

Chemistry 225 Semester 04-2016

Test on Equilibrium etc.

Attempt all of the following questions. Write your answers in the spaces provided on the question paper. You have 50 minutes. Clarity of expression is important. Underline your answers and express them to the correct number of significant figures. Working must be shown for full marks.

You may need the following information:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

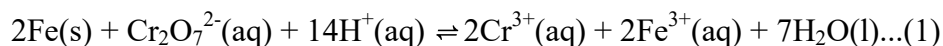
$$\Delta G^\circ = -RT \ln(K)$$

$$K_p = K_c (RT)^{\Delta n}$$

$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

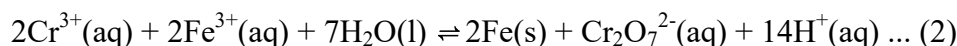
$$0^\circ \text{C} = 273 \text{ K}$$

- 1) a. Write down the equilibrium expression for the following equilibrium in the form $K_1 =$: (2 marks)



$$K_1 = \frac{[\text{Cr}^{3+}]^2 [\text{Fe}^{3+}]}{[\text{Cr}_2\text{O}_7^{2-}] [\text{H}^+]^{14}}$$

- b. Write down a relationship between the equilibrium constant (K_1) for the above reaction and that for the following reaction (K_2). Explain your answer. (2 marks)

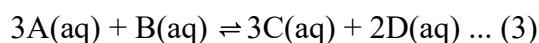


(No working required.)

$$K_1 = \frac{1}{K_2}$$

since (2) is (1) reversed.

- 2) The equilibrium constant, K_3 , for the reaction



is 8.00.

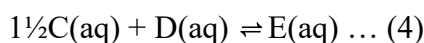
- a. If in an equilibrium mixture $[\text{A}] = 3.00 \text{ M}$, $[\text{B}] = 4.00 \text{ M}$ and $[\text{D}] = 16.00 \text{ M}$, find $[\text{C}]$ (3 marks)

$$K_3 = \frac{[\text{C}]^3 [\text{D}]^2}{[\text{A}]^3 [\text{B}]}$$

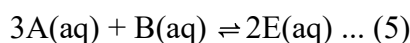
$$\therefore [\text{C}]^3 = \frac{K_3 [\text{A}]^3 [\text{B}]}{[\text{D}]^2}$$

$$\therefore [\text{C}] = \sqrt[3]{\frac{K_3 [\text{A}]^3 [\text{B}]}{[\text{D}]^2}} = \sqrt[3]{\frac{8 \times 3^3 \times 4}{16^2}} = \sqrt[3]{\frac{3^3}{2^3}} = \frac{3}{2} = \underline{\underline{1.50 \text{ M to 3 s.f.}}}$$

- b. Given that the equilibrium constant, K_4 , for

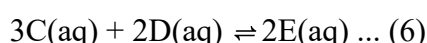


is 4.00, find the equilibrium constant, K_5 , for

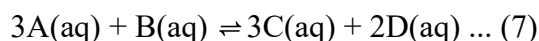


(3 marks)

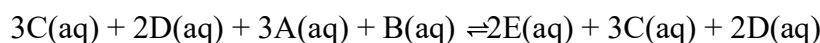
$2 \times (4)$ is



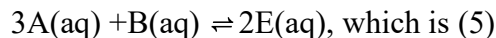
(3) is



(6) + (7) is

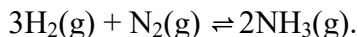


Cancelling like terms gives



$$\text{Hence } K_5 = (K_4)^2 \times (K_3) = 4^2 \times 8 = \underline{128} \text{ to 3 s.f.}$$

- 3) a. Calculate the reaction quotient (Q_p) for a mixture in which $P_{H_2} = 0.200$ atm, $P_{N_2} = 0.100$ atm, and $P_{NH_3} = 0.100$ atm. The equation for the reaction is (3 marks)



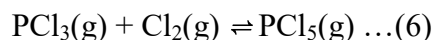
$$Q = \frac{(P_{NH_3})^2}{(P_{H_2})^3 (P_{N_2})} = \frac{(0.1)^2}{(0.2)^3 (0.1)} = \frac{(10^{-1})^2}{(2 \times 10^{-1})^3 (10^{-1})} = \frac{10^{-2}}{2^3 \times 10^{-3} \times 10^{-1}} = 0.125 \times 10^2 = \underline{12.5}$$

(Q, like K is unitless.)

- b. If $K = 49$ for the above system, compare your value of Q and predict what will happen. (2 marks)

Since $Q < K$, the system is not at equilibrium and Q must increase until it equals K . This means that reaction will occur in the forward direction.

- 4) a. Sufficient $PCl_3(g)$ and $Cl_2(g)$ were introduced into a vessel to give partial pressures, before any reaction occurred, of 1.00 atm and 2.00 atm respectively. Calculate the equilibrium partial pressure of $PCl_3(g)$ given that the equilibrium constant, K_1 , for



is 0.588 at 250 °C.

(5 marks)

+			
	$PCl_3(g)$	$Cl_2(g)$	$PCl_5(g)$
I / atm	1	2	0
C / atm	-x	-x	+x
E / atm	1-x	2-x	x

$$K_1 = \frac{x}{(1-x)(2-x)}$$

$$\therefore K_1(1-x)(2-x) = x$$

$$\therefore K_1(2-3x+x^2) = x$$

$$\therefore 2K_1 - 3K_1x + K_1x^2 = x$$

$$\therefore K_1x^2 - (3K_1+1)x + 2K_1 = 0$$

This is a quadratic in x and so

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ where}$$

$$a = K_1 = 0.588, b = -(3K_1 + 1) = -(3 \times 0.588 + 1) = -2.764 \text{ and } c = 2K_1 = 1.176 \text{ and so}$$

$$x = \frac{2.764 \pm \sqrt{(2.764)^2 - 4 \times 0.588 \times 1.176}}{2 \times 0.588} = 0.47308 \dots \text{ and } 4.2275 \dots$$

But only 0.47308 is meaningful since 1-x, the partial pressure of PCl_3 must be positive.

Hence the equilibrium partial pressure of PCl_3 is

$$1 - 0.47308 \dots = 0.5269 \dots = \underline{0.527} \text{ atm to 3 s.f.}$$

- b. Given that ΔH° for the reaction is $-92.5 \text{ kJ mol}^{-1}$, calculate the equilibrium constant (K_2) for the reaction at 300 K. (4 marks)

Given on the paper:

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

and $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

$$\ln\left(\frac{K_2}{0.588}\right) = -\frac{(-92.5)}{8.31}\left(\frac{1}{300} - \frac{1}{250+273}\right) = 15.8205\dots$$

$$\therefore \frac{K_2}{0.588} = e^{15.8205\dots} = 7.4266\dots \times 10^6$$

$$\therefore K_2 = 7.4266\dots \times 10^6 \times 0.588 = 4.36688\dots = \underline{\underline{4.37 \times 10^6}} \text{ to 3 s.f.}$$

- c. Calculate ΔG° for reaction (6) at 250 °C. Express your answer in kJ mol^{-1} . (3 marks)

$$\begin{aligned}\Delta G^\circ &= -RT \ln(K) = -8.31 \times 523 \times \ln(0.588) \\ &= 2307.92 \text{ J mol}^{-1} = \underline{\underline{2.31}} \text{ kJ mol}^{-1} \text{ to 3 s.f.}\end{aligned}$$

- d. Calculate K_c for the reaction at 250 °C. (3 marks)

$$K_p = K_c (RT)^{\Delta n}$$

where $K_p=0.588$, $R=0.081 \text{ L atm mol}^{-1} \text{ K}^{-1}$ and $T = 250 + 273 = 523 \text{ K}$

Δn is the change in the number of moles going left to right in the equation, $1 - 2 = -1$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.588}{(0.0821 \times 523)^{-1}} = 0.588 \times 0.0821 \times 523 = 25.24772\dots = \underline{\underline{25.2}} \text{ to 3 s.f.}$$