

Exam V  
CH 353 Sumer 2007

Vanden Bout

Name: KEY

Carefully read all the problems. The first page has potentially useful information. The last page is for extra writing space.

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

$$1 \text{ atm} = 1.01325 \text{ bar} \quad T/\text{K} = T/^{\circ}\text{C} + 273.15 \quad 1 \text{ atm-L} = 101.325 \text{ J} \quad 1 \text{ bar-L} = 100 \text{ J}$$

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

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Delta T = KX_B \quad K = \frac{RT_b^{*2}}{\Delta_{\text{VAP}}H} \quad \Delta T = K'X_B \quad K' = \frac{RT_m^{*2}}{\Delta_{\text{FUS}}H}$$

$$\Pi = \frac{n_B}{V} RT = [B]RT$$

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

**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.

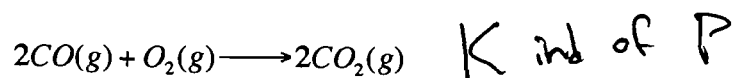
Signed: \_\_\_\_\_  
Signature Date

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

T  F The activity of a pure solid is approximately equal to one because solids are incompressible and have a small molar volume.  $\therefore$  *indep of P*

T  F For the following reaction  $\Delta_R G^\circ$  greater than zero.  
 $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$  *Yes. water is stable*

T  F For the following reaction increasing the total pressure will increase the equilibrium constant

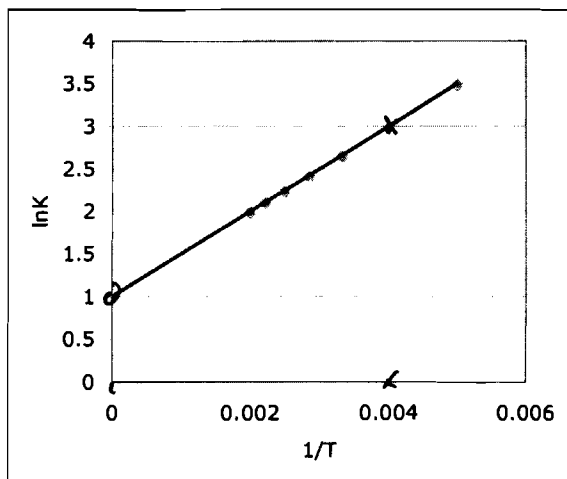


T  F When a mixture of  $NO_2$  and  $N_2O_4$  is at equilibrium, the chemical potential of  $NO_2$  is higher than that of  $N_2O_4$  ~~at equal~~

T  F If  $\Delta_R S^\circ > 0$ , the equilibrium constant for a reaction will always increase with increasing temperature  
*depend on  $\Delta H$  not  $\Delta S$*

2A. (25 points)

Below is plot of the  $\ln K$  vs  $1/T$  for a reaction. Use this plot to estimate  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  for the reaction.



$$\text{find slope} = \frac{3-1}{.004-0} = 500$$

$$-\frac{\Delta_R H^\circ}{R} = 500$$

$$\Delta_R H^\circ = -500R$$

$$\Delta_R H^\circ = -4.16 \text{ kJ mol}^{-1}$$

$$\frac{\Delta_R S^\circ}{R} = 1$$

$$\Delta_R S^\circ = R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$516^\circ$$

If you can't give a numerical answer, say whether you think each is positive, negative, or zero.

2B. (25 points)



A small amount of solid A is placed in an evacuated container (initially only A) allowed to come to chemical equilibrium at a constant temperature of 300 K. If  $\Delta_R G^\circ = -5 \text{ kJ mol}^{-1}$  for this reaction what is the total pressure at equilibrium?

$$K = \exp\left[\frac{-5,000}{(8.314)(300)}\right] = 7.42$$

$$K = P_B P_C^2 \quad P_C = 2P_B$$

$$K = P_B (2P_B)^2 = 4P_B^3 = 7.42$$

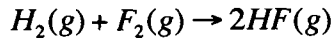
$$P_B = \sqrt[3]{\frac{7.42}{4}} = 1.23$$

$$P = P_B + 2P_B$$

$$P = 3P_B = 3.69 \text{ atm}$$

3. (50 Points)

For the following reaction



Substance	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
H <sub>2</sub> (g)	-	131
F <sub>2</sub> (g)	-	203
HF(g)	-271	174

You start with 3 moles of HF(g) at a constant temperature of 298K and a pressure of 1 bar, what is the partial pressure of H<sub>2</sub> at equilibrium?

Would you get more, less, or the same number of moles of H<sub>2</sub> if you increased the pressure to 4 bar,

SAME, same # mole gas P ∝ R

Would you get more, less, or the same number of moles of if you increased the temperature to 400K?

$\Delta H < 0 \therefore T \uparrow K \downarrow$   
more H<sub>2</sub>!

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r H^\circ = +2(-271) = -542 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = 2(174) - 203 - 131 = 17 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r G^\circ = -542,000 - (298)(17) = -547,066 \text{ J mol}^{-1}$$

$$K = \exp\left(\frac{547,066}{8.314(298)}\right) = e^{221} = 7.8 \cdot 10^{95}$$

	H <sub>2</sub>	F <sub>2</sub>	HF	Total
int	0	0	3	3
equil	+x	+x	3-2x	3
P <sub>i</sub>	$\frac{x}{3}$	$\frac{x}{3}$	$\frac{3-2x}{3}$	

$$K = \frac{\left(\frac{3-2x}{3}\right)^2}{\left(\frac{x}{3}\right)\left(\frac{x}{3}\right)} = \frac{(3-2x)^2}{x^2}$$

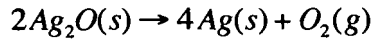
$$x \sim 0 \therefore K = \frac{9}{x^2} \quad x = \sqrt{\frac{9}{K}}$$

$$x = 3.28 \cdot 10^{-40}$$

$$P_{\text{H}_2} = \frac{x}{3} = \boxed{1.1 \cdot 10^{-40} \text{ bar}}$$

4. (50 points)

Silver oxide decomposed to silver metal and oxygen gas by the following reaction



39 g of  $\text{Ag}_2\text{O}$  is placed in an evacuated chamber with a volume of 10 L. The temperature is raised to  $175^\circ\text{C}$  and the system comes to equilibrium. At equilibrium you find there is 5.77 g of silver metal. Given that  $\Delta_r H^\circ$  for this reaction is  $+62.2 \text{ kJ mol}^{-1}$  at 450 K, what are  $\Delta_r G^\circ$  and  $\Delta_r S^\circ$  at 450K?

$$175 + 273 = 450.$$

$$\cancel{39 \text{ g } \text{Ag}_2\text{O}} \quad \frac{5.77 \text{ g Ag}}{107.87} \rightarrow 5.35 \cdot 10^{-2} \text{ mol Ag}$$

$$\frac{5.35 \cdot 10^{-2}}{4} = 1.337 \cdot 10^{-2} \text{ moles } \text{O}_2$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{V} = \frac{(1.337 \cdot 10^{-2}) (8.206 \cdot 10^{-2} \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (450 \text{ K})}{10 \text{ L}}$$

$$P_{\text{O}_2} = 4.94 \cdot 10^{-2} \text{ atm}$$

$$K = \frac{P_{\text{O}_2}}{P^\circ} = 4.94 \cdot 10^{-2}$$

$$\Delta_r G^\circ = -RT \ln K = \boxed{+11.25 \text{ kJ mol}^{-1}}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r S^\circ = \frac{\Delta_r G^\circ - \Delta_r H^\circ}{-T} = \frac{11.25 - 62.2}{-450} = \boxed{+113 \text{ J K}^{-1} \text{ mol}^{-1}}$$