Chemistry 192
Problem Set 2
Spring, 2018

1. The gas phase species NO_2 and N_2O_4 equilibrate according to the reaction

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)},$$

and it is found that at 298K in a reaction vessel of fixed volume the equilibrium concentrations of each species are $[NO_2]=2.17 \times 10^{-3}$M and $[N_2O_4]=3.64 \times 10^{-4}$M. Under different nonequilibrum conditions in the same vessel at the same temperature, NO_2 and N_2O_4 are added such that their partial pressures are P_{NO_2}=0.456 bar and $P_{N_2O_4}$=0.789 bar. Under the nonequilibrium conditions, predict whether the reaction will proceed to the right or left.

2. For the reaction between solid iodine, hydrogen gas and gas-phase hydrogen iodide

$$I_{2(s)} + H_{2(g)} \rightleftharpoons 2HI_{(g)}$$

at 298 K, the equilibrium partial pressures of hydrogen and hydrogen iodide are measured to be respectively $P_{H_2} = 32.$ bar and P_{HI}=4.0 bar. Suppose an initial non-equilibrium mixture of solid iodine, hydrogen gas and hydrogen iodide is prepared at 298 K in a closed 10.0 L container containing 68. grams of hydrogen gas, 352. grams of hydrogen iodide gas and 500. grams of solid iodine (sufficient to be in excess). Calculate the concentration equilibrium constant K_c for the reaction, and predict whether the reaction will proceed spontaneously to the right or left under the non-equilibrium conditions.

3. At 500.K and a total pressure of 5.57 bar, it is found that the degree of dissociation at equilibrium of gas-phase ammonia according to the reaction

$$NH_{3(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)}$$

is $\alpha = 0.564$. In a separate experiment at 500.K, a non equilibrium mixture is prepared by combing 1.00 moles each of gas-phase NH_3, N_2 and H_2 in a 1.00 L flask. Calculate first K_P and then K_c for the ammonia dissociation reaction, and predict the direction of the reaction for the non equilibrium mixture.

4. Consider the reaction at equilibrium

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}.$$

When a certain amount of $PCl_{5(g)}$ is heated in a 10.0 liter flask at 275.°C, analysis shows that at equilibrium the number of moles of each species is $n_{PCl_5} = 0.151$ mol, $n_{PCl_3} = 0.400$ mol and $n_{Cl_2} = 0.400$ mol. Calculate K_P and K_c for the reaction at 275.°C.

5. For the reaction given in problem 4, if for all species at 275.°C, 1.00 moles of each species were placed in the 10.0 L flask, determine whether the reaction would be favored to the left or right.

6. Consider the reaction at equilibrium between gas-phase iodine, hydrogen and hydrogen iodide

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}.$$

At 450.C° the concentration equilibrum constant for the reaction is K_c=50.0.

   (a) Calculate K_P at 450.C°.
   Answer: $K_P = 50.0$

   (b) If 2.0 moles each of iodine vapor and hydrogen are placed in a 5.0 L flask, and the gases are allowed to come to equilibrium at 450.C°, calculate the final total pressure and partial pressures of each gas in the container.
   Answer: $P_{tot} = 48.$ bar

7. For the reaction

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

it is found that $K_P = 0.171$ at 25.0°C. Calculate the degree of dissociation of N_2O_4 at 25.0C° and total pressures of 1.0 bar and 0.10 bar.
Answer: $\alpha(1.0 \text{ bar}) = 0.20, \alpha(0.10 \text{ bar}) = 0.55$

8. The degree of dissociation (the fraction of the pure substance that dissociates at equilibrium) of $NOCl_{(g)}$ at 298K and a total pressure of 2.00 bar according to the reaction

$$NOCl_{(g)} \rightleftharpoons NO_{(g)} + \frac{1}{2}Cl_{2(g)}$$

is $\alpha = 0.00307$. Calculate the pressure equilibrium constant, K_P for the reaction at 298.K.
Answer: $K_P = 1.70 \times 10^{-4}$

9. Predict the effects of increased pressure and temperature on the following reactions at equilibrium.

(a)

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad \Delta H^\circ = -41.8 \text{ kJ mol}^{-1}$$

(b)

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H^\circ = -196.5 \text{ kJ mol}^{-1}$$

(c)

$$CaCO_{3(s)} \rightleftharpoons Ca_{(s)} + CO_{2(g)} \qquad \Delta H^\circ = 179.7 \text{ kJ mol}^{-1}$$

10. At 400.K the concentration equilibrium constant for the reaction

$$HCONH_{2(g)} \rightleftharpoons NH_{3(g)} + CO_{(g)}$$

is $K_c = 4.84$. If 10.0 grams of pure gas-phase $HCONH_2$ are placed in a 10.0 liter flask at 400.K, calculate the total pressure in the flask when equilibrium is reached.
Answer: $P_{tot} = 1.47$ bar

11. When metallic lead is added to a solution of $Cr^{3+}_{(aq)}$ the following reaction occurs

$$Pb_{(s)} + 2Cr^{3+}_{(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cr^{2+}_{(aq)}$$

with associated equilibrium constant $K_c = 3.2 \times 10^{-10}$.

   (a) If solid lead is added to a 0.200 M Cr^{3+} aqueous solution, find the final concentrations of all ions in the system.
   Answer: $[Cr^{3+}]$=0.20 M, $[Pb^{2+}]$=1.5×10^{-4} M, $[Cr^{2+}] = 3.0 \times 10^{-4}$ M

   (b) If 100 mL of water are added to the solution at equilibrium, predict the direction that the equilibrium would be shifted.

12. At 145.K the the degree of dissociation of ozone in the gas-phase decomposition reaction

$$O_{3(g)} \rightleftharpoons \frac{3}{2}O_{2(g)}$$

at a total pressure of $P = 1.00$ bar is $\alpha = 0.0221$. Calculate the concentration equilibrium constant K_c of the dissociation reaction. **Answer**: 1.77×10^{-3}

13. At a temperature of 452K gas-phase isopropyl alcohol dissociates into gas-phase acetone and hydrogen according to the reaction

$$(CH_3)_2CHOH_{(g)} \rightleftharpoons (CH_3)_2CO_{(g)} + H_{2(g)}.$$

At P =2.00 bar and T = 452K, the degree of dissociation isopropyl alcohol is measured to be $\alpha = 0.182$. Calculate the concentration equilibrium constant K_c for the reaction.
Answer: 1.82×10^{-3}

14. The gas-phase decomposition of antimony pentachloride into gas-phase antimony trichloride and chlorine gas

$$\mathrm{SbCl}_{5(g)} \rightleftharpoons \mathrm{SbCl}_{3(g)} + \mathrm{Cl}_{2(g)}$$

has a concentration equilibrium constant $K_C = 2.50 \times 10^{-2}$ at a temperature of 521. K. A sample of pure SbCl_5 gas is placed in a reaction vessel of fixed volume at $T = 521.$K, and when the system attains equilibrium, the total pressure is measured to be 3.51 bar. Calculate the equilibrium degree of dissociation α (i.e. the fraction dissociated) of antimony pentachloride in the reaction vessel.
Answer: $\alpha = 0.485$

15. The equilibrium behavior of the gas-phase reaction

$$\mathrm{P}_{4(g)} \rightleftharpoons 2\mathrm{P}_{2(g)}$$

is studied at 1325.K, and the concentration equilibrium constant is measured to be $K_C = 9.08 \times 10^{-4}$. Calculate the equilibrium degree of dissociation α of P_4 at 1325.K and a total pressure of 2.00 bar.
Answer: $\alpha = 0.111$