Quiz 3

CH 353 Sumer 2010

Vanden Bout

Name: KEY

Carefully read all the problems. The exam should have 4 questions on 6 pages. The first page has potentially useful information. The last page is for extra writing space.

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ $R = 8.314\text{x}10^{-2}\ \text{L bar K}^{-1}\ \text{mol}^{-1}$ $R = 8.206\text{x}10^{-2}\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

1 atm = 1.01325 bar T/K = T/°C + 273.15 1 atm-L = 101.325 J 1 bar-L = 100 J

$g = 9.8\ \text{m s}^{-2}$ $\Pi = \rho g h$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$P_i = \chi_i P_i^*$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_M \qquad \left(\frac{\partial \mu}{\partial T}\right)_P = -S_M$$

Please sign at the bottom to certify that you have worked on your own.

I certify that I have worked the following exam without the help of others, and that the work I am turning in is my own.

Signed: ---

Signature Date

1. True/False Circle either T or F for each statement (10 points each)

(T) F At the critical point, $\Delta_{VAP}H° = 0$. Yes. $\bar{V}_{liq} = \bar{V}_{gas}$

(T) F The vapor pressure of the solid phase of a substance is never higher than the vapor pressure of the liquid phase. equal at triple point. lower at other T

T **(F)** The temperature the triple point changes dramatically with changes in the pressure since the properties of gases are strongly dependent on pressure.
Only 1 Temp @ triple point. Doesn't vary at all

(T) F The chemical potential of every substance increases with increasing pressure at constant temperature. $\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V}$ $V > 0$ $\therefore P\uparrow \mu\uparrow$

T **(F)** Given that $dA = -SdT - PdV$ and $dG = -SdT + VdP$,

then $\left(\frac{\partial A}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P$ $\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P = -S$

2A. (25 points)

Given that $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

Do you think the enthalpy of a gas that obeys the following equation will increase, decrease, or stay the same for an increase in pressure at constant temperature?

$PV_m = RT(1 + bP + cP^2)$ where b < 0 and c > 0

$V = nRT\frac{(1 + bP + cP^2)}{P}$

$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{V}{T}\right)$

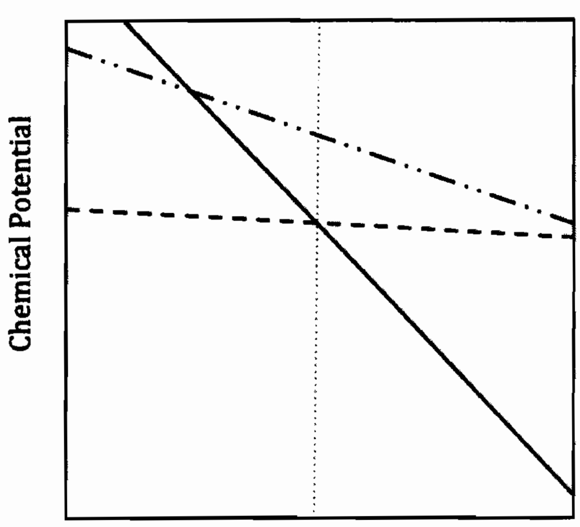
$\left(\frac{\partial V}{\partial T}\right)_P = nR\frac{(1 + bP + cP^2)}{P} = \frac{V}{T}$

$\left(\frac{\partial H}{\partial P}\right)_T = V - V = 0$

∴ H is indept of P for this gas

2B. (25 points)

The following plot show the chemical potential of different phases of a substance as a function of the temperature.
Label the phase associated with each of these lines (5 points each).
Is this diagram at a pressure above, below, or at the triple point? (5 points).
Is the temperature at the triple point above, below, or equal to the temperature marked on the diagram? (5 points)



Phase	Line
GAS	———
LIQ	—··—
SOL	- - - -

steepest slope

$\left(\frac{\partial \mu}{\partial T}\right)_P = -\bar{S}$ slope is $-\bar{S}$.

Below triple point → sublimation.
Triple point is at higher T. (last T w/ sublimation)

3A. (25 points)

Given that the density of water at 25°C is about 1 g cm^{-3}. And that the equilibrium vapor pressure of water at 25° C is approximately 25 Torr. What is the free energy difference between liquid water at 25°C and a pressure of 100 bar and gaseous water at 25°C and a pressure of 100 bar?

$$\text{Liq (100 bar)} \xrightarrow{\Delta G = ?} \text{Gas (100 bar)}$$

$$\downarrow \Delta G_1 \qquad\qquad \uparrow \Delta G_3$$

$$\text{Liq (25 Torr)} \xrightarrow[\Delta G_2 = 0]{} \text{Gas (25 Torr)}$$

$$\frac{25\ \text{Torr}}{750\ \text{Torr bar}^{-1}} = 0.033\ \text{bar}$$

use 1 mole $H_2O \rightarrow 18\,g \rightarrow .018\,L$

$$\Delta G_1 = \int_{100}^{.033} V_{liq}\, dP = V\Delta P = (.018\,L)(-99.67\ \text{bar}) = -1.8\ \text{L-bar} = -180\ J$$

$$\Delta G_3 = \int_{.033}^{100} V_{gas}\, dP = nRT \ln\left(\frac{100}{.033}\right) = (1)(8.314)(298)\ln\left(\frac{100}{.03}\right) = +19{,}861\ J$$

$$\Delta G = -180 + 0 + 19861 = \boxed{+19{,}681\ J}$$ for 1 mole. or 19.68 kJ mol^{-1}

3B (25 points)

Entropy changes with respect to temperature change and volume change is given by the following formula.

$$dS = \frac{C_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

isothermal $dT = 0$ $\quad dS = \left(\frac{\partial P}{\partial T}\right)_V dV$

What is the change in entropy for 1 mole of a van der Waals (VDW) gas that is expanded irreversibly and isothermally at 300K from an initial volume of 0.5 L to a final volume of 2 L? $\overline{C}_V = 1.5R$ and the VDW constants are a = 15 L^2-bar mol^{-2} and b = 0.1 L mol^{-1}.

$$P = \frac{RT}{\bar{V} - b} + \frac{a}{\bar{V}^2} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V} - b}$$

$$\Delta S = \int_{V_i}^{V_f} \left(\frac{\partial P}{\partial V}\right)_T dV = \int_{V_i}^{V_f} \frac{R}{\bar{V} - b} = R \ln\left(\frac{\bar{V}_f - b}{\bar{V}_i - b}\right)$$

$$\Delta S = R \ln\left(\frac{2 - .1}{.5 - .1}\right) = 8.314 \ln(4.75)$$

$$\boxed{= +12.95\ J K^{-1}}$$

4. (50 points)

The triple point of ammonia is at a temperature of 195.41 K and a pressure of 0.0608 bar. If the enthalpy of vaporization for ammonia is 23.35 kJ mol^{-1}. What is the standard boiling temperature of ammonia?

T_b is when $P_{NH_3} = 1$ bar

$$\ln\left(\frac{1}{.0608}\right) = \frac{-23{,}350}{8.314}\left[\frac{1}{T} - \frac{1}{195.41}\right]$$

$$T_b = T = 242.7 \text{ K}$$

Given that solid ammonia melts at temperature of 196.0 K at a pressure of 560 bar, $\Delta_{FUS}S° = 28.93$ J K^{-1} mol^{-1}, and the density of solid ammonia is 8.17 g cm^{-3}, what is the density of liquid ammonia?

$$\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V}$$

$P = .0608 \longrightarrow T_m = 195.41$

$P = 560 \longrightarrow T_m = 196.0$

$\Delta P = 560$ bar $\quad \Delta T = 0.59$ K

$$\frac{\Delta S}{\Delta V} = \frac{560 \text{ bar}}{0.59 \text{ K}} = 949 \text{ bar K}^{-1}$$

$$\Delta V = \frac{\Delta S}{949} \cdot \frac{.2893 \text{ L-bar K}^{-1} \text{ mol}^{-1}}{949 \text{ bar K}^{-1}}$$

$\Delta V = 3.03 \cdot 10^{-4}$ L mol^{-1}

$= 0.3$ cm^3 mol^{-1}

$\rho_{SOL} = 8.17$ g cm^{-3}

$\bar{V}_{SOL} = \frac{1}{8.17} \times 17$ g mol^{-1} = ~~0.122 cm~~ 2.08 cm^{-3} mol^{-1}

$\bar{V}_{liq} = 2.08$ cm^{-3} mol^{-1} + 0.3 cm^{-3} mol^{-1} = 2.38 cm^{-3} mol^{-1}

$$\rho_{liq} = \frac{1}{(2.38/17)} = 7.13 \text{ g cm}^{-3}$$