Name:______________________________________

First three letters of last name

Chemistry 342

ANSWERS to Second Exam
March 18, 2005
2:00 PM in C6 Lecture Center

Write all work you want graded in the spaces provided. Both the logical solution to the problem and the answer to the question are required. What is required is an answer in terms of the original numerical data, including all numerical values and units of conversion factors. Use no intermediate calculated numbers, except where such numbers arise from answers to previous parts. The solution has to be worked out in the form of complete equations, with justification or basis for the use in the specific problem. Final numerical values must include the correct units.
In other words, the instructions are the same as for Exam 1.

POSSIBLY USEFUL INFO: 1 J = 1 kg m^{-2} s^{-2} 1 atm = 101325 Pa

$(p + n^2a/V^2)(V-nb) = nRT$

R = 8.31441 J mol^{-1} K^{-1} =1.98718 cal mol^{-1} K^{-1} = 0.082057 L atm mol^{-1} K^{-1}

$(\partial \boldsymbol{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $(\partial \boldsymbol{H}/\partial p)_T = -T(\partial V/\partial T)_p + V$ $\mu_{JT} \equiv (\partial T/\partial p)_{\boldsymbol{H}}$ $(\partial \boldsymbol{H}/\partial p)_T = -C_p\mu_{JT}$

$C_p - C_V = \{p + (\partial \boldsymbol{U}/\partial V)_T\}(\partial V/\partial T)_p$

special case : $[T_f/T_i]^{Cv/R}\}= [V_i/V_f]$ only for ideal gas undergoing reversible adiabatic process

	score
1	
2	
3	
4	
5	
6	
7	
8	

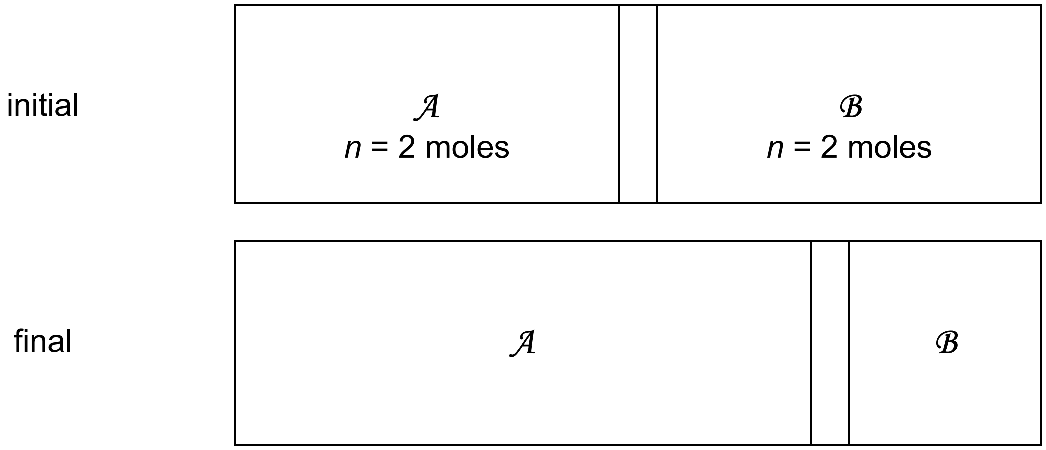
1. Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections $\mathcal{A}$ and $\mathcal{B}$. All changes in $\mathcal{B}$ are isothermal, that is a thermostat surrounds $\mathcal{B}$ to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially $T_{\mathcal{A}} = T_{\mathcal{B}} = 300$ K, $V_{\mathcal{A}} = V_{\mathcal{B}} = 2.00$ L. Heat is added to section $\mathcal{A}$ and the piston moves to the right reversibly until the final volume of section $\mathcal{B}$ is 1.00 L .

Calculate the work done by the gas in section $\mathcal{A}$. Calculate for the gas in each section: $\Delta \boldsymbol{U}$, q, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{A}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{G}$.

Calculate $\Delta \boldsymbol{S}$ of the total system and its surroundings.

Assume $\quad C_V = 20$ J K^{-1} mol^{-1} .

Ideal: $\quad C_p = 28.3144$ J K^{-1} mol^{-1} .



	section $\mathcal{A}$	*section $\mathcal{B}$*
initial *V,T, p*	$T_i = 300$ K $V_i = 2$ L $p_i = 24.6$ atm from ideal gas equation of state $pV = nRT$	$T_i = 300$ K $V_i = 2$ L total $V = 4$ L $p_i = 24.6$ atm from ideal gas equation of state $pV = nRT$
final *V,T, p*	$V_f = 3$ L by difference p_f = same as $\mathcal{B}$ $\therefore$ can find $T_f = 900$K from ideal gas equation of state	$T_f = 300$ K (isothermal) $V_f = 1$ L (given) $p_f = 49.2$ atm from ideal gas equation of state

W	W_{rev} = - 3.46 kJ from side $\mathcal{B}$ answer	Work done on the gas in section $\mathcal{B}$ $W_{\mathcal{B}} = -\int p_{op}\,\mathrm{d}V$ (reversibly) $= -\int p_{gas}\,\mathrm{d}V$ $= -\int nRT\mathrm{d}V/V$ since $p = nRT/V$, ideal $= -2 \times 8.3144 \times 300 \times \ln(1/2)$ isothermal = + 3.46 kJ W_{rev} = + 3.46 kJ
$\Delta\boldsymbol{U}$	ideal gas $\boldsymbol{U} = \boldsymbol{U}(T)$ since $(\partial \boldsymbol{U}/\partial V)_T = 0$ $\Delta\boldsymbol{U} = \int C_V\,\mathrm{d}T$ $=2\times20\times(900-300)$ = 24 kJ	ideal gas $\boldsymbol{U} = \boldsymbol{U}(T)$ since $(\partial \boldsymbol{U}/\partial V)_T = 0$ $\mathrm{d}T = 0$ $\Delta\boldsymbol{U} = 0$
q	$\Delta\boldsymbol{U} = q + W$ First Law 24 = q - 3.46 kJ q = 27.46 kJ	$\Delta\boldsymbol{U} = q + W$ First Law 0 = q + 3.46 kJ q = - 3.46 kJ
$\Delta\boldsymbol{S}$	$\mathrm{d}\boldsymbol{S} = (1/T)C_p\,\mathrm{d}T - (\partial V/\partial T)_p\,\mathrm{d}p$ $\Delta\boldsymbol{S} = n\int C_p\,\mathrm{d}T/T - n\int R\mathrm{d}p/p$ $= 2\times28.3144\times \ln(900/300)$ $- 2\times8.3144\times \ln(49.2/24.6)$ = +50.7 J K^{-1}	$\mathrm{d}\boldsymbol{S} = (1/T)C_p\,\mathrm{d}T - (\partial V/\partial T)_p\,\mathrm{d}p$ $\mathrm{d}T=0$ $\Delta\boldsymbol{S} = -n\int R\mathrm{d}p/p$ $= -2\times8.3144\times \ln(49.2/24.6)$ = - 11.53 J K^{-1}

ΔA	$A = U - TS$ definition $\Delta A = \Delta U - \Delta(TS)$ need to calculate S at initial and final states, not enough information here to get S_i and S_f separately Note that since $dT \neq 0$, $\Delta A \neq W_{rev}$ $\neq - 3.46$ kJ	$\Delta A_T = W_{rev} = W_{max} = + 3.46$ kJ or else, use $\Delta A_T = \Delta U - \Delta(TS) = \Delta U - T\Delta S$ since T = constant $= 0 - 300\times(-11.53)$ J $= 3.46$ kJ
ΔH	ideal gas $H = H(T)$ since $(\partial H/\partial p)_T = 0$ $\Delta H = n \int C_p \, dT$ $= 2\times28.3144\times (900-300)$ $= 33.98$ kJ	ideal gas $H = H(T)$ since $(\partial H/\partial p)_T = 0$ $dT = 0$ $\Delta H = 0$
ΔG	$G = H - TS$ definition $\Delta G = \Delta H - \Delta(TS)$ need to calculate S at initial and final states, not enough information here to get S_i and S_f separately If we use $dG = Vdp - SdT$, same difficulty since $dT \neq 0$	$\Delta G_T = \Delta H - \Delta(TS) = \Delta H - T\Delta S$ since T = constant $= -T\Delta S$ $= - 300\times(-11.53)$ J $= 3.46$ kJ or else use $dG = Vdp - SdT$, $dT = 0$ $\Delta G_T = n \int RT dp/p$ $= 2\times8.3144\times300\times \ln(49.2/24.6)$ $= 3.46$ kJ
ΔS_{system}	$\Delta S_{\text{system}} = \Delta S_A + \Delta S_B = +50.7 - 11.53 = + 39.2$ J K^{-1}	
$\Delta S_{\text{surrounds}}$	$- 39.2$ J K^{-1} since process was carried out reversibly	

2. The following data were obtained for hydrogen sulfide in 1936.

T (°K)	C_P (cal °K^{-1} mole^{-1})	T (°K)	C_P (cal °K^{-1} mole^{-1})
20	1.25	110	11.79
30	2.48	120	13.27
40	3.56	126.2	([b])
50	4.56	130	13.25
60	5.51	140	13.33
70	6.43	150	13.45
80	7.31	170	13.92
90	8.26	187.6	([c])
100	9.36	190	16.21
103.5	([a])	210	16.31
105	11.25	212.8	([d])

[a] Solid-state transition with $\Delta H = 368$ cal mole^{-1}.
[b] Solid-state transition with $\Delta H = 121$ cal mole^{-1}.
[c] Melting point, $\Delta H = 568$ cal mole^{-1}.
[d] Normal boiling point, $\Delta H = 4463$ cal mole^{-1}.

Below 20 K the heat capacity obeys the law $C_p = aT^3$.
Calculate the absolute entropy of hydrogen sulfide gas at 1 atm and 212.8 K.

$\boldsymbol{S}$ (gas, 1 atm, 212.8 K) = $\boldsymbol{S}$ (0 K) + $\Delta\boldsymbol{S}$ (solid I, 0 K→20 K) + $\Delta\boldsymbol{S}$ (solid I, 20 K→103.5 K)
+ $\Delta\boldsymbol{S}_{\text{trans}}$ (solid I to solid II at 103.5 K) + $\Delta\boldsymbol{S}$ (solid II, 103.5 K→126.2 K)
+ $\Delta\boldsymbol{S}_{\text{trans}}$ (solid II to solid III, at 126.2 K) + $\Delta\boldsymbol{S}$ (solid III, 126.2 K→187.6 K)
+ $\Delta\boldsymbol{S}_{\text{trans}}$ (solid III to liquid at 187.6 K) + $\Delta\boldsymbol{S}$ (liquid, 187.6 K→212.8 K)
+ $\Delta\boldsymbol{S}_{\text{trans}}$ (liquid to gas at 212.8 K), all at 1 atm so that dp = 0 for every step and for one mole
Use d$\boldsymbol{S}$ = d$\boldsymbol{q}_{\text{rev}}/T$ or else d$\boldsymbol{S}$ = $(C_p/T)\mathrm{d}T + (\partial \boldsymbol{S}/\partial p)_T\mathrm{d}p$ to obtain each $\Delta\boldsymbol{S}$:

$\boldsymbol{S}$ (0 K) = 0 Third Law of thermodynamics
Debye T-cubed law: $C_p = a\,T^3$, thus, a 20^3 = 1.25 cal K^{-1} mol^{-1}
$\Delta\boldsymbol{S}$ (solid I, 0 K→20 K) = $\int_0^{20} (aT^3/T)\,\mathrm{d}T = a\,(1/3)[T^3]_0^{20} = (1/3)1.25$ = 0.42 cal K^{-1} mol^{-1}
$\Delta\boldsymbol{S}$ (solid I, 20 K→103.5 K) = $\int_{20}^{103.5} (C_p/T)\mathrm{d}T$
≈ sum over increments of C_p/T over T= 20 to 103.5 good enough approximation for this test
≈{1.25/20 + 2.48/30 + 3.56/40 + 4.56/50 + 5.51/60 + 6.43/70 + 7.31/80 + 8.26/90
+ 9.36/100}×10 + (9.36/103.5) ×3.5
≈ 7.26 cal K^{-1} mol^{-1}
(Of course, we could use a graphical method of integration, or for better accuracy, fit the C_p values to a polynomial function in T and then do analytical integration.)

$\Delta \boldsymbol{S}_{\text{trans}}$ (solid I to solid II at 103.5 K) = $\boldsymbol{q}_{\text{rev}}/T = \boldsymbol{q}_{\text{p}}/T = \Delta \boldsymbol{H}_{\text{trans}}/T = +368/103.5$

$= 3.55 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}$ (solid II, 103.5 K$\rightarrow$126.2 K) = $\int_{103.5}^{126.2} (C_p/T)\mathrm{d}T$

$\approx$ sum over increments of C_p/T over T= 103.5 to 126.2 K

$\approx 11.25/105\times1.5 + 11.79/110\times5 + 13.27/120\times10 + 13.27/126.2\times6.2 \qquad \approx 2.45 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}_{\text{trans}}$ (solid II to solid III, at 126.2 K) = $\boldsymbol{q}_{\text{rev}}/T = \boldsymbol{q}_{\text{p}}/T = \Delta \boldsymbol{H}_{\text{trans}}/T = +121/126.2$

$= 0.96 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}$ (solid III, 126.2 K$\rightarrow$187.6 K) = $\int_{126.2}^{187.6} (C_p/T)\mathrm{d}T$

$\approx$ sum over increments of C_p/T over T= 126.2 to 187.6 K

$\approx 13.25/130\times4.8 + 13.33/140\times10 + 13.45/150\times10 + 13.92/170\times20 + 13.92/187.6\times17.6$

$\approx 5.28 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}_{\text{trans}}$ (solid III to liquid at 187.6 K) = $\boldsymbol{q}_{\text{rev}}/T = \boldsymbol{q}_{\text{p}}/T = \Delta \boldsymbol{H}_{\text{trans}}/T = +568/187.6$

$= 3.03 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}$ (liquid, 187.6 K$\rightarrow$212.8 K) = $\int_{187.6}^{212.8} (C_p/T)\mathrm{d}T$

$\approx$ sum over increments of C_p/T over T= 187.6 to 212.8 K

$\approx 16.21/190\times2.4 + 16.31/210\times20 + 16.31/212.8\times2.8 \qquad \approx 1.97 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\Delta \boldsymbol{S}_{\text{trans}}$ (liquid to gas at 212.8 K) = $\boldsymbol{q}_{\text{rev}}/T = \boldsymbol{q}_{\text{p}}/T = \Delta \boldsymbol{H}_{\text{trans}}/T = +4463/212.8$

$= 20.97 \text{ cal K}^{-1} \text{ mol}^{-1}$

$\boldsymbol{S}$ (gas, 1 atm, 212.8 K) = $0 + 0.42 + 7.26 + 3.55 + 2.45 + 0.96 + 5.28 + 3.03 + 1.97 + 20.97$

$= 45.89 \text{ cal K}^{-1} \text{ mol}^{-1}$

3. Assume that a gas obeys the equation $p(V\text{-b}) = \mathrm{R}T$, where b is a constant, independent of T and p. Derive an expression for the fugacity of a real gas as a function of T and p, starting from $\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$. Apply the derived equation to this particular equation of state.

$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$

For a particular temperature T and one mole of ideal gas,

$\mathrm{d}\mu_{\text{ideal}} = V_{\text{ideal}}\mathrm{d}p$ for an ideal gas

When integrated from p =1 atm to p this gives

$$\mu_{\text{ideal}} - \mu^{\circ}(T) = \int_1^p (\mathrm{R}T/p)\,\mathrm{d}p = \mathrm{R}T\ln(p/1) \qquad (1)$$

$\mathrm{d}\mu = V\mathrm{d}p$ for a real gas in which $V = \mathrm{R}T\,\mathrm{Z}/p$

$\mathrm{d}\mu_{\text{ideal}} = V_{\text{ideal}}\mathrm{d}p$ for an ideal gas

Subtract one equation from the other,

$\mathrm{d}(\mu - \mu_{\text{ideal}}) = (V - V_{\text{ideal}})\,\mathrm{d}p$

Integrate between the limits p^* and p : $(\mu - \mu_{\text{ideal}}) = \int_{p^*}^{p} (V - V_{\text{ideal}})\,\mathrm{d}p$

Now let $p^* \to 0$; in this limit as $p^* \to 0$, $\mu \to \mu_{\text{ideal}}$

$$\text{Thus the equation becomes } (\mu - \mu_{\text{ideal}}) = \int_0^p (V - V_{\text{ideal}})\,\mathrm{d}p \qquad (2)$$

But we have $\mu_{\text{ideal}} = \mu^{\circ}(T) + \mathrm{R}T\ln(p/1)$ from (1)

from which we define fugacity (to have an equation that has the same form)

$\mu = \mu^{\circ}(T) + \mathrm{R}T\ln(f/1)$

from (2) we write $(\mu - \mu_{\text{ideal}}) = \mathrm{R}T\ln(f/1) - \mathrm{R}T\ln(p/1) = \int_0^p (V - V_{\text{ideal}})\,\mathrm{d}p$

$\therefore\ \mathrm{R}T\ln(f/p) = \int_0^p \{\mathrm{R}T\,\mathrm{Z}/p - \mathrm{R}T/p\}\,\mathrm{d}p = \mathrm{R}T\int_0^p \{(\mathrm{Z}-1)/p\}\,\mathrm{d}p$

$\ln(f/p) = \int_0^p \{(\mathrm{Z}-1)/p\}\,\mathrm{d}p$ for any real gas

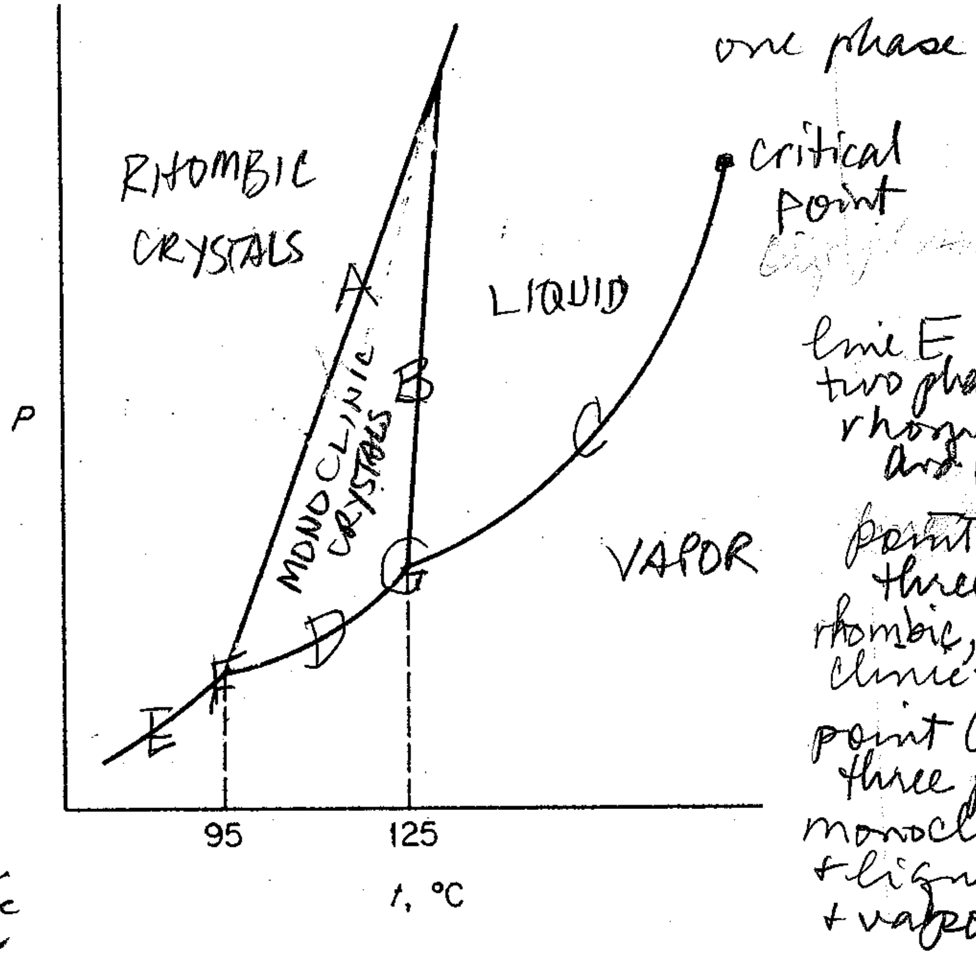
For the given equation of state $p(V\text{-b}) = \mathrm{R}T$: $V = \mathrm{b} + (\mathrm{R}T/p)$

$\mathrm{R}T\ln(f/p) = \int_0^p (V - V_{\text{ideal}})\,\mathrm{d}p = \int_0^p \{\mathrm{b} + \mathrm{R}T/p - \mathrm{R}T/p\}\,\mathrm{d}p = \mathrm{b}\int_0^p \mathrm{d}p = \mathrm{b}p$

$\ln(f/p) = \mathrm{b}p/\mathrm{R}T$

$f = p\exp[\mathrm{b}p/\mathrm{R}T]$

4. The p versus t °C phase diagram for sulfur is shown below: (Possible phases are rhombic crystalline, monoclinic crystalline, liquid, and gas, and the stable form of the element is rhombic.)



Line A
two phases
rhombic &
monoclinic

Line B
two phases
monoclinic,
and liquid

Line C
two phases
Liquid and
vapor

Line D
two phases.
monoclinic
and vapor

line E
two phases
rhombic
and vapor

point F
three phases
rhombic, mono-
clinic + vapor

point G
three phases
monoclinic
+ liquid
+ vapor

(a) On the figure given above, identify all the areas, points, and lines (curved or straight) with the correct <u>phase descriptions</u> (i.e., which phases are present).

(b) Where more than one phase is present, derive the Clapeyron equation that describes the constraint that links the pair of variables p and T, i.e., the equation that describes the area, line or point (where you have placed an identifying mark such as A, B, C, D, E, ...) Use explicit symbols and define each of the symbols you use.

We start from the general $d\mathbf{G} = Vdp - \mathbf{S}dT$ and write the equation for both phase α and phase β:

$d\mathbf{G}_\alpha = V_\alpha dp - \mathbf{S}_\alpha dT$

$d\mathbf{G}_\beta = V_\beta dp - \mathbf{S}_\beta dT$

Impose the condition that the two phases are in equilibrium: $d\mathbf{G}_\alpha = d\mathbf{G}_\beta$

$V_\alpha dp - \mathbf{S}_\alpha dT = V_\beta dp - \mathbf{S}_\beta dT$

Rearrange to get:

$(V_\alpha - V_\beta)\, dp = (\mathbf{S}_\alpha - \mathbf{S}_\beta)\, dT$

$dp/dT = (\mathbf{S}_\alpha - \mathbf{S}_\beta)/(V_\alpha - V_\beta)$ This is the general Clapeyron equation which applies to any two phases that are in equilibrium.

Curved line A = Coexistence of rhombic and monoclinic crystalline phases:
$dp/dT = (\boldsymbol{S}_{\mathrm{rhombic}} - \boldsymbol{S}_{\mathrm{monoclinic}})/(V_{\mathrm{rhombic}} - V_{\mathrm{monoclinic}})$

Curved line B = coexistence of monoclinic crystalline phase and liquid phase:
$dp/dT = (\boldsymbol{S}_{\mathrm{liquid}} - \boldsymbol{S}_{\mathrm{monoclinic}})/(V_{\mathrm{liquid}} - V_{\mathrm{monoclinic}})$

Curved line C = coexistence of liquid and vapor:
$dp/dT = (\boldsymbol{S}_{\mathrm{liquid}} - \boldsymbol{S}_{\mathrm{vapor}})/(V_{\mathrm{liquid}} - V_{\mathrm{vapor}})$

Curved line D = coexistence of monoclinic crystals and vapor phase:
$dp/dT = (\boldsymbol{S}_{\mathrm{monoclinic}} - \boldsymbol{S}_{\mathrm{vapor}})/(V_{\mathrm{monoclinic}} - V_{\mathrm{vapor}})$

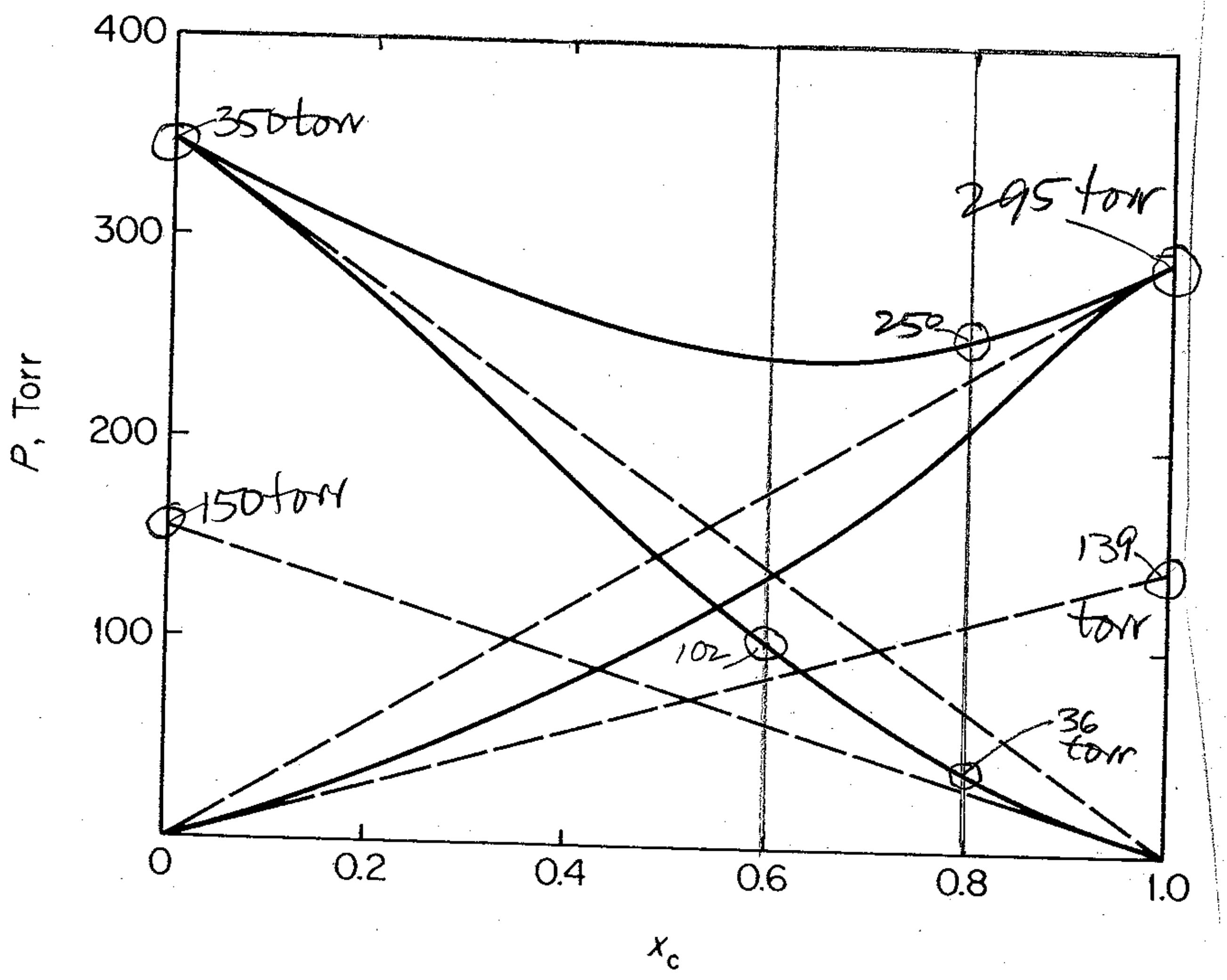
Curved line E = coexistence of rhombic crystals and vapor phase:
$dp/dT = (\boldsymbol{S}_{\mathrm{rhombic}} - \boldsymbol{S}_{\mathrm{vapor}})/(V_{\mathrm{rhombic}} - V_{\mathrm{vapor}})$

(c) Where more than two phases are present, provide the equations that have to be solved for a unique set of coordinates (T, p). Again, unless already defined in part (b), define each of the symbols you use.

Point F = coexistence of rhombic crystals, monoclinic crystals and vapor:
At this special (T,p), equations for curves A, D, and E all have to hold:
$dp/dT = (\boldsymbol{S}_{\text{rhombic}} - \boldsymbol{S}_{\text{monoclinic}})/(V_{\text{rhombic}} - V_{\text{monoclinic}})$ curve A
$dp/dT = (\boldsymbol{S}_{\text{monoclinic}} - \boldsymbol{S}_{\text{vapor}})/(V_{\text{monoclinic}} - V_{\text{vapor}})$ curve D
$dp/dT = (\boldsymbol{S}_{\text{rhombic}} - \boldsymbol{S}_{\text{vapor}})/(V_{\text{rhombic}} - V_{\text{vapor}})$ curve E
Because of the quantities that appear in common in 2 equations at a time, only the intersection of any two of the three equations define the unique set (T,p). That is, given the temperature dependence and pressure dependence of $\boldsymbol{S}$ and V for each of the three phases, integrate two of the three equations to get $p = f(T)$ and $p = g(T)$. Then solve for the value of T_{triple}. Put this value of T_{triple} back into $p = f(T)$ and solve for p. This value is p_{triple} for point F, at which rhombic, monoclinic and vapor are in equilibrium.

Point G = coexistence of monoclinic crystals, liquid, and vapor:
At this special (T,p), equations for curves B, C, and D all have to hold:
$dp/dT = (\boldsymbol{S}_{\text{liquid}} - \boldsymbol{S}_{\text{monoclinic}})/(V_{\text{liquid}} - V_{\text{monoclinic}})$ curve B
$dp/dT = (\boldsymbol{S}_{\text{liquid}} - \boldsymbol{S}_{\text{vapor}})/(V_{\text{liquid}} - V_{\text{vapor}})$ curve C
$dp/dT = (\boldsymbol{S}_{\text{monoclinic}} - \boldsymbol{S}_{\text{vapor}})/(V_{\text{monoclinic}} - V_{\text{vapor}})$ curve D
Do the same as above, that is, given the temperature dependence and pressure dependence of $\boldsymbol{S}$ and V for each of the three phases, integrate two of the three equations to get $p = r(T)$ and $p = s(T)$. Then solve for the value of T_{triple}. Put this value of T_{triple} back into $p = r(T)$ and solve for p. This value is p_{triple} for point G, at which liquid, monoclinic and vapor are in equilibrium.

5. The vapor pressures over a liquid solution of acetone and chloroform are described by the graph below, where the x axis reads from 0 to 1 in mole fraction of chloroform.



Find the numerical values and attach the proper units to each number:

the vapor pressure of pure chloroform	295 Torr
the vapor pressure of pure acetone	350 Torr
the Henry's Law constant of acetone dissolved in chloroform	150 Torr
the Henry's Law constant of chloroform dissolved in acetone	139 Torr
partial pressure of acetone in the vapor over a liquid solution having 40 mole per cent acetone	102 Torr
total vapor pressure of a solution containing 20 mole per cent acetone	250 Torr
mole fraction of acetone in the vapor over a liquid solution which is 20 mole per cent acetone	0.144 (see below)

Use this space for computations, if any are required beyond reading numbers off the graph.
All numbers are read off the graph directly except for:
$y_a = p_a / p_{tot} = 36 \text{ Torr} / 250 \text{ Torr} = 0.144$

6. Consider the following system: Pure liquid A has a vapor pressure equal to p_A^* at 300 K while pure liquid B has a vapor pressure equal to p_B^* at 300 K. The molecules of type A have an electric dipole moment equal to 3.2 debye and are capable of forming 1 hydrogen bond per molecule. On the other hand, B molecules do not have a dipole moment at all. B molecules have a greater electric polarizability than A molecules but are incapable of forming hydrogen bonds. ***Use only this information to answer the following.*** For some of the questions, quantitative results will have to wait until we have studied colligative properties. ***Which of the following are likely to be true (select all correct ones) about the vapor pressures, boiling temperatures, and compositions of this system?***

A ✓ $p_A^* < p_B^*$ at 300 K
B $p_A^* \approx p_B^*$ at 300 K
C $p_A^* > p_B^*$ at 300 K
D $T_{b,A}^* < T_{b,B}^*$ at 1 atm
E $T_{b,A}^* \approx T_{b,B}^*$ at 1 atm
F ✓ $T_{b,A}^* > T_{b,B}^*$ at 1 atm

For a 50-50 mol % solution of A and B:

G $p_{total} < \frac{1}{2}(p_A^* + p_B^*)$ at 300 K
H $p_{total} = \frac{1}{2}(p_A^* + p_B^*)$ at 300 K
I ✓ $p_{total} > \frac{1}{2}(p_A^* + p_B^*)$ at 300 K
J ✓ $p_A < p_A^*$ at 300 K
K ✓ $p_A > \frac{1}{2}p_A^*$ at 300 K
L ✓ the vapor pressure of A exceeds that given by Raoult's law
M the vapor pressure is depressed compared to that predicted by Raoult's law
N $T_b > T_{b,B}^*$ at 1 atm
O $T_b > T_{b,A}^*$ at 1 atm
P ✓ $T_b < \frac{1}{2}(T_{b,A}^* + T_{b,B}^*)$ at 1 atm
Q $T_b = \frac{1}{2}(T_{b,A}^* + T_{b,B}^*)$ at 1 atm
R $T_b > \frac{1}{2}(T_{b,A}^* + T_{b,B}^*)$ at 1 atm
S ✓ mole fraction of A in the vapor < ½
T mole fraction of A in the vapor = ½
U mole fraction of A in the vapor > ½
V mole fraction of A in the vapor $< p_A/(p_A + p_B)$
W ✓ mole fraction of A in the vapor $= p_A/(p_A + p_B)$
X mole fraction of A in the vapor $> p_A/(p_A + p_B)$
Y mole fraction of A in the vapor $< p_A^*/(p_A^* + p_B^*)$
Z mole fraction of A in the vapor $= p_A^*/(p_A^* + p_B^*)$
Σ ✓ mole fraction of A in the vapor $> p_A^*/(p_A^* + p_B^*)$
Φ fractional distillation leads to pure A in the pot and pure B coming off the distillation column
Δ fractional distillation leads to pure B in the pot and pure A coming off the distillation column
Ω fractional distillation leaves a constant-boiling mixture of A and B in the pot

Circle the letters corresponding to all the correct answers in the boxes below:

(A)	B	C	D	E	**(F)**	G	H	**(I)**	**(J)**	**(K)**	**(L)**	M	N	O
(P)	Q	R	**(S)**	T	U	V	**(W)**	X	Y	Z	**(Σ)**	Φ	Δ	Ω

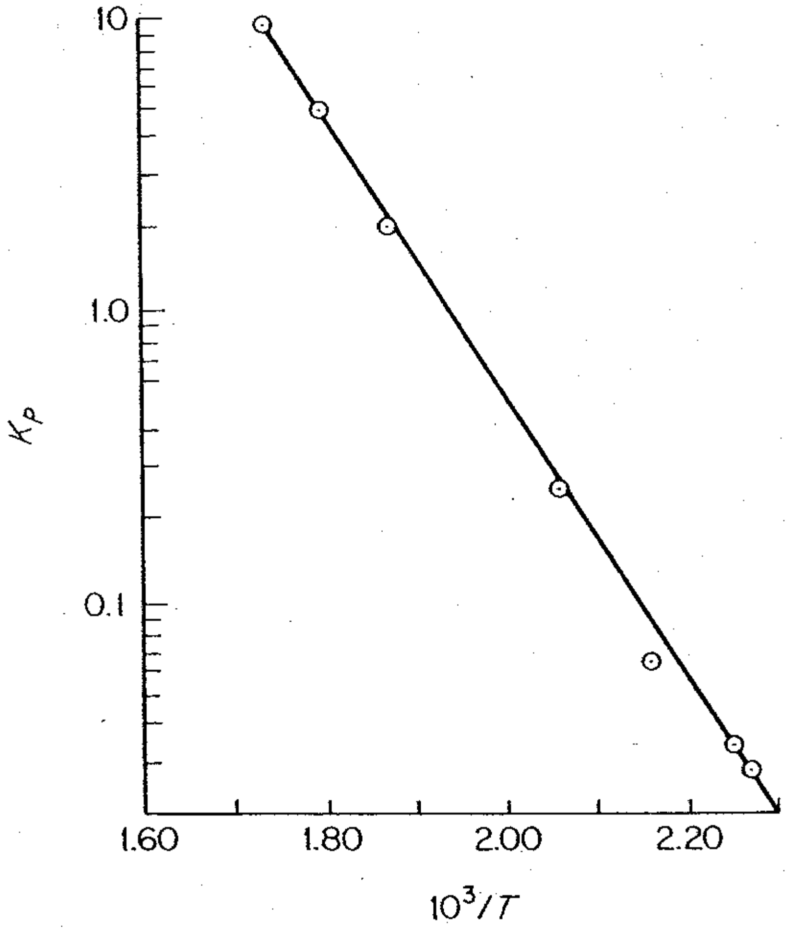
7. The variation with temperature of K_p for the gas-phase equilibrium

$$PCl_5(g) = PCl_3(g) + Cl_2(g)$$

has been measured and is shown below, in table and graphical form. Reading the plot carefully, we see that $K_p = 10$ at $1/T = 1.73\times10^{-3}\ K^{-1}$ and $K_p = 0.1$ for $1/T = 2.15\times10^{-3}\ K^{-1}$.

The $PCl_5 = PCl_3 + Cl_2$ *Equilibrium*

T (°K)	α	K_P (atm)
439	0.124	0.0269
443	0.196	0.0329
462	0.244	0.0633
485	0.431	0.245
534	0.745	1.99
556	0.857	4.96
574	0.916	9.35
613	0.975	40.4



(a) Derive an equation that will provide a determination of the $\Delta \boldsymbol{H}_{\text{rxn}}^\circ$ for this chemical reaction in the temperature range shown.

[HINT: Start with the definition of ***G***. Also take a hint from the plot that (1/T) is a convenient explicit factor to include in your derivation. Assume that each gas behaves ideally, so that K_p can be written in pressures rather than in fugacities. Later in the course, we will consider 'true' equilibrium constants in terms of fugacities.]

Derivation here:

Consider $\boldsymbol{G}/T$: $\partial(\boldsymbol{G}/T)/\partial T = -\boldsymbol{G}/T^2 + (1/T)(\partial \boldsymbol{G}/\partial T)_p$

Substitute $\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$ into the right side of above eqn. to get

$\partial(\boldsymbol{G}/T)/\partial T = -(\boldsymbol{H} - T\boldsymbol{S})/T^2 + (1/T)(\partial \boldsymbol{G}/\partial T)_p$

But, from $\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$ we see that $-\boldsymbol{S}$ can be identified as $(\partial \boldsymbol{G}/\partial T)_p$

$\partial(\boldsymbol{G}/T)/\partial T = -(\boldsymbol{H} - T\boldsymbol{S})/T^2 - \boldsymbol{S}(1/T)$

$\partial(\boldsymbol{G}/T)/\partial T = -\boldsymbol{H}/T^2$ This is the Gibbs-Helmholtz eqn.

For reactants : $\partial(\boldsymbol{G}_{\text{reactants}}/T)/\partial T = -\boldsymbol{H}_{\text{reactants}}/T^2$

For products : $\partial(\boldsymbol{G}_{\text{products}}/T)/\partial T = -\boldsymbol{H}_{\text{products}}/T^2$

From which: $\partial(\Delta \boldsymbol{G}_{\text{rxn}}/T)/\partial T = -\Delta \boldsymbol{H}_{\text{rxn}}/T^2$

which can also be written as $(\partial(\Delta \boldsymbol{G}_{\text{rxn}}/T)/\partial(1/T))_p = +\Delta \boldsymbol{H}_{\text{rxn}}$

With reactants and products in their standard states, $(\partial(\Delta \boldsymbol{G}_{\text{rxn}}^\circ/T)/\partial(1/T))_p = \Delta \boldsymbol{H}_{\text{rxn}}^\circ$

Now we need to find where K_p fits into this.

At a given temperature, by integrating $\mathrm{d}\boldsymbol{G} = V\mathrm{d}p$, for an ideal gas,

$\boldsymbol{G}_{\text{C}}(p_{\text{C}}) = \boldsymbol{G}_{\text{C}}(1\ \text{atm}) + RT\ln(p_{\text{C}}/1)$

For a reaction aA +bB = cC + dD in the gas phase, at equilibrium, the value of p_{C} is the equilibrium partial pressure of C in the reaction vessel, and similarly for the others.

For a reaction aA +bB = cC + dD in the gas phase, at equilibrium $\boldsymbol{G}_{\text{products}} = \boldsymbol{G}_{\text{reactants}}$

Thus, we can write

$c\boldsymbol{G}_{\text{C}} + d\boldsymbol{G}_{\text{D}} = c\{\boldsymbol{G}_{\text{C}}(1\ \text{atm}) + RT\ln(p_{\text{C}}/1)\} + d\{\boldsymbol{G}_{\text{D}}(1\ \text{atm}) + RT\ln(p_{\text{D}}/1)\}$

$= a\boldsymbol{G}_{\text{A}} + b\boldsymbol{G}_{\text{B}} = a\{\boldsymbol{G}_{\text{A}}(1\ \text{atm}) + RT\ln(p_{\text{A}}/1)\} + b\{\boldsymbol{G}_{\text{B}}(1\ \text{atm}) + RT\ln(p_{\text{B}}/1)\}$

Collecting all the $\boldsymbol{G}_{\text{reactant or product}}(1\ \text{atm})$ terms together, and all the ln terms together, we get

$c\boldsymbol{G}_{\text{C}}^\circ + d\boldsymbol{G}_{\text{D}}^\circ - \{a\boldsymbol{G}_{\text{A}}^\circ + b\boldsymbol{G}_{\text{B}}^\circ\} = -RT\ln[(p_{\text{C}}^{c} \bullet p_{\text{D}}^{d})/p_{\text{A}}^{a} \bullet p_{\text{B}}^{b}]$

$\Delta \boldsymbol{G}_{\text{rxn}}^\circ = -RT\ln K_p$

$\Delta \boldsymbol{G}_{\text{rxn}}^\circ/T = -R\ln K_p$

Since we see above that $(\partial(\Delta \boldsymbol{G}_{\text{rxn}}^\circ/T)/\partial(1/T))_p = \Delta \boldsymbol{H}_{\text{rxn}}^\circ$, a plot of $\ln K_p$ versus 1/T should have a slope equal to $-\Delta \boldsymbol{H}_{\text{rxn}}^\circ/R$

(b) Apply your equation to the data to find the numerical value of $\Delta \boldsymbol{H}_{rxn}°$. Here, ° means the standard state, 1 atm, of course.

Calculations here:

From the given: " $K_p = 10$ at $1/T = 1.73\times10^{-3}\ K^{-1}$ and $K_p = 0.1$ for $1/T = 2.15\times10^{-3}\ K^{-1}$ "
we have the slope
$[\ln(10) – \ln(0.1)]/ [1.73\times10^{-3}\ K^{-1} - 2.15\times10^{-3}] = - 4.605/0.42\times10^{-3} = -10964$
This is equal to $- \Delta \boldsymbol{H}_{rxn}°/R$.
Thus, $\Delta \boldsymbol{H}_{rxn}° = +10964 \bullet 1.987 =$ 21,786 cal, call it 21,800 cal

Note: The graph was given only to provide a visual hint towards deriving the correct relation. You need not read any values from it.

8. Consider the following systems. In each case calculate the pressure which must be applied to $\mathcal{B}$ in order that equilibrium be established between $\mathcal{A}$ and $\mathcal{B}$ at the given temperature.

$\mathcal{A}$	$\mathcal{B}$	Calculations for *p,* atm
(a)		
rhombic sulfur density 1.5×10^3 g L^{-1} $\Delta \boldsymbol{G}°_f = 0$ *p* atm $V = \frac{32\ \text{g mol}^{-1}}{1.5\times10^3\ \text{g L}^{-1}}$ L mol^{-1}	monoclinic sulfur density 1.2×10^3 g L^{-1} $\Delta \boldsymbol{G}°_f = 0.023$ kcal mol^{-1} *p* atm $V = \frac{32\ \text{g mol}^{-1}}{1.2\times10^3\ \text{g L}^{-1}}$ L mol^{-1}	For all of (a)-(c) the following apply: $d\boldsymbol{G} = Vdp - \boldsymbol{S}dT$; $dT = 0$; and μ(side $\mathcal{A}$)= μ(side $\mathcal{B}$) in particular, μ(rh, *p* atm)= μ(mo, *p* atm), $\mu(\text{rh},1\text{ atm}) + \int_{1atm}^{p} V_{rh}dp = \mu(\text{mo},1\text{ atm}) + \int_{1atm}^{p} V_{mo}dp$ $0 + \int_{1atm}^{p}\frac{32}{1.5\times10^3}dp = 0.023 + \int_{1atm}^{p}\frac{32}{1.2\times10^3}dp$ $0.023\times10^3 = \left(\frac{32}{1.5\times10^3}-\frac{32}{1.2\times10^3}\right)(p-1)\frac{1.987}{0.08205}$ Solve for *p* = atm

(b) ***This Pd membrane allows only H_2 to pass***

↓

H_2 (g) 1 atm	$N_2(g) + H_2(g)$ $4N_2 : 1H_2$ mixture *p* atm	μ_{H2} (side $\mathcal{A}$) = μ_{H2} (side $\mathcal{B}$) since H_2 can pass through μ_{H2}(1 atm) = μ_{H2}(1 atm) + RT ln(p_{H2}/1 atm) $p_{H2} = 0.20\bullet p$ atm (Dalton's law of partial pressures) 0= RT ln (p_{H2}/1 atm) or ln ($0.20\bullet p$/1 atm) =0 $0.20\bullet p$/1 atm =1 ∴ p = 5 atm

(c) ***This semi-permeable membrane allows only H_2O to pass***

↓

pure liquid H_2O 1 atm vapor pressure $p_w{}^*$ $V_w = 0.018$ Lmol^{-1}	0.1 mole percent solution of sucrose in H_2O vapor pressure according to Raoult's law *p* atm Raoult's law: $p_w = x_w\, p_w{}^*$ $=(1\text{-}0.001)p_w{}^*$ $V_{soln} \approx 0.018$ Lmol^{-1}	μ_{H2O}(side $\mathcal{A}$)=μ_{H2O}(side $\mathcal{B}$) since H_2O can pass through μ_{H2O}(pure liquid H_2O, 1 atm)=μ_{H2O}(H_2O in solution, *p* atm) Think of pure liquid H_2O in equilibrium with its vapor: μ_{H2O}(in liquid H_2O,1 atm) = μ_{H2O}(in H_2O vapor) = μ_{H2O}(in H_2O vapor, 1atm) + R*T* ln ($p_w{}^*$/1) Think of liquid solution in equilibrium with its vapor: μ_{H2O}(in liquid soln, p_w) = μ_{H2O}(in H_2O vapor over the soln) = μ_{H2O}(in H_2O vapor, 1atm) + R*T* ln (p_w/1) = μ_{H2O}(in H_2O vapor, 1atm) + R*T* ln (0.999$p_w{}^*$/1) However, here side $\mathcal{B}$ is not under its vapor pressure $p_w{}^*$, but a pressure equal to *p* atm therefore we need to add $\int_{1atm}^{p} V_w dp$: Thus, μ_{H2O}(in liquid soln, *p*) = μ_{H2O}(in H_2O vapor, 1atm) +R*T* ln (0.999$p_w{}^*$/1)+ $\int_{1atm}^{p} V_{sol} dp$ ∴ R*T* ln ($p_w{}^*$/1)= R*T* ln (0.999$p_w{}^*$/1) + $\int_{1atm}^{p} V_{sol} dp$ $0.08205T \ln(0.999) = 0.018(p-1)$ Given *T*, solve for *p*