

1. Pure water boils at 1.00 atm and 100.0 °C. The enthalpy of vaporization is 44.0 kJ mol⁻¹.
- Calculate the boiling point of water one mile above sea level (e.g., Denver, Colorado) where atmospheric pressure is 0.83 bar. Can you suggest why cooking takes longer at high altitudes?
 - Calculate the boiling point of water inside a pressure cooker at 2.00 bar. Why is cooking food at 2.00 bar significantly more rapid than cooking under atmospheric pressure (\approx 1 bar)?

2. The following vapor pressures have been measured for *n*-propanol:

<i>t</i> / °C	40.0	60.0	80.0	100.0
<i>p</i> / kPa	6.69	19.6	50.1	112.3

Use the data (*Hint!* $\ln p$ plotted against $1/T$ is a straight line) to calculate the:

- enthalpy of vaporization
- normal boiling point (at 1.00 atm)
- standard boiling point (at 1.00 bar)
- vapor pressure of *n*-propanol at 25 °C.

3. The vapor pressures of solid and liquid uranium hexafluoride are represented by the equations

$$\ln(p_{\text{solid}}/\text{Pa}) = 29.411 - (5893.5 \text{ K})/T$$

$$\ln(p_{\text{liquid}}/\text{Pa}) = 22.254 - (3479.9 \text{ K})/T$$

- Calculate the temperature and pressure at the triple point of UF₆.
- Calculate the enthalpy of fusion, sublimation, and vaporization of UF₆.
- Why is UF₆ (and information about its properties) of considerable technical importance?

4. Suppose you have an organic compound dissolved in chloroform and you need to remove the chloroform by distillation. Because the compound is heat-sensitive, the temperature cannot be raised above 0 °C so you decide on vacuum distillation. At what pressure does pure chloroform boil at 0 °C? *Data:* Pure chloroform boils at 1.00 atm and 61.2 °C with $\Delta H_{\text{vap,in}} = 29.4 \text{ kJ mol}^{-1}$.
5. Estimate the melting point of ice at a pressure of 2040 atm under a glacier. (The measured melting point at this pressure is -22 °C.) *Data:* At 0 °C and 1 bar the densities of ice and liquid water are 0.915 g cm⁻³ and 0.9998 g cm⁻³. The enthalpy of fusion is 6010 J mol⁻¹.

6. The following p - V_m data are for xenon gas at 600 K.

p / bar	V_m / L mol $^{-1}$	Z	$(Z - 1)/p$ / bar $^{-1}$
9.936	4.9884	0.9936	-0.000643
57.90	0.8314	0.9651	-0.000603
103.7	0.4535	0.9431	-0.000549
148.6	0.3118	0.9288	-0.000479
193.9	0.2375	0.9237	-0.000393
294.4	0.1609	0.9498	-0.000170
428.8	0.1217	1.0457	0.000107
521.1	0.1084	1.1328	0.000255
641.2	0.0978	1.2574	0.000401
802.7	0.0891	1.4334	0.000540
1026.	0.0818	1.6823	0.000665

- a) Calculate the fugacity coefficient γ for xenon as a function of pressure at 600 K.

Suggestion! Excel (or other software) and regression can be used to fit $(Z-1)/p$ to a polynomial in p , such as $(Z-1)/p = a_0 + a_1 p + a_2 p^2 + a_3 p^3 + a_4 p^4$, then integrate:

$$\ln \gamma = \ln \frac{f}{p} = \int_0^p \frac{Z-1}{p} dp$$

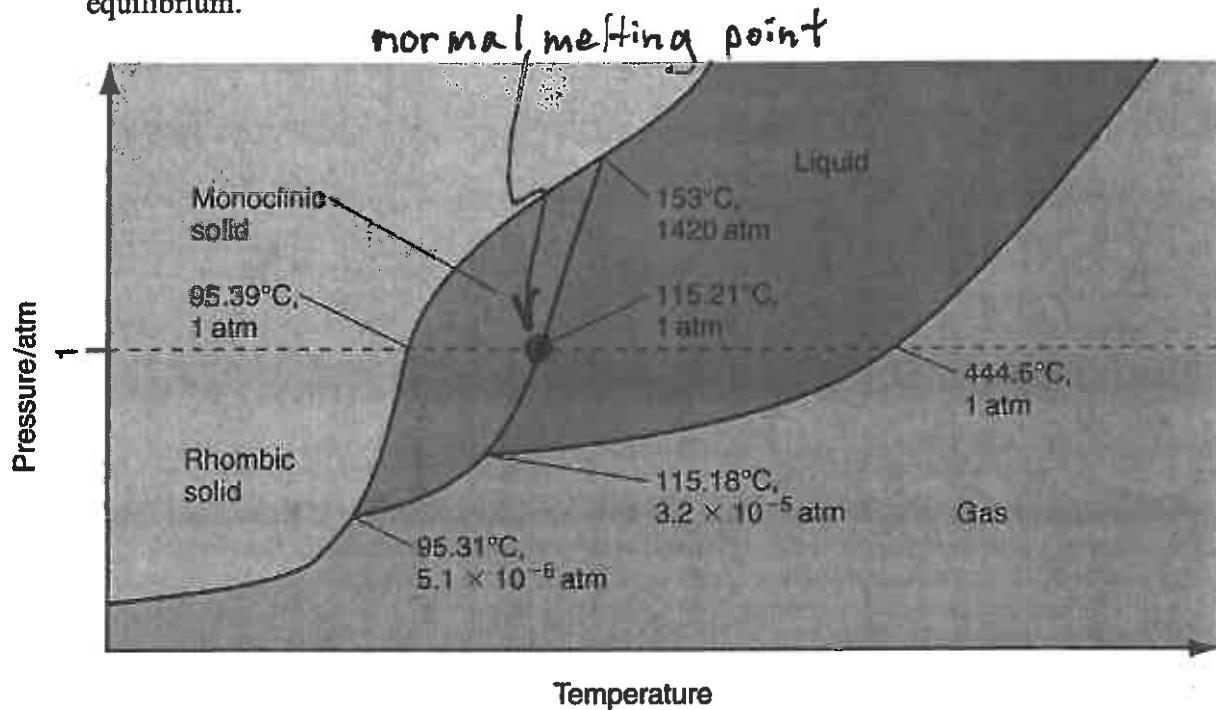
- b) The chemical potential of xenon ($\mu = G_m$) is less than μ^{ideal} (the chemical potential of an ideal gas) at low pressures, but larger than μ^{ideal} at high pressures. Does this behavior "make sense"?

- c) Show $(Z - 1)/p \rightarrow B(T)/RT$ in the limit $p \rightarrow 0$. (Reminder! $B(T)$ is the second virial coefficient.)

7. Use the phase rule $F = C - P + 2$ to determine the number of degrees of freedom for each of the following systems. And for each system, give a variable for each degree of freedom to conveniently describe the state of each system (such as temperature T and pressure p for liquid water, $C = 1$).

- a) liquid water in equilibrium with its vapor
- b) liquid water in equilibrium with its vapor and ice
- c) a liquid methanol + water mixture in equilibrium with its vapor
- d) sugar dissolved in water
- e) a tin-lead solder (a solid solution of lead and tin)
- f) an aqueous solution of NaCl (dissociated to form Na^+ and Cl^- ions)
- g) aqueous solution of acetic acid (partially dissociated to H^+ and CH_3COO^- ions)

8. Use the p - T phase diagram for sulfur shown below to answer this question.
- What is the stable form of sulfur at 25 °C and 1 atm?
 - Give the normal melting point of sulfur. Does solid sulfur float or sink in the liquid sulfur? Justify your answer.
 - Describe the phases present at each triple point.
 - Give the range of temperature and pressure over which monoclinic sulfur can exist at equilibrium.



9. One mole of bulk liquid water (volume 18.0 cm³, negligible surface area) is converted to a mist of droplets of radius 10 nm at 25 °C.
- Calculate the surface work w for this process. Use 0.072 N m⁻¹ for the surface tension.
 - Calculate the pressure inside the droplets. Assume the external pressure is 1.00 bar.
 - Calculate the vapor pressure of the water in the droplets. The vapor pressure of bulk ($r = \infty$) liquid water at 25 °C is 0.0316 bar.
10. Suppose you are asked to measure surface tensions in the range $0.02 < \gamma < 0.08$ N m⁻¹. Calculate a suitable capillary diameter to give a minimum capillary rise (h) of 2.00 cm for solutions with densities $0.70 < \rho < 1.00$ g cm⁻³.

1. a) Calculate the boiling point of water at a pressure of 0.83 bar

1.01325 bar

Data: The vapor pressure of water is 1.00 atm at 100°C
 where $\Delta H_{vap,m}^{\circ} = 44.0 \text{ kJ mol}^{-1}$

373.15 K

Use the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = -\frac{\Delta H_{vap,m}^{\circ}}{R} \approx \text{constant}$$

$$\frac{\ln p_2 - \ln p_1}{T_2 - T_1} = -\frac{\Delta H_{vap,m}^{\circ}}{R}$$

$T_1 = 373.15 \text{ K}$
 $p_1 = 1.01325 \text{ bar}$
 $T_2 = ?$
 $p_2 = 0.83 \text{ bar}$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta H_{vap,m}^{\circ}} (\ln p_2 - \ln p_1) = \frac{1}{T_1} - \frac{R}{\Delta H_{vap,m}^{\circ}} \ln \left(\frac{p_2}{p_1} \right)$$

$$\frac{1}{T_2} = \frac{1}{373.15 \text{ K}} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{44000 \text{ J mol}^{-1}} \ln \left(\frac{0.83}{1.01325} \right)$$

$$T_2 = 367.97 \text{ K} \quad (94.8 \text{ }^{\circ}\text{C})$$

Cooking is a chemical-reaction process with rate constants depending exponentially on the temperature, so even a relatively small decrease in temperature ($\approx 5 \text{ K}$) can significantly slow down cooking rates (especially "baking" that involves vapor generation)

(1 cont.)

b) Boiling point of water at 2.00 bar?

$$P_1 = 1.01325 \text{ bar}$$

$$P_2 = 2.00 \text{ bar}$$

$$T_1 = 373.15 \text{ K}$$

$$T_2 = ?$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta H_{vap,m}^{\circ}} \ln\left(\frac{P_2}{P_1}\right) = \frac{1}{373.15} - \frac{8.314}{44000} \ln\left(\frac{2.00}{1.01325}\right)$$

$$\frac{1}{T_2} = 0.0025517$$

$$T_2 = 391.9 \text{ K} \quad (118.8^\circ\text{C})$$

2. Plot $\ln P$ against $1/T$ for n-propanol
(see next page) units: K

straight line!

$$\text{slope} = \frac{-\Delta H_{vap,m}^{\circ}}{R}$$

$$\boxed{\ln(P/\text{kPa}) = 19.4718 - 5499.15 \frac{1}{T}} \quad \text{"from regression"}$$

(least-squares fitting)

a) $\frac{-\Delta H_{vap,m}^{\circ}}{R} = -5499.15 \text{ K}$

$$\Delta H_{vap,m}^{\circ} = R(5499.15 \text{ K}) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(5499.15 \text{ K}) \\ = 45720 \text{ J mol}^{-1}$$

b) normal boiling point $P = 1 \text{ atm} = 101.325 \text{ kPa}$

$$\text{solve } \ln(101.325) = 19.4718 - \frac{5499.15 \text{ K}}{T}$$

$$T = 370.23 \text{ K}$$

$$97.1^\circ\text{C}$$

(Q2 cont.)

c) standard boiling point of n-propanol

$$P = 100.00 \text{ kPa} (1.000 \text{ bar})$$

$$\text{solve } \ln(100.00) = 19.4718 - \frac{5499.15}{T}$$

$$T = 369.90 \text{ K} \quad (96.7^\circ\text{C})$$

0.33°C lower
than the normal
boiling point

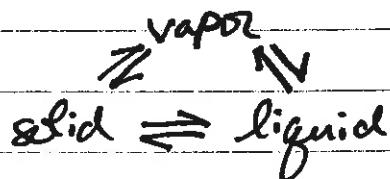
d) 25°C 298.15 K

$$\ln(P/\text{kPa}) = 19.4718 - \frac{5499.15}{298.15} = 1.0276$$

$$P = 2.794 \text{ kPa}$$

(Q3) a) at the triple point, the solid and liquid (and the vapor) are in equilibrium (same vapor pressure)

$$P_{\text{solid}} = P_{\text{liquid}}$$



$$\ln(P_{\text{solid}}/\text{Pa}) = \ln(P_{\text{liquid}}/\text{Pa})$$

$$29.411 - \frac{5893.5}{T_{tp}} = 22.254 - \frac{3479.9}{T_{tp}}$$

$$\text{solve } T_{tp} = 337.2 \text{ K} \quad \text{where } \ln P_{\text{solid}} = \ln P_{\text{liquid}} = 11.935$$

$$P_{\text{solid}} = P_{\text{liquid}} = e^{11.935} \text{ Pa} = 152,500 \text{ Pa} = 152.5 \text{ kPa}$$

(Q3 cont.)

b) $\ln(P_{\text{solid}}/\text{Pa}) = 29.411 - \frac{5893.5 \text{ K}}{T}$

$$\frac{d \ln(P_{\text{solid}}/\text{Pa})}{dT} = -5893.5 \text{ K} = -\frac{\Delta H_{\text{sub,m}}^{\circ}}{R}$$

$$\begin{aligned}\Delta H_{\text{sub,m}}^{\circ} &= (5893.5 \text{ K})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 48.998 \text{ kJ mol}^{-1}\end{aligned}$$

Similarly:

$$\ln(P_{\text{liquid}}) = 22.254 - \frac{3479.9 \text{ K}}{T}$$

$$\begin{aligned}\Delta H_{\text{vap,m}}^{\circ} &= (3479.9 \text{ K})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 28.932 \text{ kJ mol}^{-1}\end{aligned}$$

$$UF_6(s) = UF_6(l) \quad \Delta H_{\text{fus,m}}^{\circ}$$

$$UF_6(l) = UF_6(g) \quad \Delta H_{\text{vap,m}}^{\circ}$$

$$UF_6(s) = UF_6(g) \quad \Delta H_{\text{sub,m}}^{\circ}$$

$$\Delta H_{\text{sub,m}}^{\circ} = \Delta H_{\text{fus,m}}^{\circ} + \Delta H_{\text{vap,m}}^{\circ}$$

$$\begin{aligned}\Delta H_{\text{fus,m}}^{\circ} &= \Delta H_{\text{sub,m}}^{\circ} - \Delta H_{\text{vap,m}}^{\circ} \\ &= 48.998 - 28.932 \\ &= 20.066 \text{ kJ mol}^{-1}\end{aligned}$$

slightly denser

c) gas centrifuges are used to separate $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$

to purify ^{235}U for nuclear power reactor fuel

^{238}U isotope (most abundant) does not fission easily

vapor pressure of chloroform at 0 °C?

4. Use the Clausius-Clapeyron equation

$$\frac{dp}{dT} = -\frac{\Delta H_{vap,m}^{\circ}}{R} \approx \frac{\ln p_2 - \ln p_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$T_1 = 334.35 \text{ K} \quad (61.2^\circ\text{C})$$

$$p_1 = 1.00 \text{ atm}$$

$$T_2 = 273.15 \text{ K} (0^\circ\text{C})$$

$$p_2 = ?$$

$$\ln p_2 = \ln p_1 - \frac{\Delta H_{vap,m}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$= \ln(1.00) - \frac{29400}{8.314} \left(\frac{1}{273.15} - \frac{1}{334.35} \right)$$

$$\ln p_2 = -2.370$$

$$p_2 = e^{-2.370} \text{ atm} = 0.0934 \text{ atm}$$

don't use the Clausius-Clapeyron equation - no gas phase here!

5. Ice melts at 0 °C and 1 atm, but what is the melting point at 2040 atm under a glacier?

Clapeyron equation $\frac{dp}{dT} = \frac{\Delta H_{fus,m}}{T \Delta V_{fus,m}}$

$$\frac{dp}{dT} = \frac{6010 \text{ J mol}^{-1}}{(273.15 \text{ K})(-1.67 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}$$

$$\frac{dp}{dT} = -1.318 \times 10^7 \text{ Pa K}^{-1}$$

$$\frac{dp}{dT} = \left(-1.318 \times 10^7 \frac{\text{Pa}}{\text{K}} \right) \frac{1 \text{ atm}}{101325 \text{ Pa}} = -130 \frac{\text{atm}}{\text{K}}$$

$$\Delta T \approx \Delta P / (-130 \text{ atm K}^{-1}) = 2039 \text{ atm} / (-130 \text{ atm K}^{-1}) \\ = -15.7 \text{ K} \quad \approx -15.7^\circ\text{C}$$

at 0 °C and 1 atm:

$$T = 273.15 \text{ K}$$

$$\Delta H_{fus,m} = 6010 \text{ J mol}^{-1}$$

$$\Delta V_{fus,m} = V_m(l) - V_m(s)$$

$$= \frac{M}{\rho_l} - \frac{M}{\rho_s}$$

$$= \frac{18.015}{0.9998} - \frac{18.015}{0.915}$$

$$= -1.67 \frac{\text{cm}^3}{\text{mol}}$$

6.

Okay, okay, this is a tough one!

But this question shows how attractive and repulsive intermolecular forces influence the chemical potential, one of the most important thermodynamic quantities, especially for chemists.

a) As suggested, plot $(z-1)/\rho$ against the pressure ρ .

(See next page)

Regression (least-squares fitting) gives:

$$(z-1)/\rho = a_0 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 + a_4 \rho^4$$

$$a_0 = -0.00064958 \text{ bar}^{-1}$$

$$a_1 = 3.82769 \times 10^{-7} \text{ bar}^{-2}$$

$$a_2 = 6.8865 \times 10^{-9} \text{ bar}^{-3}$$

$$a_3 = -1.06065 \times 10^{-11} \text{ bar}^{-4}$$

$$a_4 = 4.62878 \times 10^{-15} \text{ bar}^{-5}$$

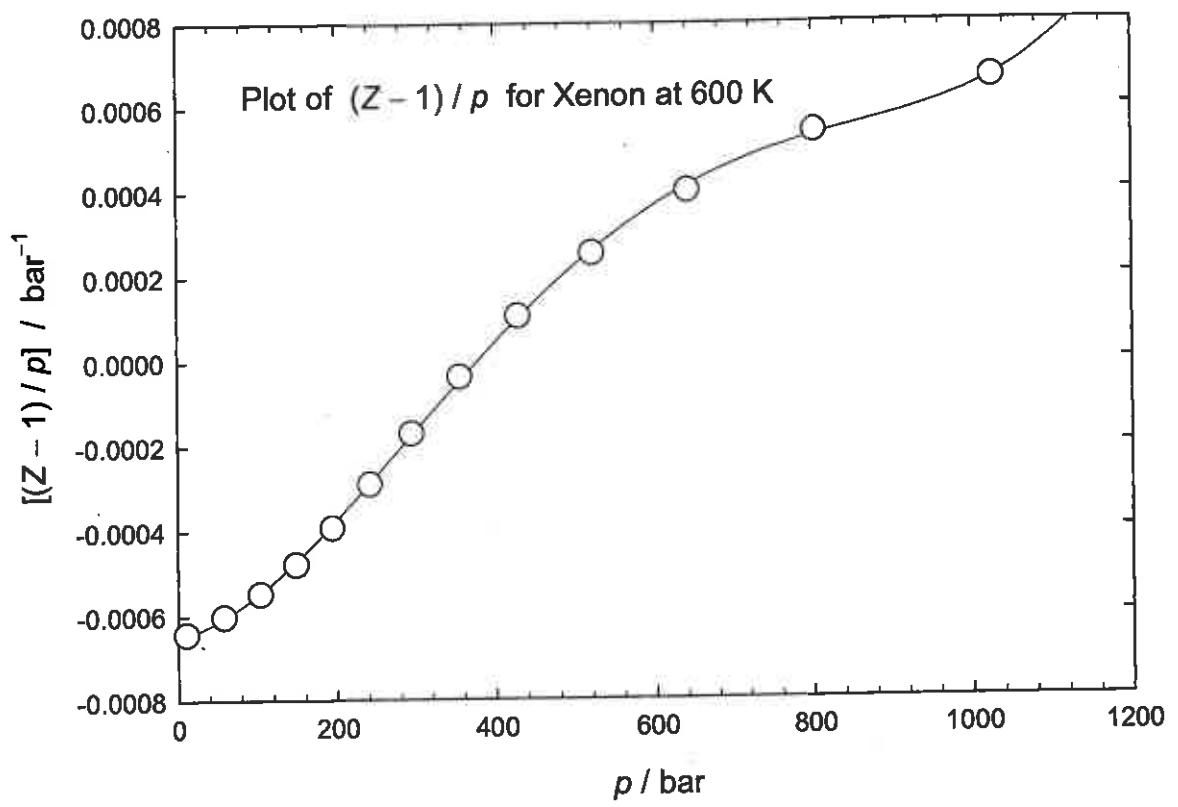
$$\ln \gamma = \ln \left(\frac{f}{P} \right) = \int_0^P \frac{z-1}{P} d\rho = \int_0^P (a_0 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 + a_4 \rho^4) d\rho$$

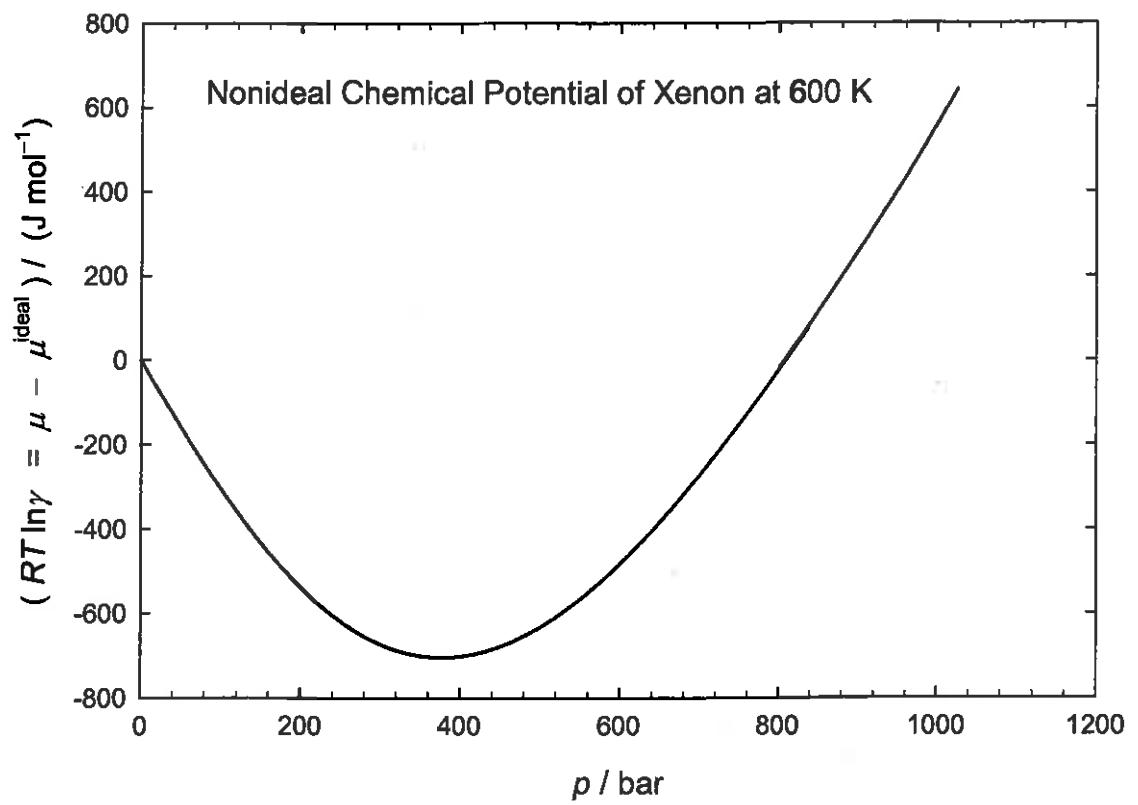
$$\ln \gamma = a_0 P + \frac{a_1}{2} P^2 + \frac{a_2}{3} P^3 + \frac{a_3}{4} P^4 + \frac{a_4}{5} P^5$$

$$RT \ln \gamma = RT \ln(f/P) = RT \ln f - RT \ln P$$

$$= \mu - \mu^{\text{ideal}} = \text{nonideal chemical potential of Xe}$$

see graph
RTlnγ vs P





(6 cont.)

$$\mu = \underbrace{\mu^0 + RT \ln P}_{\text{ideal}} + \underbrace{RT \ln \delta}_{\text{nonideal}}$$

b) in the limit $P \rightarrow 0$, the gas is ideal:

$$\mu \rightarrow \mu^0 + RT \ln P \quad RT \ln \delta \rightarrow 0$$

$$0 < P < 800 \text{ bar}$$

$$RT \ln \delta < 0$$

$$\mu < \mu^{\text{ideal}}$$

attractive forces reduce the chemical potential

$$P > 800 \text{ bar}$$

$$RT \ln \delta > 0$$

$$\mu > \mu^{\text{ideal}}$$

repulsive forces increase the chemical potential

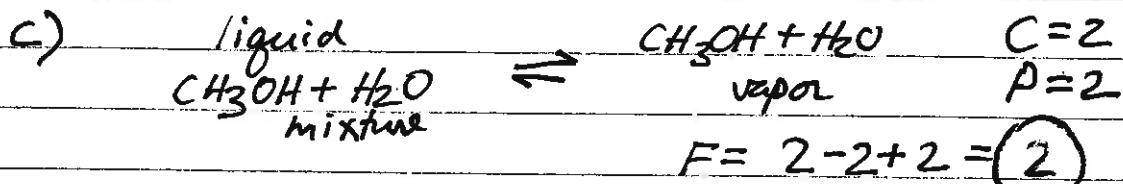
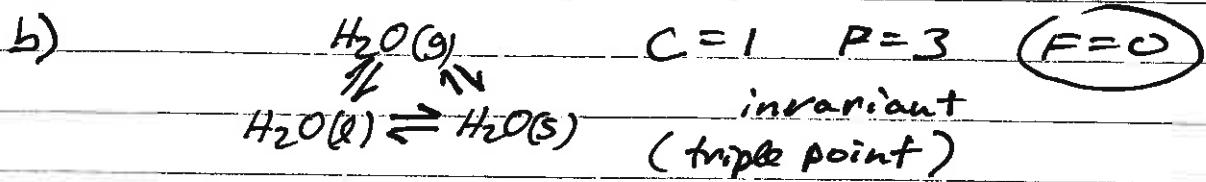
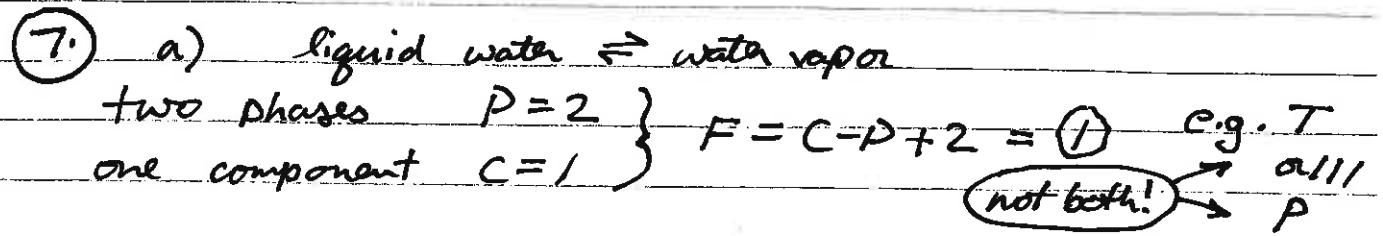
c) $Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots$ virial equation

$$\frac{Z-1}{P} = \frac{\frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots}{P}$$

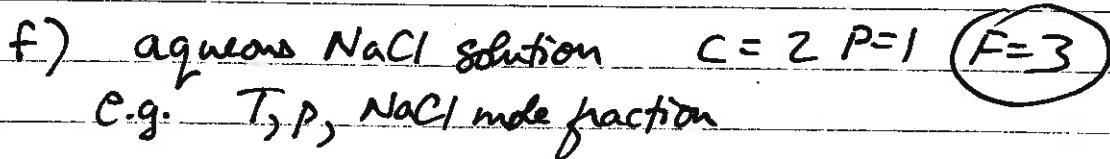
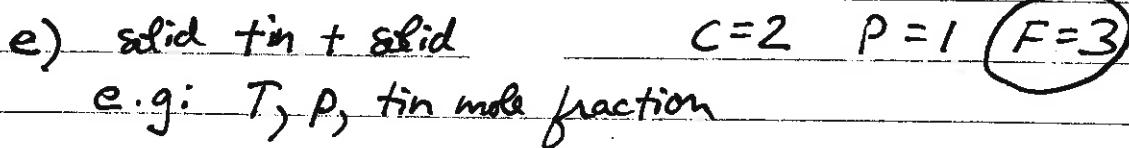
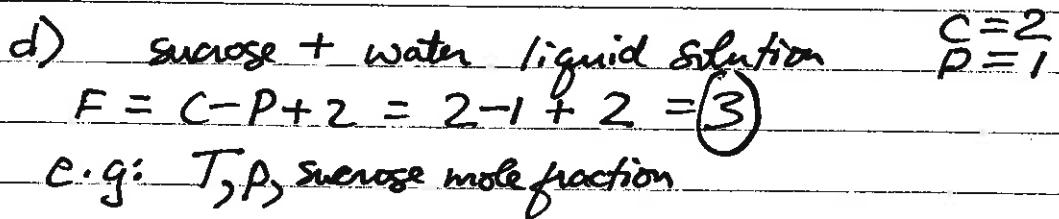
$$= \frac{B(T)}{PV_m} + \frac{C(T)}{PV_m V_m} + \dots$$

$$\lim_{P \rightarrow 0} P \rightarrow 0$$

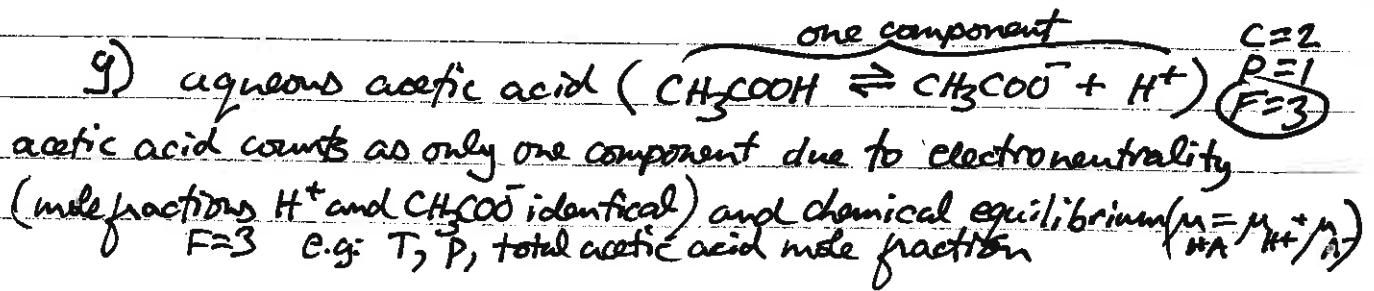
$$\frac{PV_m}{V_m} \rightarrow RT \quad \frac{Z-1}{P} = \frac{B(T)}{RT}$$



variables: T and methanol mole fraction in the liquid
 or // T and P



Na^+ and Cl^- don't count as two components because
 mole fraction $Na^+ =$ mole fraction Cl^- (electroneutrality)



(8.) a) sulfur at 25 °C and 1 atm
rhombic S(s) (see diagram)

b) melting point at 1 atm
solid sinks (see diagram)
115.21 °C

c) 95.31 °C \Rightarrow S(s) rhombic + S(g) +
 5.1×10^{-6} atm S(s) monoclinic

115.18 °C \Rightarrow S(s) monoclinic + S(l) + S(g)
 3.2×10^{-5} atm

153 °C \Rightarrow S(s) monoclinic + S(s) rhombic
1420 atm + S(l)

d) 95.31 to 153 °C \Rightarrow monoclinic
stable
 5.1×10^{-6} to 1420 atm S(s)

at the normal melting point (1 atm, 95.39 °C):

notice that $\frac{dP}{dT} > 0$ for the monoclinic solid \rightleftharpoons liquid
coexistence line
(positive slope)

from the Clapeyron equation for melting the solid

$$\frac{dP}{dT} = \frac{\Delta S_{fus}}{\Delta V_{fus}} = \frac{\Delta H_{fus}}{T \Delta V_{fus}} \quad \therefore \Delta V_{fus} > 0$$

+ve +ve

S(s) expands on melting
solid denser and sinks

$$(r = 10 \times 10^{-9} \text{ m} = 10 \times 10^{-7} \text{ cm})$$

9. One mole of "bulk" (negligible surface area) liquid water is dispersed, forming a mist of 10-nm radius droplets

$\downarrow \text{surface tension } \gamma$

$\downarrow \text{surface area } A$

a) surface tension work $d\omega = \gamma dA$

surface tension $\gamma = 0.072 \text{ N/m}$ (assumed constant)

$$\omega = \int d\omega = \int_{A_i}^{A_f} \gamma dA = \gamma (A_f - A_i)$$

initial area for a cube of liquid of volume 180 cm^3

$$V = L^3 \quad L = V^{1/3} = \text{edge length}$$

six faces $L = 2.62 \text{ cm}$



$$A_i = 6L^2 = 6(2.62)^2 \text{ cm}^2 = 41.2 \times 10^{-4} \text{ m}^2 \quad \text{initial surface area}$$

final area volume of one droplet $= \frac{4}{3}\pi r^3$

area of one droplet $= 4\pi r^2$

total area $= (\text{number of droplets})(\text{area per droplet})$

(surface area of the mist) $= \frac{\text{total volume}}{\text{volume per droplet}} \text{ area per droplet}$

$$= \frac{18.0 \text{ cm}^3}{\frac{4}{3}\pi(10 \times 10^{-7} \text{ cm})^3} 4\pi r^2$$

$$A_f = \frac{V}{\frac{4}{3}\pi r^3} 4\pi r^2$$

$$A_f = 3V/r$$

$$= (4.297 \times 10^{18} \text{ droplets}) 4\pi (10 \times 10^{-9} \text{ m})^2$$

$A_f = 5400 \text{ m}^2$ final area of droplets

(9 a cont.)

$$\text{surface work} = (\text{surface tension}) \times (\text{change in surface area})$$

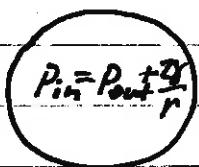
$$= \gamma (A_f - A_i)$$

$$= (0.072 \text{ N m}^{-1}) / (5400 \text{ m}^2 - 0.0041 \text{ m}^2)$$

$$w = 389 \text{ J to form the mist}$$

\uparrow negligible

b)



$$P_{\text{out}} = 1 \text{ bar} = 10^5 \text{ Pa}$$

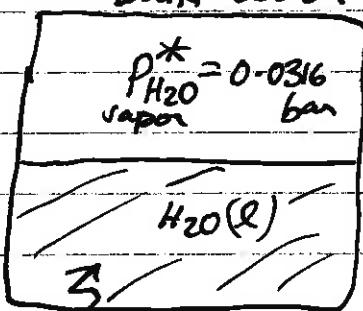
$$P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r}$$

$$= 10^5 \text{ Pa} + \frac{2(0.072 \text{ N m}^{-1})}{10 \times 10^{-9} \text{ m}} \quad (\text{SI units})$$

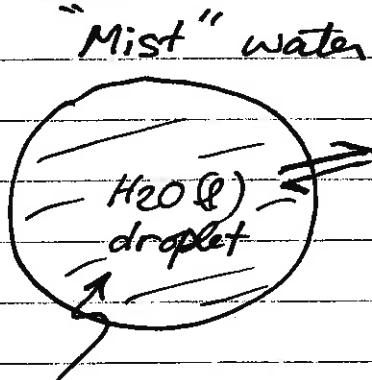
$$= 10^5 \text{ Pa} + 1.44 \times 10^7 \text{ Pa}$$

$$= 1.45 \times 10^7 \text{ Pa} = 145 \text{ bar}$$

c) the vapor pressure of liquid water "bulk" phase ($r=\infty$) is 0.0316 bar



at a pressure
of 0.0316 bar



at a pressure
of 145 bar

$$\Delta P = 145 - 0.0316 \text{ bar} \approx 145 \text{ bar}$$

$$P = P^* e^{V_m \Delta P / RT}$$

(all SI)

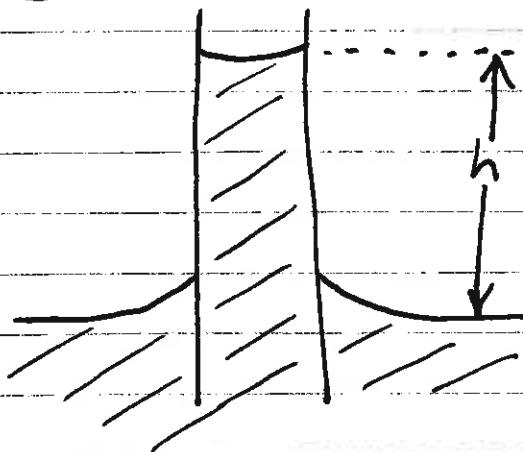
$$(18 \times 10^{-6} \text{ m}^3 / (145 \times 10^5 \text{ Pa}) / (8.34) / 298)$$

$$= (0.0316 \text{ bar}) e^{0.105}$$

$$= (0.0316 \text{ bar}) 1.111 = 0.0351 \text{ bar}$$

$$= 145 \times 10^5 \text{ Pa}$$

10.

capillary rise h 

$$h = \frac{2\gamma}{\rho g r} \quad (\text{assume } \theta=0)$$

$$\text{minimum } h = 2.00 \text{ cm}$$

min. h for min. γ (0.02 Nm^{-1})
and max ρ (1.00 g cm^{-3})

capillary radius $r = \frac{2\gamma}{\rho g h}$

$$= \frac{2(0.02 \text{ Nm}^{-1})}{(1000 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2})(0.020 \text{ m})}$$

$$= 2.04 \times 10^{-4} \text{ m}$$

$$= 0.204 \text{ mm}$$