B	2
$\mu_{A,vapor} = \mu^{\ominus}_{A,T} + RT\ln(p_A/1)$	For an ideal gas at temperature T (We assume ideal vapor for this problem ; if non-ideal must use f_A instead of p_A)	3
$\mu_{A,vapor} = \mu^{\ominus}_{A,T} + RT\ln(p_A/1)$	For ideal vapor over a solution of A and B	4
$\mu^*_{A,vapor} = \mu^{\ominus}_{A,T} + RT\ln(p^*_A/1)$	For ideal vapor over pure liquid A	5
$\mu_{A,\ liquid\ solution} - \mu^*_{A,liquid} = \{\mu^{\ominus}_{A,T} + RT\ln(p_A/1)\} - \{\mu^{\ominus}_{A,T} + RT\ln(p^*_A/1)\}$	Eq 2 minus Eq 1	6
$\mu_{A,\ liquid\ solution} - \mu^*_{A,liquid} = RT\ln(p_A/p^*_A)$		7
$(p_A/p^*_A) = x_A$	For an ideal solution, Raoult's law holds , where x_A is the mole fraction of A in the liquid solution	8
$\mu_{A,\ liquid\ solution} - \mu^*_{A,liquid} = RT\ln x_A$		9
$\mu^*_{w,\ liquid}\ (T,p)$	For water in pure liquid water under pressure p and temperature T	10
$\mu_{w,\ liquid\ solution}\ (T,\ p+\pi,x_w) - \mu^*_{w,liquid}\ (T,\ p+\pi) = RT\ln x_w$	For water in solution in which its mole fraction is x_w under pressure $p+\pi$ and temperature T	11
$\mu^*_{w,\ liquid}\ (T,p) = \mu_{w,\ liquid\ solution}\ (T,p+\pi,x_w)$	At equilibrium, chemical potential of water is the the same on both sides of the membrane	12

$\mu^*_{w,\,liquid}(T,p) - \mu^*_{w,liquid}(T,\, p+\pi) = RT \ln x_w$	Substitute Eq 12 into Eq 11	13
$\mu^*_{w,liquid}(T,\, p+\pi) - \mu^*_{w,\,liquid}(T,p) = - RT \ln x_w$	Rearrange	14
$d\mathbf{G} = Vdp - \mathbf{S}dT$	one of the four fundamental equations of thermodynamics	15
$d\mu = (\partial\mu/\partial p)_T dp + (\partial\mu/\partial T)_p dT$ $d\mu = (\partial\mu/\partial p)_T dp = Vdp$	$\mu = \mu(T,p)$ apply it to constant temperature as in this problem and identify $(\partial\mu/\partial p)_T$	16
$\mu^*_{w,liquid}(T,\, p+\pi) - \mu^*_{w,\,liquid}(T,p)$ $= \int_p^{p+\pi} (\partial\mu/\partial p)_T dp$ $= \int_p^{p+\pi} Vdp = V(p+\pi-p) = V\pi$	Identify the integral which produced the LHS of Eq 14	17
$V\pi = - RT \ln x_w$	From Eq 14 and 15	18
$\ln x_w = \ln(1-x_G) \approx -x_G - (1/2)x_G^2 - (1/3)x_G^3 - \ldots$	Use the sum of mole fractions = 1 and expand the *ln* in a series	19
$V\pi = RT\, x_G$	The relation between molar volume of liquid water the osmotic pressure and the mole fraction (of glucose in this problem).	20
$\pi = \rho g h$ $\rho = 1$ g cm^{-3} $\pi = 1$ g cm$^{-3}\times 980.66$ cm s$^{-2}\times$ h cm $\times$ 10^{-3} kg/g $\times 10^2$ cm/m $\pi = 1 \times 98.066 \times h$	In this problem, the additional pressure is provided by the hydrostatic pressure exerted by the column of solution of height h cm and density ρ of the solution in the column Given g =980.66 cm s^{-2} Pascal = kg m^{-1} s^{-2} π is in Pascal and h in cm	
$x_G = n_{glucose}/(n_{glucose} + n_{water})$ $n_{glucose} = 1$ g /180 g mol^{-1} = 0.0055 mol $n_{water} = \dfrac{(h \bullet 1)\ \text{cm}^3 \bullet 1\ \text{g cm}^{-3}}{18.0\ \text{g mol}^{-1}}$ $n_{total} \approx n_{water}$ $x_G = \dfrac{(1/180)\bullet 18.0}{h \bullet 1 \bullet 1} = \dfrac{0.1}{h}$	definition of mole fraction molar mass of $C_6H_{12}O_6$ is $(6\times 12.01+12\times 1.01+6\times 15.99) = 180$ mass of water is volume of water $\times$ 1 g cm^{-3} volume of water in the column is h cm $\times$ 1 cm^2 molar mass of H_2O is $2\times 1.01+15.99 = 18.0$ since we found $n_{glucose}$ very small	
$V = 18.0$ g mol^{-1}/(1 g cm^{-3}) $= 18.0$ cm^3 mol^{-1} $= 18.0 \times 10^{-6}$ m^3 mol^{-1}	molar volume of liquid water	
$V\pi = RT\, x_G$ 18.0×10^{-6} m^3 mol$^{-1}\times 98.066$ h Pa = 8.3145 Pa m^3 K^{-1} mol^{-1} 298K$\times$(0.1/ h)	T= 25 +273 given substituting T, V, π and x_G	

$h^2 = \frac{8.3145 \bullet 298 \bullet 0.1}{18.0 \times 10^{-6} \bullet 98.066}$	Rearrange	
h = 375 cm	Solve for h	
π = 36700 Pa	Substituting h into $\pi = 1 \times 98.066 \times h$	

2. Given a binary ideal solution

Equation	Basis for the equation	Eq. #
$\mu^*_{A,liquid} = \mu^*_{A,vapor}$	For pure liquid A in equilibrium with its own vapor at temperature T (* means pure)	1
$\mu_{A,\ liquid\ solution} = \mu_{A,vapor}$	For A in solution of A and B, in equilibrium with the vapor containing both A and B	2
$\mu_{A,vapor} = \mu^{\ominus}_{A,T} + RT \ln(p_A/1)$	For an ideal gas at temperature T (We assume ideal vapor for this problem ; if non-ideal must use $\hat{f}_A$ instead of p_A)	3
$\mu_{A,vapor} = \mu^{\ominus}_{A,T} + RT \ln(p_A/1)$	For ideal vapor over a solution of A and B	4
$\mu^*_{A,vapor} = \mu^{\ominus}_{A,T} + RT \ln(p^*_A/1)$	For ideal vapor over pure liquid A	5
$\mu_{A,\ liquid\ solution} - \mu^*_{A,liquid} = \{ \mu^{\ominus}_{A,T} + RT \ln(p_A/1)\} - \{\mu^{\ominus}_{A,T} + RT \ln(p^*_A/1)\}$	Eq 2 minus Eq 1	6
$\mu_{A,\ liquid\ solution} - \mu^*_{A,liquid} = RT \ln(p_A/p^*_A)$		7
$(p_A/p^*_A) = x_A$ $p_A = x_A\ p^*_A$ $p_B = x_B\ p^*_B$ $p_{tot} = x_A\ p^*_A + x_B\ p^*_B = x_A\ p^*_A + (1-x_A)\ p^*_B$ $p_{tot} = p^*_B + (p^*_A - p^*_B)\ x_A$ p_{tot} is a linear function of x_A **Q.E.D.** Similarly can show $p_{tot} = p^*_A + (p^*_B - p^*_A)\ x_B$	For an ideal solution, Raoult's law holds, where x_A is the mole fraction of A in the liquid solution	8 9 10 11
$y_A = p_A / p_{tot}$	Dalton's law in the vapor phase	12
$y_A = \frac{x_A\ p^*_A}{x_A\ p^*_A + (1-x_A)\ p^*_B}$. $y_A \bullet \{ x_A\ p^*_A + (1-x_A)\ p^*_B \} = x_A\ p^*_A$	Substitute Eq 9 $p_A = x_A\ p^*_A$ into Eq 12	13
$x_A = \frac{y_A p^*_B}{-y_A p^*_A + y_A p^*_B + p^*_A}$.	Solve for x_A	14

$p_A = \frac{y_A p^*_B p^*_A}{-y_A p^*_A + y_A p^*_B + p^*_A}$.	Substitute Eq 14 into Eq 9 $p_A = x_A p^*_A$	15
$p_{tot} = p_A/y_A$ $p_{tot} = \frac{p^*_B p^*_A}{-y_A p^*_A + y_A p^*_B + p^*_A}$.	Rearrange Eq. 12 Substitute Eq. 15 into Eq 16	16
$\frac{1}{p_{tot}} = \frac{-y_A p^*_A + y_A p^*_B + p^*_A}{p^*_B p^*_A}$ $= 1/p^*_B + y_A \bullet (p^*_B - p^*_A)/p^*_B p^*_A$ $(1/p_{tot})$ is a linear function of y_A **Q.E.D.** We can show $1/p_{tot} = 1/p^*_A + y_B \bullet (p^*_A - p^*_B)/p^*_B p^*_A$	Taking the reciprocal By a similar series of steps	17

3. Given an ideal binary solution

Equation	Basis for the equation	Eq. #
$p = p_1 + p_2$	Given	1
$p_1 = n_1 RT/V$ $p_2 = n_2 RT/V$	Assume gases 1 and 2 are ideal gases	2 3
$p_1 {}^* V_{m,1}{}^* = RT$ $p_2 {}^* V_{m,2}{}^* = RT$	Given, where subscript m means for 1 mol, * means pure	4 5
$x_1 = p_1/p^*_1$ $x_2 = p_2/p^*_2$	Given, Raoult's law applies	6 7
$x_1 = (n_1 RT/V) \bullet (V_{m,1}{}^*/RT) = n_1 V_{m,1}{}^*/V$	Substitute Eq 2 and 4 into Eq 6	8
$x_2 = (n_2 RT/V) \bullet (V_{m,2}{}^*/RT) = n_2 V_{m,2}{}^*/V$	Substitute Eq 3 and 5 into Eq 7	9
$x_1 + x_2 = 1$ $(n_1 V_{m,1}{}^*/V) + (n_2 V_{m,2}{}^*/V) = 1$	Sum of molefractions is 1	10 11
$n_1 V_{m,1}{}^* + n_2 V_{m,2}{}^* = V$ **Q.E.D.**	Multiply Eq 11 by V	

4. Given an ideal binary solution

Equation	Basis for the equation	Eq. #
$y_1 = \frac{x_1 p^*_1}{x_1 p^*_1 + (1-x_1) p^*_2}$.	Derived in problem 2	1
$y_1 - x_1 = \frac{x_1 p^*_1}{x_1 p^*_1 + (1-x_1) p^*_2}$. $- x_1$	Find expression for $y_1 - x_1$	2

$y_1-x_1 = \frac{x_1 p^*_1 - x_1^2 p^*_1 - x_1(1-x_1)p^*_2}{x_1 p^*_1 + (1-x_1) p^*_2}$ $= \frac{[p^*_1 - p^*_2][x_1 - x_1^2]}{x_1 [p^*_1 - p^*_2] + p^*_2}$		3
$(d/x_1)(y_1-x_1) = \{x_1 [p^*_1 - p^*_2] + p^*_2\}\bullet$ $[p^*_1 - p^*_2][1 - 2 x_1] - [p^*_1 - p^*_2][x_1 - x_1^2] \bullet [p^*_1 - p^*_2]$ we leave out the denom^{-2} because we will set derivative to zero anyway. $\{x_1 [p^*_1 - p^*_2] + p^*_2\}\bullet$ $[p^*_1 - p^*_2][1 - 2x_1] - [p^*_1 - p^*_2][x_1 - x_1^2]$ $\bullet[p^*_1 - p^*_2] = 0$ Divide out $[p^*_1 - p^*_2]$ $\{x_1 [p^*_1 - p^*_2]+p^*_2\}\bullet[1-2x_1] - [x_1 - x_1^2] \bullet$ $[p^*_1 - p^*_2] = 0$ $x_1^2 [p^*_1 - p^*_2] + 2x_1 p^*_2 - p^*_2 = 0$ $x_1 = \frac{- p^*_2 \pm [p^*_1 p^*_2]^{1/2}}{[p^*_1 - p^*_2]}$ **Answer**	Find the extremum by differentiating the function y_1-x_1 and then setting the derivative to zero. Solve Eq 5 for x_1	4 5 6 7
$p_{tot} = x_1 p^*_1 + (1-x_1) p^*_2$ $= p^*_2 + x_1 [p^*_1 - p^*_2]$ At this value of x_1, $p_{tot} = p^*_2 + \{- p^*_2 \pm [p^*_1 p^*_2]^{1/2}\}$ $p_{tot} = [p^*_1 p^*_2]^{1/2}$ **Answer**	Total vapor pressure when Raoult's law holds Substitute Eq 6 value of x_1 at the extremum Extremum in y_1-x_1 for ideal solution at this p_{tot}	8 9

5. For some non-ideal solution: Instead of Raoult's law: $p_1 = x_1 p^*_1$; $p_1 = x_1 p^*_1$

we have $p_1 = (x_1)^a p^*_1$ and $p_2 = (x_2)^a p^*_2$

Equation	Basis for the equation	Eq. #
$p_{tot} = p_1 + p_2$ $p_1 = (x_1)^a p^*_1$; $p_2 = (x_2)^a p^*_2$ $p_{tot} = (x_1)^a p^*_1 + (x_2)^a p^*_2$ $p_{tot} = (x_1)^a p^*_1 + (1-x_1)^a p^*_2$	Dalton's law of partial pressures Given Substitute Eq 2 into Eq 1	1 2 3
(dp_{tot}/dx_1) $= a (x_1)^{a-1} p^*_1 - a (1-x_1)^{a-1} p^*_2 = 0$	Find the extremum	4
$[x_1/(1-x_1)]^{a-1} = p^*_2 / p^*_1$	Solve for x_1 to find the composition where p_{tot} is an extremum	5

(d^2p_{tot}/dx_1^2) $= a\,(x_1)^{a-1}\,p^*_1 - a\,(1-x_1)^{a-1}\,p^*_2$ $(d^2p_{tot}/dx_1^2) = a(a-1)\,(x_1)^{a-2}\,p^*_1$ $+ a(a-1)(1-x_1)^{a-2}\,p^*_2$	Find the sign of the second derivative to see if minimum or maximum	6
$(d^2p_{tot}/dx_1^2) > 0$ if $a > 1$ (concave upwards or minimum) **Q.E.D.** $(d^2p_{tot}/dx_1^2) < 0$ if $a < 1$ (concave downwards or maximum) **Q.E.D.**	since x_1 , $1-x_1$, p^*_1 , p^*_2 are all positive quantities, the sign of the second derivative will be determined by the sign of (a-1)	7

6.

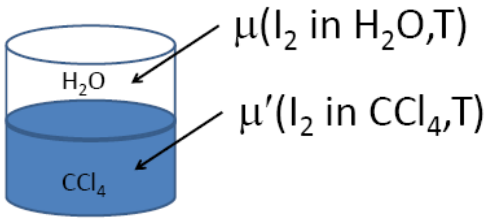
Equation	Basis for the equation	Eq. #
d**G** = Vdp - **S**dT	one of the four fundamental equations of thermodynamics	1
$V_{liq}dp - S_{liq}dT = V_{vap}dp - S_{vap}dT$	To maintain equilibrium between the pure liquid under the equil. vapor pressure & the pure vapor	2
$dp/dT = (\mathbf{S}_{vap}-\mathbf{S}_{liq})/(V_{vap}-V_{liq})$ We can replace $(\mathbf{S}_{vap}-\mathbf{S}_{liq}) = (\mathbf{H}_{vap}-\mathbf{H}_{liq})/T$	Clapeyron equation for pure substance vapor and liquid at equilibrium at T, $\Delta\mathbf{S} = q_{REV}/T$	3
$dp/p = (\mathbf{H}_{vap}-\mathbf{H}_{liq})dT/RT^2$ $\ln(p/1atm) = [1/T_{boil} - 1/T]\bullet(\mathbf{H}_{vap}-\mathbf{H}_{liq})/R$ $\ln(p/1atm)=(\mathbf{H}_{vap}-\mathbf{H}_{liq})/RT_{boil}]\bullet[1-T_{boil}/T]$ $= [(\mathbf{S}_{vap}-\mathbf{S}_{liq})_1/R]\bullet[1-T_{boil}/T]$ $(\mathbf{S}_{vap}-\mathbf{S}_{liq})_1/R$ $= 21\ cal\ K^{-1}mol^{-1}/1.987 cal\ K^{-1}mol^{-1}$ $= 10.57$ $\ln(p/1atm) = 10.57[1-T_{boil}/T]$ $(p/1atm) = \exp\{10.57[1-T_{boil}/T]\}$	$V_{vap}-V_{liq} \approx V_{vap} \approx RT/p$ Another form of the Clausius-Clapeyron eq when $(\mathbf{H}_{vap}-\mathbf{H}_{liq}) \approx$ indep of T Given relates vapor pressure of pure liquid to boiling T	4 5 6
$(p^*_b/1atm) = \exp\{10.57[1-353.2/T]\}$ $(p^*_t/1atm) = \exp\{10.57[1-383.7/T]\}$	Applying Eq 6 Vapor pressure of pure benzene as a function of T Vapor pressure of pure toluene as a function of T	7 8
$p_{tot} = p_b + p_t$	Dalton's law of partial pressures for the vapor	9
$p_b = x_b p^*_b$ $p_t = x_t p^*_t = (1-x_b)p^*_t$	If Raoult's law holds for the solution	10
$p_{tot} = x_b p^*_b + (1-x_b)p^*_t$	Total vapor pressure of this ideal solution	11
$(p_{tot}/1\ atm) = x_b\bullet\exp\{10.57[1-353.2/T]\}$ $+ (1-x_b)\bullet\exp\{10.57[1-383.7/T]\}$ $1 = x_b\bullet\exp\{10.57[1-353.2/T]\}$ $+ (1-x_b)\bullet\exp\{10.57[1-383.7/T]\}$ **Answer**	Subtituting Eq 7 & 8 into Eq 11 Boiling temperature of the liquid solution is T at which p_{tot} = 1 atm. This Eq relates the boiling point T of the mixture with mole fraction of benzene.	12 13
$1= x_b\bullet\exp\{10.57(1-353.2/368.1)\}$ $+ (1-x_b)\bullet\exp\{10.57(1-383.7/368.1)\}$	Substitute boiling temperature is 95 °C or 368.1 K	14

$1 = x_b \bullet \exp(0.42785) + (1-x_b) \bullet \exp(-0.44795)$ $x_b = 0.40$ **Answer**	Solve for x_b	

7. ideal dilute solution, Raoult's law holds for solvent and Henry's law holds for the solute

Equation	Basis for the equation	Eq. #
$p_2 = K_H x_2$	Given Henry's law for the solute 2	1
$p_1 = x_1 p^*_1 = (1-x_2)\, p^*_1$	Given Raoult's law holds for solvent	2
$p_{tot} = p_1 + p_2$	Assume Dalton's law of partial pressures holds for the vapor	3
$p_{tot} = (1-x_2)p^*_1 + K_H x_2$ **Answer**	Substituting Eq 1 and 2 into Eq 3	4
$y_1 = p_1/p_{tot}$	Mole fraction in the vapor assuming Dalton's law holds	5
$y_1 = \frac{(1-x_2)\, p^*_1}{(1-x_2)p^*_1 + K_H x_2}$ **Answer** or else $y_1 = \frac{x_1\, p^*_1}{x_1 p^*_1 + K_H(1-x_1)}$ **Answer**		6

8. ideal dilute solutions of iodine in H_2O and iodine in CCl_4

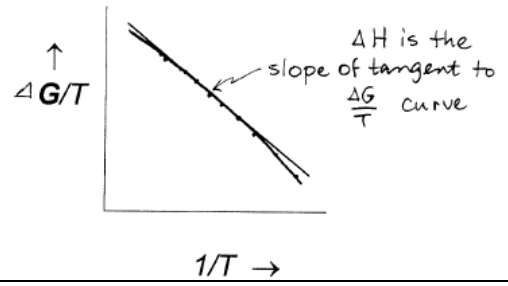


Equation	Basis for the equation	Eq. #
$\mu_{H2O,T} = \mu_{H2O,T}^* + RT\ln a_{H2O}$ $\mu_{CCl4,T} = \mu_{CCl4,T}^* + RT\ln a_{CCl4}$ where $a_{H2O} = p_{H2O}/p^*_{H2O}$ $a_{CCl4} = p_{CCl4}/p^*_{CCl4}$	For solvent in both solutions, where * means pure, $\mu^{\ominus}_{H2O,T} = \mu_{H2O,T}^*$; $\mu^{\ominus}_{CCl4,T} = \mu_{CCl4,T}^*$ For ideal aqueous solution, activity coefficient $\gamma = a_{H2O} / x_{H2O} = 1$; $x_{H2O} = p_{H2O}/p^*_{H2O}$ Similarly for a CCl_4 solution $x_{CCl4} = p_{CCl4}/p^*_{CCl4}$	
for I_2 in H_2O, $\mu_{I2\ in\ H2O,T} = \mu^{\ominus}_{I2\ in\ H2O,T} + RT\ \ln a_{I2\ in\ H2O}$ for I_2 in CCl_4, $\mu_{I2'\ in\ CCl4,T} = \mu^{\ominus}_{I2\ in\ CCl4,T} + RT\ \ln a_{I2\ in\ CCl4}$	For a "non-volatile" solute in an ideal solution $\mu_{solute,T} = \mu^{\ominus}_{solute,T} + RT\ \ln a_{solute}$ where $\mu^{\ominus}_{solute,T}$ is the chemical potential of a fictitious Henry's law solution having $p_{solute} = K_H$	1 2

$\mu_{I2'\ in\ CCl4,T} - \mu_{I2\ in\ H2O,T}$ $= \mu^{\ominus}_{I2\ in\ CCl4,T} - \mu^{\ominus}_{I2\ in\ H2O,T}$ $+ RT \ln a_{I2\ inCCl4}$ $- RT \ln a_{I2\ inH2O}$	Eq 2 minus Eq 1	3
$\mu_{I2'\ in\ CCl4,T} = \mu_{I2\ in\ H2O,T}$ $0 = \Delta G^{\ominus}_T + RT \ln a_{I2\ inCCl4}$ $- RT \ln a_{I2\ inH2O}$ where the standard free energy change is $\Delta G^{\ominus}_T = \mu^{\ominus}_{I2\ in\ CCl4,T} - \mu^{\ominus}_{I2\ in\ H2O,T}$	When I_2 is in equilibrium	4 5 6
$\frac{a_{I2\ inCCl4}}{a_{I2\ inH2O}} = \exp[-\Delta G^{\ominus}_T/RT]$ **Q.E.D.** $\frac{a_{I2\ inCCl4}}{a_{I2\ inH2O}}$ is the partition coefficient	Note that $\exp[-\Delta G^{\ominus}_T/RT]$ does not depend on the concentration of I_2 , only on temperature, therefore the partition coefficient does not depend on concentration of the solute.	7
In the limit that $a_{I2} = x_{I2}$ for an ideal solution $\frac{x_{I2\ inCCl4}}{x_{I2\ inH2O}} = \exp[-\Delta G^{\ominus}_T/RT]$	Define $\gamma = a_{I2\ inH2O} / x_{I2\ inH2O}$ As $x_{I2} \rightarrow 0$, $a_{I2} \rightarrow x_{I2}$, $\gamma_{I2} \rightarrow 1$ ideal In this limit, $\frac{x_{I2\ inCCl4}}{x_{I2\ inH2O}}$ is the partition coefficient	8
For concentrations in terms of molality		
In the limit that $a_{I2} = m_{I2}$ for an ideal solution $\frac{m_{I2\ inCCl4}}{m_{I2\ inH2O}} = \exp[-\Delta G^{\ominus}_T/RT]$	Define $\gamma = a_{I2\ inH2O} / m_{I2\ inH2O}$ As $m_{I2} \rightarrow 0$, $a_{I2} \rightarrow m_{I2}$, $\gamma_{I2} \rightarrow 1$ In this limit, $\frac{m_{I2\ inCCl4}}{m_{I2\ inH2O}}$ is the partition coefficient	8
In this case, the standard free energy change is $\Delta G^{\ominus}_T = \mu^{\ominus}_{I2\ in\ CCl4,T} - \mu^{\ominus}_{I2\ in\ H2O,T}$	except that $\mu^{\ominus}_{solute,T}$ is the chemical potential of a fictitious Henry's law solution having unit molality and obeys Henry's law: $p_{solute} = m_{solute} K_H$	

9. water(liquid) $\Leftrightarrow$ ice

Equation	Basis for the equation	Eq. #
$\mathbf{G} = \mathbf{H} - T\mathbf{S}$	Definition	1
$\mathbf{G}/T = \mathbf{H}/T - \mathbf{S}$	Divide Eq 1 by T	2
$(\partial[\mathbf{G}/T]/\partial T)_p = (\partial[\mathbf{H}/T]/\partial T)_p - (\partial \mathbf{S}/\partial T)_p$ $= -(\mathbf{H}/T^2) + (1/T)(\partial \mathbf{H}/\partial T)_p - (\partial \mathbf{S}/\partial T)_p$	Taking $(\partial/\partial T)_p$ of Eq 2 Differentiating Eq 3	3 4
$(\partial[\mathbf{G}/T]/\partial T)_p = -(\mathbf{H}/T^2)$	Applying $(\partial \mathbf{H}/\partial T)_p = C_p$ and $(\partial \mathbf{S}/\partial T)_p = C_p/T$ to	5

This is the Gibbs-Helmholtz equation	Eq 4. Note that this expression was derived using the temperature dependence of both **H** and **S**, just that the two terms are equal and opposite in sign.	
$(\partial[\Delta\mathbf{G}/T]/\partial T)_p = -(\Delta\mathbf{H}/T^2)$ $(\partial[\Delta_{fus}\mathbf{G}/T]/\partial T)_p = -(\Delta_{fus}\mathbf{H}/T^2)$	Applying Eq 5 to both $\mathbf{G}_{initial}$ and $\mathbf{G}_{final}$ Apply it to fusion	6 7
$[\Delta_{fus}\mathbf{G}/T]_2 - [\Delta_{fus}\mathbf{G}/T]_1 = \Delta_{fus}\mathbf{H}\{T_2^{-1} - T_1^{-1}\}$ 	If we integrate Eq 7over a range of temperatures AND assume that $\Delta_{fus}\mathbf{H}$ is independent of temperature in this temperature range.	
A phase(T_1, p_1) → B phase(T_1, p_1) (a) A phase(T_2, p_2) → A phase(T_1, p_1) (b) B phase(T_1, p_1) → B phase(T_2, p_2) (c) A phase(T_2,p_2) → B phase(T_2, p_2) (d) $\Delta\mathbf{H}(d) = \Delta\mathbf{H}(a) + \Delta\mathbf{H}(b) + \Delta\mathbf{H}(c)$ For water(liquid) ⇔ ice $\Delta_{fus}\mathbf{H}$(270,1 atm) = $\Delta_{fus}\mathbf{H}$(273,1 atm) + $\int_{270}^{273} C_p$(liq,1 atm)dT + $\int_{273}^{270} C_p$(ice,1 atm)dT = 79.7 + 1.00(273-270) + 0.48(270-273) cal g^{-1} = 81.3 cal g^{-1} **Answer** $\Delta_{fus}\mathbf{S}$(270,1 atm) = q_{REV}(273,1 atm)/273 + $\int_{270}^{273} C_p$(liq,1 atm)dT/T + $\int_{273}^{270} C_p$ (ice,1 atm)dT/T = $\Delta_{fus}\mathbf{H}$(273,1 atm)/273 + 1.00 ln(273/270) + 0.48 ln(270/273) = 79.7/273 +(1.00-0.48)(0.011) = 0.298 cal K^{-1} g^{-1} **Answer** $\Delta_{fus}\mathbf{G}$(270,1 atm) = $\Delta_{fus}\mathbf{H}$(270,1 atm) - 270$\Delta_{fus}\mathbf{S}$(270,1 atm) = 81.3 - 270 (0.298) cal g^{-1} = 0.84 cal g^{-1} **Answer**	The temperature or pressure dependence of the change in a thermodynamic property **H**, **S**, **A**, **G** for any phase transformation can be obtained by doing the transformation in steps and summing up the thermodynamic property changes for each step. **H** = **H**(T,p) $d\mathbf{H} = C_p dT + (\partial\mathbf{H}/\partial p)_T dp$ Here dp = 0 so just need to integrate over $C_p dT$ for steps (b) and (c) **S** = **S**(T,p) $d\mathbf{S} = C_p dT/T + (\partial\mathbf{S}/\partial p)_T dp$ Here dp = 0 so just need to integrate over $C_p dT/T$ for stgeps (b) and (c). This phase change is reversible at (273, 1 atm) $q_{REV} = \Delta_{fus}\mathbf{H}$(273,1 atm)/273 **G** = **H** - T**S** definition at constant T, $\Delta\mathbf{G} = \Delta\mathbf{H} - T\Delta\mathbf{S}$	8

10. To find the heat capacity of a vapor heated along such a path that its pressure is always equal to p_T, the equilibrium vapor pressure at that temperature

vapor $(p_{T1},T_1) \rightarrow$ vapor (p_{T2},T_2)

Equation	Basis for the equation	Eq. #
(a) $C = C_p - T(\partial V/\partial T)_p dp/dT$	Given	1
$dp/dT = (\mathbf{S}_{vap}-\mathbf{S}_{liq}) /(V_{vap}-V_{liq})$	Given Clapeyron Eq (derived above in prob 6)	2
$C = C_p - T(\partial V/\partial T)_p(\mathbf{S}_{vap}-\mathbf{S}_{liq}) /(V_{vap}-V_{liq})$	Substituting dp/dT from Eq 2 into Eq 1	3
$(\mathbf{S}_{vap}-\mathbf{S}_{liq})= (\mathbf{H}_{vap}-\mathbf{H}_{liq})/T$	vapor and liquid at equilibrium at T, $\Delta\mathbf{S} = q_{REV}/T$	4
$C = C_p - (\partial V/\partial T)_p(\mathbf{H}_{vap}-\mathbf{H}_{liq}) /(V_{vap}-V_{liq})$ **Q.E.D.**		5
(b) $(V_{vap}-V_{liq}) \approx V_{vap}$	For $V_{liq} << V_{vap}$ (given)	6
$V_{vap} = RT/p$	Vapor is an ideal gas (given)	7
$(\partial V/\partial T)_p = R/p$	Differentiating Eq 7	8
$C = C_p - (\mathbf{H}_{vap}-\mathbf{H}_{liq})R/pV_{vap}$ $C = C_p - (\mathbf{H}_{vap}-\mathbf{H}_{liq})/T$ **Q.E.D.**	Substituting Eq 7 & 8 into Eq 5	9 10
(c) $C = 9 - 9720/373$ $= -17.06$ cal K^{-1} mol^{-1} **Answer**	Given: T = 373 K; C_p = 9 cal K^{-1} mol^{-1}, $\Delta_{vap}\mathbf{H} = (\mathbf{H}_{vap}-\mathbf{H}_{liq})$ = 9720 cal mol^{-1} Substitute these into Eq 10 C_p and C_V are always positive, that is, for constant p (and constant V) processes, **H** (and **U**) increase when the temperature of the system is increased by adding heat ($q_{SYS} > 0$). On the other hand, this negative value of C means that $(dq/dT) < 0$, that is, as the temperature increases, the amount of input heat required to maintain equilibrium between the liquid and vapor decreases.	