

## CHEMISTRY 225 SEMESTER 04-2011 HOMEWORK ON EQUILIBRIA - GENERAL

1) Write an expression for the equilibrium constant (K) for each of the following reactions:

- a)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- b)  $\text{Cl}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightleftharpoons 2\text{ClF}_3(\text{g})$
- c)  $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$
- d)  $5\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) \rightleftharpoons 4\text{H}_2\text{O}(\text{l}) + \text{Mn}^{2+}(\text{aq}) + 5\text{Fe}^{3+}(\text{aq})$
- e)  $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightleftharpoons 4\text{H}_2\text{O}(\text{g}) + 3\text{Fe}(\text{s})$
- f)  $2\text{Fe}(\text{s}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^{+}(\text{aq}) \rightleftharpoons 2\text{Fe}^{3+}(\text{aq}) + 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$
- g)  $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(\text{g})$
- h)  $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$
- i)  $\text{Ag}(\text{s}) + \text{Fe}^{3+}(\text{aq}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Fe}^{2+}(\text{aq})$
- j)  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{CaO}(\text{s})$
- k)  $\text{Pb}(\text{s}) + 2\text{H}^{+}(\text{aq}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- l)  $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$
- m)  $\text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_3(\text{g})$
- n)  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
- o)  $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
- p)  $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$
- q)  $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

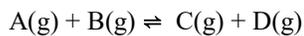
2) For the system:



state the effect on individual concentrations, equilibrium position, reaction rates and the value of  $K_c$  of

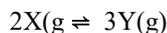
- a) adding more oxygen.
  - b) increasing the pressure.
  - c) adding finely divided platinum, which acts as a catalyst.
  - d) increasing the temperature.
- 3) Chemical equilibrium is often described as *dynamic equilibrium*. Contrast dynamic equilibrium with static equilibrium, giving non-chemical examples in each case, and explain why chemical equilibrium is correctly described as dynamic.
- 4) Hydrogen and iodine are introduced into a sealed vessel at a temperature at which both are gases and allowed to react until equilibrium is reached. Sketch a graph of concentration against time showing the concentrations of hydrogen, iodine and hydrogen iodide. Sketch a second graph showing the rate of production of hydrogen iodide (one curve) and the rate of its reaction (ie. destruction) as a function of time.

- 5) The equilibrium constant ( $K_c$ ) for the reaction



is 4. If in an equilibrium mixture  $[A] = 5$ ,  $[B] = 2$  and  $[D] = 4$ , find  $[C]$

- 6) The equilibrium constant ( $K_p$ ) for the reaction

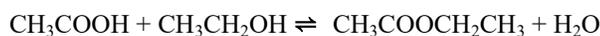


is  $1/8$ . If  $P_x = 8$  atm, find  $P_y$

- 7) For the equilibrium  $X(g) \rightleftharpoons Y(g) + Z(g)$ , a  $500 \text{ cm}^3$  flask contains 1 mol X, 1.5 mol Z and 2.5 mol Y in equilibrium together at  $0^\circ\text{C}$ . Find  $K_p$  for the reaction. If a second equilibrium mixture at the same temperature has  $P_x = 10$  atm and  $P_y = 6$  atm, find  $P_z$ .

- 8) When 60 g of ethanoic acid,  $\text{CH}_3\text{COOH}$ , are mixed with 46 g of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , the equilibrium amount of ethylethanoate,  $\text{CH}_3\text{COOCH}_2\text{CH}_3$  formed is 58.7 g.

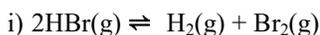
a) Calculate  $K_c$  for the system:



where water is NOT the solvent.

b) What mass of ethylethanoate would be formed at the same temperature if 60 g of ethanoic acid are mixed with 23 g of ethanol?

- 9) a) An equilibrium mixture contains 2.0 mol of bromine, 1.25 mol of hydrogen and 0.5 mol of hydrogen bromide at a fixed temperature. Determine the equilibrium constants ( $K_c$  and  $K_p$ ) for the reactions represented by

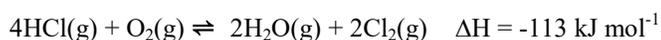


b) In another experiment conducted at this temperature, some HBr was admitted into an evacuated  $2000 \text{ cm}^3$  vessel and when equilibrium was attained some had decomposed yielding 6.32 mol of bromine as one product.

i) What was the concentration of each species present at equilibrium?

ii) What mass of HBr was originally let into the vessel?

- 10) Suppose 3 mol of HCl and 2 mol of  $\text{O}_2$  are introduced into a  $5000 \text{ cm}^3$  vessel and the temperature held constant at  $450^\circ\text{C}$  until equilibrium is attained according to the reaction:



a) From this data, could the equilibrium constant be calculated? If so, find its value. If not, what further data would be needed?

b) How will the value of  $K_p$  for the system at  $450^\circ\text{C}$  and 1 atm compare with that at  $550^\circ\text{C}$  and 1 atm?

c) If the temperature is maintained at  $450^\circ\text{C}$ , but the system is permitted to expand so that the pressure is reduced to 0.5 atm, how will the relative concentrations at equilibrium compare with those at  $450^\circ\text{C}$  and 1 atm pressure?

d) How will the value of  $K_p$  for the system at  $450^\circ\text{C}$  and 1 atm compare with that at  $450^\circ\text{C}$  and 0.5 atm?

e) Show how the equilibrium constant expression for this reaction is related to those for the reactions:



- 11) In the following questions, consider the equilibrium:



for which  $K_p = 1.70$  at  $250^\circ\text{C}$

- a) If  $\text{PCl}_5$  is 48.5% dissociated at  $200^\circ\text{C}$ , 1 atm, and 97% dissociated at  $300^\circ\text{C}$ , 1 atm, explain whether the decomposition reaction is exothermic, or endothermic.
- b) If 1 mol of  $\text{PCl}_5(\text{g})$  is placed in a  $1000\text{ cm}^3$  flask at  $250^\circ\text{C}$  and allowed to come to equilibrium, find the equilibrium partial pressure of each species present.
- c) If 5 mol of  $\text{PCl}_5(\text{g})$  were initially present as in (b) calculate the equilibrium partial pressure of each species.
- d) Using your results from (b) and (c) or otherwise calculate the degree of dissociation of the  $\text{PCl}_5$  in each case.
- e) Proceed as in (b) and (c) for the following initial mixtures of species:
- 1 mol of  $\text{PCl}_3$  and 1 mol of  $\text{Cl}_2$ .
  - 0.5 mol of  $\text{PCl}_5$  and 1 mol of  $\text{Cl}_2$ .
- 12) Calculate the reaction quotients in each of the following cases and decide whether the mixture has a tendency to form reactants or products.
- a) A mixture that is 4.8 mM in  $\text{H}_2(\text{g})$ , 2.4 mM in  $\text{I}_2(\text{g})$ , and 2.4mM in  $\text{HI}(\text{g})$  if  $K_c = 49$  for
- $$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
- b) Equal concentrations of the three gases that appear in (a).
- c) A mixture that is 1.0 M in ethanoic acid, 2.0 M in ethanol, 0.50 M in ethyl ethanoate, and 5.0 M in water in a non-aqueous solution.  $K_c = 4.0$
- 13) 1g of ethanoic acid, when released into a  $1500\text{ cm}^3$  vessel and allowed to evaporate completely at  $25^\circ\text{C}$  gave rise to a pressure of 26.1 kPa. Calculate the degree of association of the ethanoic acid. (Ans. 0.103)
- 13) 0.92 g of a certain gaseous dimer occupies a volume of  $342\text{ cm}^3$  at  $25^\circ\text{C}$  and 1 atm pressure. If the dimer is 40% dissociated under these conditions, calculate the molar mass of the dimer and hence the monomer. (Ans. 92,  $46\text{ gmol}^{-1}$ )
- 15) At elevated temperatures, aluminium chloride,  $\text{Al}_2\text{Cl}_6$ , reacts to form  $\text{Al}_3\text{Cl}_9$  according to the equation:
- $$3\text{Al}_2\text{Cl}_6(\text{g}) \rightleftharpoons 2\text{Al}_3\text{Cl}_9(\text{g})$$
- In an experiment at 454 K, the equilibrium partial pressure of  $\text{Al}_2\text{Cl}_6$  is 1.00 atm, and the equilibrium partial pressure of  $\text{Al}_3\text{Cl}_9$  is  $1.02 \times 10^{-2}$  atm. Calculate the equilibrium constants,  $K_p$  and  $K_c$  of the above reaction at 454 K.
- 16) The compound 1,3-di-*t*-butylcyclohexane exists in two forms that are known as the "chair" and "boat" conformations because the shapes of the molecules resemble these objects. Equilibrium exists between these forms, represented by the equation:
- $$\text{chair} \rightleftharpoons \text{boat}$$
- At 580 K, 6.42% of the molecules are in the chair form. Calculate the equilibrium constant ( $K_c$ ) for the reaction as written above.