

Quiz 5  
CH 353 Sumer 2009  
Vanden Bout

Name: KEY

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

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

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

$$750 \text{ Torr} = 1 \text{ bar} \quad 1 \text{ bar} = 10^5 \text{ Pa}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad \ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta_R H^\circ}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad \Delta_R G = \Delta_R G^\circ + RT \ln Q \quad \Delta_R G^\circ = -RT \ln K$$

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

**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

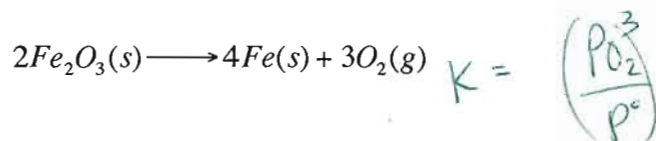
1. True/False Circle either T or F for each statement (10 points each)

T  F If  $\Delta_R H^\circ > 0$  then K increases with increasing temperature "  
*endothermic, T is reactant*"

T  F The activity of an ion in a 1 M solution is less than the concentration.

T  F The activity of an ideal gas is measured relative to the standard state of 1 M.  
~~1 bar~~

T  F If  $\Delta_R G^\circ > 0$  at room temperature for the following reaction, then the partial pressure of oxygen at equilibrium is less than 1 bar.

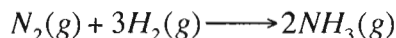


*If  $\Delta G > 0$ ,  $\ln K < 0$   
 $\Delta G = -RT \ln K$   
so  $K < 1$*

T  F The equilibrium constant  $K_p$  is independent of pressure.

2A. (25 points)

Nitrogen and hydrogen gases reaction to form ammonia gas by the following reaction



At 400°C a mixture of 3 moles of  $\text{N}_2$ , 0.5 moles of  $\text{H}_2$  and 0.045 moles of ammonia are found to be in equilibrium in a 3 L container. What is  $\Delta_r G^\circ$  for this reaction?

45

$$PV = nRT \quad n_{\text{tot}} = 3.545 \quad P_{\text{tot}} = \frac{(3.545)(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(673 \text{ K})}{3 \text{ L}}$$

$$y_{\text{N}_2} = \frac{3}{3.545} \quad P_{\text{N}_2} = \frac{3}{3.545} (66.1 \text{ bar}) = 55.95 \text{ bar} \quad P_{\text{tot}} = 66.1 \text{ bar}$$

$$P_{\text{H}_2} = \frac{0.5}{3.545} (66.1) = 9.32 \text{ bar} \quad 45$$

$$P_{\text{NH}_3} = \frac{0.045}{3.545} (66.1) = 0.839 \text{ bar}$$

$$P^\circ = 1 \text{ bar}$$

$$K = \frac{a_{\text{NH}_3}^2}{a_{\text{N}_2} a_{\text{H}_2}^3} = \frac{(P_{\text{NH}_3}/P^\circ)^2}{(P_{\text{N}_2}/P^\circ)(P_{\text{H}_2}/P^\circ)^3}$$

410

$$K = 1.55 \times 10^{-5}$$

$$\Delta_r G^\circ = -RT \ln K = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} (673 \text{ K}) \ln K$$

$$\Delta_r G^\circ = +41.9 \text{ kJ mol}^{-1}$$

2B. For the following reaction



At a particular temperature you find the system is at equilibrium at a particular temperature when you have one mole of  $\text{N}_2\text{O}_4$  and 0.1 moles of  $\text{NO}_2$  at a total pressure of 1 bar. At the same temperature you have a different mixture with 0.8 moles of  $\text{N}_2\text{O}_4$  and 0.3 moles of  $\text{NO}_2$  at a total pressure of 0.1 bar. Is this second system at equilibrium? (justify your answer mathematically)

$$K = \frac{a_{\text{NO}_2}^2}{a_{\text{N}_2\text{O}_4}}$$

45

$Q \neq K$ , 2nd system not at equilibrium

Case I (equil)

$$n_{\text{tot}} = 1.1 \text{ mol} \quad P = 1 \text{ bar} \quad 410$$

$$y_{\text{N}_2\text{O}_4} = P_{\text{N}_2\text{O}_4} = \frac{1}{1.1} = 0.909$$

$$y_{\text{NO}_2} = P_{\text{NO}_2} = \frac{0.1}{1.1} = 0.0909$$

$$K = \frac{(P_{\text{NO}_2}/P^\circ)^2}{(P_{\text{N}_2\text{O}_4}/P^\circ)} = \frac{(0.0909)^2}{(0.909)} = 9.09 \times 10^{-3}$$

$$Q = \frac{(0.0273)^2}{0.0727}$$

410

Case II:  $n_{\text{tot}} = 0.8 + 0.3 = 1.1$

$$P = 0.1 \text{ bar}$$

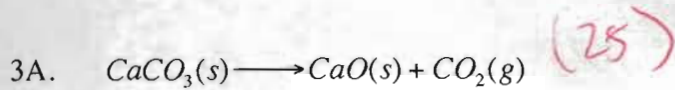
$$y_{\text{N}_2\text{O}_4} = 0.8/1.1 = 0.727$$

$$y_{\text{NO}_2} = 0.3/1.1 = 0.273$$

$$P_{\text{N}_2\text{O}_4} = (0.1 \text{ bar})(0.727) = 0.0727$$

$$P_{\text{NO}_2} = 0.1 \text{ bar}(0.273) = 0.0273$$

$$Q = 1.025 \times 10^{-3}$$



$\Delta_R G^\circ = 83.7 \text{ kJ mol}^{-1}$

Given that atmosphere has a partial pressure of 38 Pascal  $\text{CO}_2$ , if you have a chunk of calcium carbonate at  $25^\circ\text{C}$  sitting out in the atmosphere, will it decompose to calcium oxide and carbon dioxide? Why or why not?

$\Delta_R G^\circ = -RT \ln K$

(7/10)  $K = \exp(-\Delta G / RT) = \exp(-83.7(10^3) / [8.314(298)])$

$K = 2.13 \times 10^{-15}$

(+10)  $Q = a_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{P^\circ} = \frac{38 \text{ Pa} \left( \frac{1 \text{ bar}}{10^5 \text{ Pa}} \right)}{1 \text{ bar}} = 3.8 \times 10^{-4}$

(+5)  $Q \gg K$ , favors reactants, NO

(25) 3B. Given the following plot of the temperature dependence of an equilibrium constant for a reaction.

(+5) Is this reaction exothermic or endothermic? exothermic slope =  $-\Delta H/R$

(+10) What is  $\Delta_R H^\circ$  for this reaction?

(+10) What is  $\Delta_R S^\circ$  for this reaction?

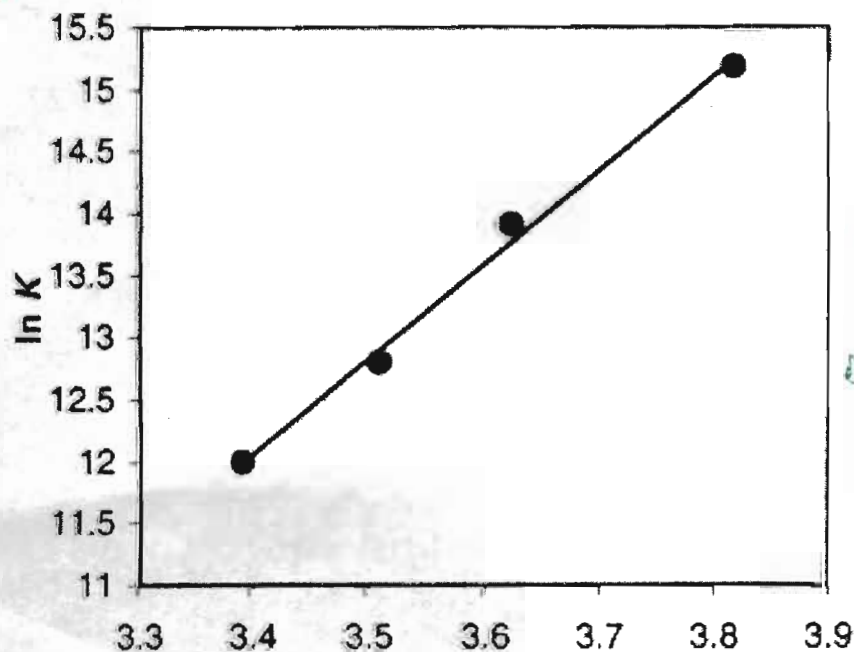
$\frac{15.25 - 12}{(3.85 \times 10^{-3} - 3.4 \times 10^{-3})} = \frac{-\Delta H}{R}$   
 $= 7.22 \times 10^3$

$\Delta H^\circ = -60 \text{ kJ mol}^{-1}$

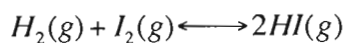
$\Delta_R G^\circ = -RT \ln K$   
 $= -8.314(294.1)(12) = -29.3 \text{ kJ mol}^{-1}$

$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$

$\Delta S^\circ = \frac{-60 + 29.3}{294.1} = -70.4 \text{ J K}^{-1} \text{ mol}^{-1}$



4. (50 Points)



Data at 298 K	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_p^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
H <sub>2</sub> (g)	0	130.7	28.8
I <sub>2</sub> (g)	62.4	260.7	37.6
HI(g)	26.50	206.6	29.2

You start with 1 mole pure HI and raised to a temperature of 600K at constant pressure of 1 bar.

What are the partial pressures of H<sub>2</sub> and I<sub>2</sub> at equilibrium? (you can assume  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are independent of temperature)

What is  $\Delta U$  in going from the initial state to equilibrium?

(+5)  $\Delta_r H^\circ = 2(26.5) - 62.4 = -9.4 \text{ kJ mol}^{-1}$

(+5)  $\Delta_r S^\circ = 2(206.6) - 260.7 - 130.7 = 21.8 \text{ JK mol}^{-1}$

(+5)  $\Delta_r G^\circ(600K) = -9.4 - 600(21.8)(10^3) = -22.48$

$K(600K) = \exp(22.48(10^3) / [8.314(600)]) = 90.6$

H <sub>2</sub>	I <sub>2</sub>	HI	total moles	
0	0	1	1	I
+x	+x	-2x	0	c
x	x	1-2x	1	e

$$\sqrt{\frac{(1-2x)^2}{x^2}} = \sqrt{90.6}$$

$$1-2x = (90.6)^{1/2} x$$

~~1 = 90.6 + 2x~~  
 $1 = 9.5 + 2x$

$$x = 0.0868 = 0.087$$

$$P = 1 \text{ bar}$$

(+5)  $P_{H_2} = P_{I_2} = (1 \text{ bar})(0.087)$

$$= 0.087 \text{ bar}$$

(+10)  $\Delta U = q + w = -x \Delta_r H + -\Delta n_r T$

$$= (0.0868)(9.4) = 0.82 \text{ kJ}$$

Must be positive since reverse rxn is occurring.