5

Chemical Equilibrium

5.1 For the reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$, $K = 1.60 \times 10^{-4}$ at 400 °C. Calculate (a) $\Delta_r G^o$ and (b) $\Delta_r G$ when the pressures of N_2 and H_2 are maintained at 10 and 30 bar, respectively, and NH_3 is removed at a partial pressure of 3 bar. (c) Is the reaction spontaneous under the latter conditions?

SOLUTION

(a) $\Delta_r G^o = - RT \ln K$

$$= - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(673 \text{ K}) \ln 1.60 \times 10^{-4} = 48.9 \text{ kJ mol}^{-1}$$

(b) $\Delta_r G = \Delta_r G^o + RT \ln \dfrac{(P_{NH_3}/P^o)^2}{(P_{N_2}/P^o)(P_{H_2}/P^o)^3}$

$$= 48.9 + (8.314 \times 10^{-3})(673) \ln \dfrac{3^2}{10(30)^3} = - 8.78 \text{ kJ mol}^{-1}$$

(c) Yes

5.2 At 1:3 mixture of nitrogen and hydrogen was passed over a catalyst at 450 °C. It was found that 2.04% by volume of ammonia was formed when the total pressure was maintained at 10.13 bar. Calculate the value of K for $\frac{3}{2} H_2(g) + \frac{1}{2} N_2(g) = NH_3(g)$ at this temperature.

SOLUTION

At equilibrium $P_{H_2} + P_{N_2} + P_{NH_3} = 10.13$ bar

$P_{NH_3} = (10.13 \text{ bar})(0.0204) = 0.207$ bar

$P_{H_2} + P_{N_2} = 10.13 \text{ bar} - 0.207 \text{ bar} = 9.923$ bar

$P_{H_2} = 3P_{N_2}$ because this initial ratio is not changed by reaction

$P_{N_2} = \dfrac{9.923 \text{ bar}}{4} = 2.481$ bar

$P_{H_2} = \frac{3}{4}(9.923 \text{ bar}) = 7.442$ bar

$$K = \frac{(P_{NH_3}/P^o)}{(P_{H_2}/P^o)^{3/2}(P_{N_2}/P^o)^{1/2}}$$

$$= \frac{0.207}{7.442^{3/2}\ 2.482^{1/2}} = 6.47 \times 10^{-3}$$

5.3   At 55 °C and 1 bar the average molar mass of partially dissociated N_2O_4 is 61.2 g mol^{-1}. Calculate (a) ξ and (b) K for the reaction $N_2O_4(g) = 2NO_2(g)$. (c) Calculate ξ at 55 °C if the total pressure is reduced to 0.1 bar.

SOLUTION

(a) $\xi = \dfrac{M_1 - M_2}{M_2} = \dfrac{92.0 - 61.2}{61.2} = 0.503$

$K = \dfrac{4\xi^2(P/P^o)}{1 - \xi^2} = \dfrac{4(0.503)^2}{1 - 0.503^2} = 1.36$

(c) $\dfrac{\xi^2}{1 - \xi^2} = \dfrac{K}{4(P/P^o)} = \dfrac{1.36}{4(0.1)}$

$\xi = 0.879$

(Note that ξ is the dimensionless extent of reaction.)

5.4   A 1 liter reaction vessel containing 0.233 mol of N_2 and 0.341 mol of PCl_5 is heated to 250 °C. The total pressure at equilibrium is 29.33 bar. Assuming that all the gases are ideal, calculate K for the only reaction that occurs.
$PCl_5(g) = PCl_3(g) + Cl_2(g)$

SOLUTION

	PCl_5	=	PCl_3	+	Cl_2	
initial	0.341		0		0	
eq.	0.341 - ξ		ξ		ξ	total = 0.341 + ξ

$$K = \frac{\xi^2(P/P^o)^2}{(0.341 + \xi)(0.341 - \xi)}$$

$$= \frac{\xi^2(P/P^o)}{0.341^2 - \xi^2} \text{ where } P = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$$

Calculate the equilibrium pressure of the reacting gases by subtracting the partial pressure of nitrogen from the total pressure.

$$P = 29.33 \text{ bar} - \frac{(0.233 \text{ mol})(0.08314 \text{ L bar K}^{-1}\text{mol}^{-1})(523 \text{ K})}{1 \text{ L}}$$

$$= 19.20 \text{ bar} = \frac{(0.341 + \xi)(0.08314)(523)}{1}$$

$$\xi = 0.1005$$

$$K = \frac{(0.1005)^2(19.2)}{0.341^2 - 0.1005^2} = 1.83$$

5.5   An evacuated tube containing 5.96×10^{-3} mol L^{-1} of solid iodine is heated to 973 K. The experimentally determined pressure is 0.496 bar. Assuming ideal gas behavior, calculate K for $I_2(g) = 2I(g)$.

SOLUTION

$$P = \frac{n}{V}RT$$

$$0.496 \text{ bar} = (1 + \xi)(5.96 \times 10^{-3} \text{ L}^{-1})\text{x}(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(973 \text{ K})$$

$$\xi = \frac{0.496 \text{ bar}}{(5.96 \times 10^{-3} \text{ mol L}^{-1})(0.08314 \text{ L bar}^{-1} \text{ K}^{-1} \text{ mol}^{-1})(973 \text{ K})} - 1$$

$$= 0.0288$$

$$K = \frac{4\xi^2(P/P^o)}{1 - \xi^2} = \frac{4(0.0288)^2(0.496)}{1 - 0.0287^2} = 1.64 \times 10^{-3}$$

5.6   Nitrogen trioxide dissociates according to the reaction
$N_2O_3(g) = NO_2(g) + NO(g)$
When one mole of $N_2O_3(g)$ is held at 25 °C and 1 bar total pressure until equilibrium is reached, the extent of reaction is 0.30. What is $\Delta_r G^o$ for this reaction at 25 °C?

SOLUTION

	$N_2O_3(g)$	$=$	$NO_2(g)$	$+ NO(g)$	
init.	1		0	0	
eq.	$1 - \xi$		ξ	ξ	total $= 1 + \xi$
mole fr.	$\dfrac{1 - \xi}{1 + \xi}$		$\dfrac{\xi}{1 + \xi}$	$\dfrac{\xi}{1 + \xi}$	

$$K = \frac{\xi^2 P^2(1 + \xi)}{(1 + \xi)^2(1 - \xi)P} = \frac{\xi^2 P}{1 - \xi^2} = \frac{0.30^2}{0.91} \cdot 1 = 0.099$$

$$\Delta_r G^o = -RT \ln K = -8.314 (298) \ln 0.099 = 5.73 \text{ kJ mol}^{-1}$$

*5.7   For the reaction
$$2HI(g) = H_2(g) + I_2(g)$$
at 698.6 K, $K = 1.83 \times 10^{-2}$. (a) How many grams of hydrogen iodide will be formed when 10 g of iodine and 0.2 g of hydrogen are heated to this temperature in a 3 L vessel? (b) What will be the partial pressures of H_2, I_2, and HI?

SOLUTION

(a)   Pressures due to reactants prior to reaction:

$$P_{I_2} = \frac{(10 \text{ g})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(698.6 \text{ K})}{(254 \text{ g mol}^{-1})(3 \text{ L})} = 0.762 \text{ bar}$$

$$P_{H_2} = \frac{(0.2)(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(698.6 \text{ K})}{2 \times 3} = 1.936 \text{ bar}$$

$$K = \frac{(0.762 - x)(1.936 - x)}{(2x)^2} = 1.83 \times 10^{-2}$$

$$x = 0.730 \text{ bar}$$

(b) $P_{H_2} = 1.936 - 0.730 = 1.206 \text{ bar}$

$P_{I_2} = 0.762 - 0.730 = 0.032 \text{ bar}$

$P_{HI} = 1.460 \text{ bar}$

5.8   Express K for the reaction
$$CO(g) + 3H_2(g) = CH_4(g) + H_2O(g)$$
in terms of the equilibrium extent of reaction ξ when one mole of CO is mixed with one mole of hydrogen.
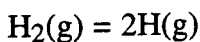
SOLUTION

	CO	+	$3H_2$	=	CH_4	+	H_2O	
initial	1		1		0		0	
equilibrium	$1 - \xi$		$1 - 3\xi$		ξ		ξ	total $= 2 - 2\xi$

$$K = \frac{\left(\frac{\xi}{2 - 2\xi}\right)^2 \left(\frac{P}{P^o}\right)^2}{\left(\frac{1 - \xi}{2 - 2\xi}\right)\left(\frac{1 - 3\xi}{2 - 2\xi}\right)^3 \left(\frac{P}{P^o}\right)^4}$$

$$K = \frac{(\xi)^2 (2 - 2\xi)^2}{(1 - \xi)(1 - 3\xi)^3 (P/P^o)^2}$$

5.9   What are the percentage dissociations of $H_2(g)$, $O_2(g)$, and $I_2(g)$ at 2000 K and a total pressure of 1 bar?
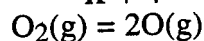
SOLUTION

$H_2(g) = 2H(g)$
$\Delta_r G^o = 2(106,760 \text{ J mol}^{-1})$
$\quad = - RT \ln K$
$\quad = - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(2000 \text{ K}) \ln K$
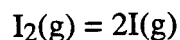
$$K = 2.65 \times 10^{-6} = \frac{4\xi^2}{1 - \xi^2}$$

$$\xi = \left(\frac{K}{K + 4}\right)^{1/2} = \left(\frac{2.65 \times 10^{-6}}{4}\right)^{1/2} = 0.000814 \text{ or } 0.0814\%$$

$O_2(g) = 2O(g)$
$\Delta_r G^o = 2(121,552 \text{ J mol}^{-1})$

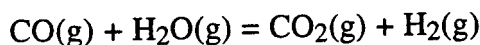$K = 4.48 \times 10^{-7}$ $\xi = 0.0335\%$

$I_2(g) = 2I(g)$
$\Delta_r G^o = 2(- 29,410 \text{ J mol}^{-1})$

$K = 34.37$ $\xi = 94.6\%$

5.10   In order to produce more hydrogen from "synthesis gas" ($CO + H_2$) the water gas shift reaction is used.

$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

Calculate K at 1000 K and the equilibrium extent of reaction starting with an equimolar mixture of CO and H_2O.

SOLUTION

$\Delta G^o = - 395,886 - - 200,275) - (- 192,590) = -3021 \text{ J mol}^{-1}$
$\quad = - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ K}) \ln K$

$$K = 1.44 = \frac{P_{H_2} P_{CO_2}}{P_{CO} P_{H_2O}} = \frac{\xi^2}{(1 - \xi)^2}$$

$\xi = 0.545$

(Note that this reaction is exothermic so that there will be a larger extent of reaction at lower temperatures. In practice this reaction is usually carried out at about 700 K.)

5.11   Calculate the extent of reaction ξ of 1 mol of $H_2O(g)$ to form $H_2(g)$ and $O_2(g)$ at 2000 K and 1 bar. (Since the extent of reaction is small, the calculation may be simplified by assuming that $P_{H_2O} = 1$ bar.)

SOLUTION

$$H_2O(g) \quad = \quad H_2(g) + \frac{1}{2}O_2(g)$$

init.	1	0	0
eq.	$1 - \xi$	ξ	$\frac{1}{2}\xi$

$\Delta_r G^o = 135{,}528 \text{ J mol}^{-1}$

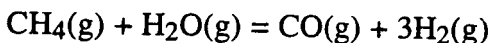$\quad = - (8.1315 \text{ J K}^{-1} \text{ mol}^{-1})(2000 \text{ K}) \ln K$

$K = 2.887 \times 10^{-4}$

$$K = \frac{\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{O_2}}{P^o}\right)^{1/2}}{\left(\frac{P_{H_2O}}{P^o}\right)} \; ; \quad \frac{P_{O_2}}{P^o} = \frac{P_{H_2}}{2P^o}$$

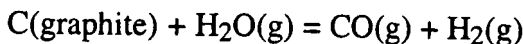$$\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{H_2}}{2P^o}\right)^{1/2} = \frac{1}{\sqrt{2}}\left(\frac{P_{H_2}}{P^o}\right)^{3/2}$$

$$\xi = \left(\frac{P_{H_2}}{P^o}\right) = (\sqrt{2}\, K)^{2/3} = 0.0055$$

5.12   At 500 K CH_3OH, CH_4 and other hydrocarbons can be formed from CO and H_2. Until recently the main source of the CO mixture for the synthesis of CH_3OH was methane.
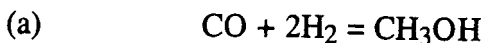
$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$$

When coal is used as the source, the "synthesis gas" has a different composition.

$$C(graphite) + H_2O(g) = CO(g) + H_2(g)$$

Suppose we have a catalyst that catalyzes only the formation of CH_3OH. (a) What pressure is required to convert 25% of the CO to CH_3OH at 500 K if the "synthesis gas" comes from CH_4? (b) If the synthesis gas comes from coal?

SOLUTION

(a) $\quad\quad\quad CO + 2H_2 = CH_3OH$

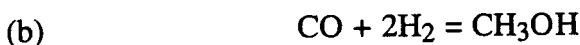| Initial	1	3	0	
Equil.	$1 - \xi$	$3 - 2\xi$	ξ	Total $= 4 - 2\xi$

$$K = \frac{y_{CH_3OH}}{y_{CO}y_{H_2}^2 P^2} = \frac{\xi(4 - 2\xi)^2}{(1 - \xi)(3 - 2\xi)^2 P^2}$$

$$\Delta_r G^o = -134.27 - (-155.41) = 22.14 \text{ kJ mol}^{-}$$

$$K = 6.188 \times 10^{-3}$$

$$P = \left[\frac{\xi(4 - 2\xi)^2}{K(1 - \xi)(3 - 2\xi)^2} \right]^{1/2}$$

$$= \left[\frac{(0.25)(3.5)^2}{6.188 \times 10^{-3}(0.75)(2.5)^2} \right]^{1/2} = 10.3 \text{ bar}$$

(b) $CO + 2H_2 = CH_3OH$

Initial   1   1   0

Equil. $1 - \xi$ $1 - 2\xi$ ξ Total $= 2 - 2\xi$

$$K = \frac{\xi(2 - 2\xi)^2}{(1 - \xi)(1 - 2\xi)^2 P^2}$$

$$P = \left[\frac{(0.25)(1.5)^2}{K(0.75)(0.5)^2} \right]^{1/2} = 22.0 \text{ bar}$$

5.13   Many equilibrium constants in the literature were calculated with a standard state pressure of 1 atm (1.01325 bar). Show that the corresponding equilibrium constant with a standard pressure of 1 bar can be calculated using

$$K(\text{bar}) = K(\text{atm})(1.01325)^{\Sigma v_i}$$

where the v_i are the stoichiometric numbers of the gaseous reactants.

SOLUTION

$$K(\text{bar}) = \prod_i [P_i/(1 \text{ bar})]^{v_i}$$

$$K(\text{atm}) = \prod_i [P_i/(1 \text{ atm})]^{v_i}$$

$$\frac{K(\text{bar})}{K(\text{atm})} = \prod_i \left(\frac{1 \text{ atm}}{1 \text{ bar}} \right)^{v_i} = \left(\frac{1 \text{ atm}}{1 \text{ bar}} \right)^{\Sigma v_i}$$

$$= 1.01325^{\Sigma v_i}$$

5.14   Older tables of chemical thermodynamic properties are based on a standard state pressure of 1 atm. Show that the corresponding $\Delta_f G_i^o$ with a standard state pressure of 1 bar can be calculated using

$$\Delta_f G_j^o(\text{bar}) = \Delta_f G_j^o(\text{atm}) - (0.109 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) T \Sigma v_i$$

where the ν_i are the stoichiometric numbers of the gaseous reactants and products in the formation reaction.
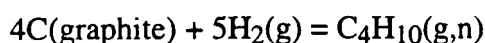
SOLUTION

$$\Delta_f G_j^\circ(\text{bar}) = -RT \ln\left\{ \prod_i [P_i/(1 \text{ atm})]^{\nu_i} \right\}$$

$$= -RT \ln\left\{ \prod_i [P_i/(1 \text{ bar})]^{\nu_i}[(1 \text{ atm})/(1 \text{ bar})]^{\Sigma \nu_i} \right\}$$

$$= -RT \ln\left\{ \prod_i [P_i/(1 \text{ atm})]^{\nu_i} \right\} - RT \ln\left[(1 \text{ atm})/(1 \text{ bar})\right]^{\Sigma \nu_i}$$

$$= \Delta_f G_j^\circ(\text{atm}) - RT \ln (1.01325)^{\Sigma \nu_i}$$

5.15   Show that the equilibrium mole fractions of n-butane and iso-butane are given by

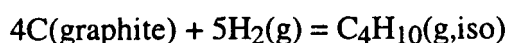$$y_n = \frac{e^{-\Delta_f G_n^\circ/RT}}{e^{-\Delta_f G_n^\circ/RT} + e^{-\Delta_f G_{iso}^\circ/RT}}$$

$$y_{iso} = \frac{e^{-\Delta_f G_{iso}^\circ/RT}}{e^{-\Delta_f G_n^\circ/RT} + e^{-\Delta_f G_{iso}^\circ/RT}}$$

SOLUTION

$$4C(\text{graphite}) + 5H_2(g) = C_4H_{10}(g,n)$$

$$K_n = P_n/P_{H_2}^5 = e^{-\Delta_f G_n^\circ/RT}$$

$$4C(\text{graphite}) + 5H_2(g) = C_4H_{10}(g,iso)$$

$$K_{iso} = P_{iso}/P_{H_2}^5 = e^{-\Delta_f G_{iso}^\circ/RT}$$

$$y_n = \frac{P_n}{P_n + P_{iso}} = \frac{P_{H_2}^5 e^{-\Delta_f G_n^\circ/RT}}{P_{H_2}^5 \left(e^{-\Delta_f G_n^\circ/RT} + e^{-\Delta_f G_{iso}^\circ/RT} \right)}$$

$$= \frac{e^{-\Delta_f G_n^\circ/RT}}{e^{-\Delta_f G_n^\circ/RT} + e^{-\Delta_f G_{iso}^\circ/RT}}$$

*5.16   Calculate the molar Gibbs energy of butane isomers for extents of reaction of 0.2, 0.4, 0.6, and 0.8 for the reaction

n-butane = iso-butane

at 1000 K and 1 bar. At 1000 K,

$\Delta_f G^o$ (n-butane) = 270 kJ mol^{-1}

$\Delta_f G^o$ (iso-butane) = 276.6 kJ mol^{-1}

Make a plot and show that the minimum corresponds with the equilibrium extent of reaction.

SOLUTION

n-butane = iso-butane

1	0	moles at $t = 0$
$1 - \xi$	ξ	moles at equilibrium; $n_T = 1$ mol

$G = n_n \mu_n + n_i \mu_i = n_n \mu_n^o + n_n RT \ln(x_n) + n_i \mu_i^o + n_i RT \ln(x_i)$

$\quad = (1 - \xi) \Delta_f G_n^o + (1 - \xi) RT \ln(1 - \xi) + \xi \Delta_f G_i^o + \xi RT \ln(\xi)$

$\quad = 270 + (276.6 - 270) \, \xi + RT[(1 - \xi)\ln(1 - \xi) + \xi \ln(\xi)]$

$G(\xi) = 270 + 6.6\xi + 8.314[(1 - \xi)\ln(1 - \xi) + \xi \ln(\xi)]$ kJ mol^{-1}

$G(0.2) = 267.2 \qquad G(0.6) = 268.4$
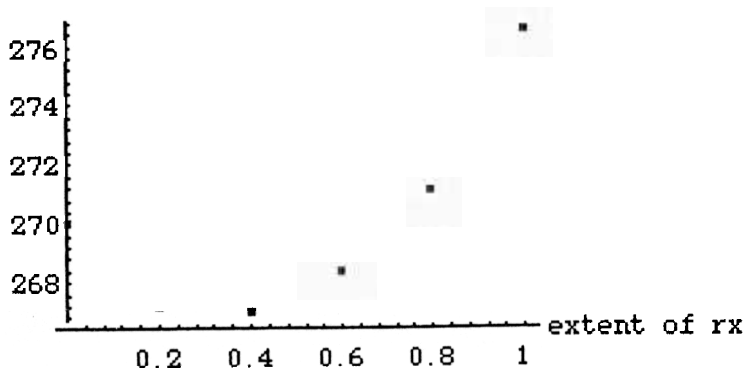
$G(0.4) = 267.0 \qquad G(0.8) = 271.1 \qquad$ in kJ/mol

$\Delta G^o = \Delta_f G_i^o - \Delta_f G_n^o = 6.6$ kJ mol^{-1} = $- RT \ln K$

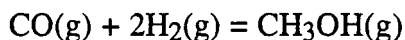$K = \dfrac{\xi}{1 - \xi} = \exp\left[\dfrac{- \Delta_r G^o}{RT}\right] = 0.4521 \quad (T = 10^3 \text{ K})$

$\xi = 0.311$

$G(0.311) = 266.9$ kJ/mol corresponds to the minimum of the following graph of $G(\xi)$ versus extent of reaction

5.17   In the synthesis of methanol by $CO(g) + 2H_2(g) = CH_3OH(g)$ at 500 K, calculate the total pressure required for a 90% conversion to methanol if CO and H_2 are initially in a 1:2 ratio. Given: $K = 6.09 \times 10^{-3}$.

SOLUTION

$$CO(g) + 2H_2(g) = CH_3OH(g)$$

initial moles   1   2   0

equil. moles   0.1   0.2   0.9   total 1.2

$$K = \frac{(P_{CH_3OH}/P^o)}{(P_{CO}/P^o)(P_{H_2}/P^o)^2} = 6.09 \times 10^{-3}$$

$$= \frac{\dfrac{0.9}{1.2}\dfrac{P}{P^o}}{\dfrac{0.1}{1.2}\dfrac{P}{P^o}\left(\dfrac{0.2}{1.2}\dfrac{P}{P^o}\right)^2}$$

$$\frac{P}{P^o} = \sqrt{\frac{(0.9)(1.2)^2}{(0.1)(0.04)(6.09 \times 10^{-3})}} = 231$$

$P = 231$ bar = total pressure for 90% conversion to CH_3OH

5.18   At 1273 K and at a total pressure of 30.4 bar the equilibrium in the reaction $CO_2(g) + C(s) = 2CO(g)$ is such that 17 mole % of the gas is CO_2. (a) What percentage would be CO_2 if the total pressure were 20.3 bar? (b) What would be the effect on the equilibrium of adding N_2 to the reaction mixture in a closed vessel until the partial pressure of N_2 is 10 bar? (c) At what pressure of the reactants will 25% of the gas be CO_2?

SOLUTION

(a) $P_{CO_2} = (30.4 \text{ bar})(0.17) = 5.2$ bar

$P_{CO} = (30.4 \text{ bar})(0.83) = 25.2$ bar

$$K = \frac{(25.2)^2}{5.2} = 122$$

Let x = mole fraction CO_2
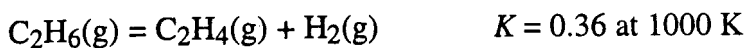
$$K = \frac{[20.3(1 - x)]^2}{20.3x} = 122$$

$x = 0.127$

Percentage CO_2 at equilibrium = 12.7%

(b)   No effect for ideal gases because the partial pressures of the reactants are not affected.
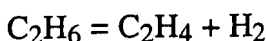
(c) $K = \dfrac{[0.75(P/P^o)]^2}{0.25(P/P^o)}$

$P = 54$ bar

5.19   When alkanes are heated up, they lose hydrogen and alkenes are produced. For example,

$C_2H_6(g) = C_2H_4(g) + H_2(g)$ $K = 0.36$ at 1000 K

If this is the only reaction that occurs when ethane is heated to 1000 K, at what total pressure will ethane be (a) 10% dissociated and (b) 90% dissociated to ethylene and hydrogen?

SOLUTION

$C_2H_6 = C_2H_4 + H_2$

Init.   1   0   0

Equil. $1 - \xi$ ξ ξ total $= 1 + \xi$

$K = \dfrac{\xi^2(P/P^o)}{(1 + \xi)(1 - \xi)} = \dfrac{\xi^2(P/P^o)}{1 - \xi^2}$
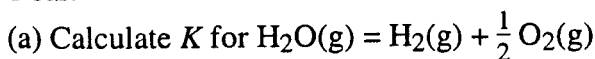
(a) $0.36 = \dfrac{0.1^2(P/P^o)}{1 - 0.1^2} = \dfrac{0.01(P/P^o)}{0.99}$

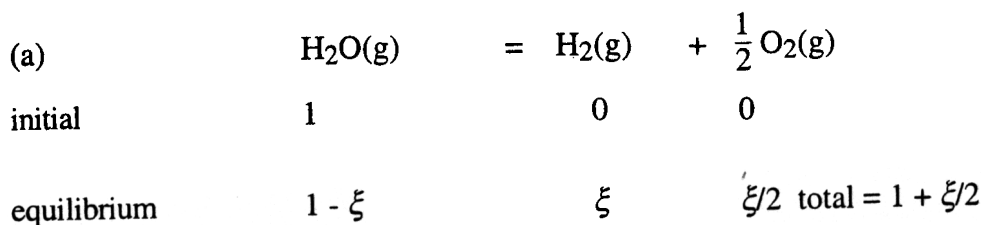$\dfrac{P}{P^o} = \left[\dfrac{(0.99)(0.36)}{0.01}\right] = 35.6$

(b) $0.36 = \dfrac{0.9^2(P/P^o)}{1 - 0.9^2} = \dfrac{0.81(P/P^o)}{0.19}$

$P = \left[\dfrac{(0.19)(0.36)}{0.81}\right] = 0.084$ bar

5.20   At 2000 °C water is 2% dissociated into oxygen and hydrogen at a total pressure of 1 bar.

(a) Calculate K for $H_2O(g) = H_2(g) + \frac{1}{2}O_2(g)$

(b) Will the extent of reaction increase or decrease if the pressure is reduced? (c) Will the extent of reaction increase or decrease if argon gas is added, holding the total pressure equal to 1 bar? (d) Will the extent of reaction change if the pressure is raised by addition of argon at constant volume to the closed system containing partially dissociated water vapor? (e) Will the extent of reaction increase or decrease if oxygen is added while holding the total pressure constant at 1 bar?

SOLUTION

(a)

$$H_2O(g) \quad = \quad H_2(g) \quad + \quad \frac{1}{2}O_2(g)$$

initial   1   0   0

equilibrium $1 - \xi$ ξ $\xi/2$ total $= 1 + \xi/2$

$$P_{H_2O} = \frac{1 - \xi}{1 + \frac{\xi}{2}} P \qquad P_{H_2} = \frac{\xi}{1 + \frac{\xi}{2}} P \qquad P_{O_2} = \frac{\xi/2}{1 + \frac{\xi}{2}} P$$

$$K = \frac{\left[\frac{\xi/2}{1 + \xi/2}\frac{P}{P^o}\right]^{1/2}\left[\frac{\xi}{1 + \xi/2}\frac{P}{P^o}\right]}{\frac{1 - \xi}{1 + \xi/2}\frac{P}{P^o}} = \frac{\xi^{3/2}(P/P^o)^{1/2}}{\sqrt{2}(1 + \xi/2)^{1/2}(1 - \xi)}$$

$$= \frac{0.02^{3/2}\, 1^{1/2}}{\sqrt{2}\,(1.01)^{1/2}\,(0.98)} = 2.03 \times 10^{-3}$$

(b)   If the total pressure is reduced, the extent of reaction will increase because the reaction will produce more molecules to fill the volume.

(c)   If argon is added at constant pressure, the extent of reaction will increase because the partial pressure due to the reactants will decrease.

(d)   If argon is added at constant volume, the extent of reaction will not be changed because the partial pressure due to the reactants will not change.

(e)   If oxygen is added at constant total pressure, the extent of reaction of H_2O will decrease because the reaction will be pushed to the left.

5.21   At 250 °C PCl_5 is 80% dissociated at a pressure of 1.013 bar, and so $K = 1.80$. What is the extent of reaction at equilibrium after sufficient nitrogen has been added at constant pressure to produce a nitrogen partial pressure of 0.9 bar? The total pressure is maintained at 1 bar.
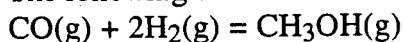
SOLUTION

$$K = \frac{0.8^2 (1.013)}{1 - 0.64} = 1.80$$

$$K = \frac{\xi^2(0.1)}{1 - \xi^2}$$

$\xi = 0.973$ or 97.3% dissociated.

5.22   The following exothermic reaction is at equilibrium at 500 K and 10 bar.
       $CO(g) + 2H_2(g) = CH_3OH(g)$
       Assuming the gases are ideal, what will happen to the amount of methanol at equilibrium when (a) the temperature is raised, (b) the pressure is increased, (c) an

inert gas is pumped in at constant volume, (d) an inert gas is pumped in at constant pressure, and (e) hydrogen gas is added at constant pressure?

SOLUTION

(a) $n(CH_3OH)$ decreases because heat is involved.

(b) $n(CH_3OH)$ increases because there are fewer molecules of gas in the product.

(c)   No effect.

(d) $n(CH_3OH)$ decreases because the volume increases.

(e) $n(CH_3OH)$ increases because there is more of a reactant. Note: the effect of the addition of CO is more complicated.

5.23   The following reaction is nonspontaneous at room temperature and endothermic.
$$3C(graphite) + 2H_2O(g) = CH_4(g) + 2CO(g)$$
As the temperature is raised, the equilibrium constant will become equal to unity at some point. Estimate this temperature using data from Appendix C.3.

SOLUTION

At 1000 K

$\Delta_r G^\circ = 19.492 + 2(- 200.275) - 2(- 192.590) = 4.122$ kJ mol^{-1}

$= - (8.3145 \times 10^{-3}$ kJ K^{-1} mol$^{-1})(1000$ K$) \ln K$

$K = 0.609$

$\Delta_r H^\circ = - 89.849 + 2(-111.983) - 2(-247.857) = 181.899$ kJ mol^{-1}

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

$$\ln \frac{1}{0.609} = \frac{181\ 899 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{1000 \text{ K}} - \frac{1}{T_2} \right)$$

$$T_2 = \frac{1}{\dfrac{1}{\text{----}} - \dfrac{8.3145}{181899} \ln \dfrac{1}{0.609}} = 1023 \text{ K}$$

5.24   The measured density of an equilibrium mixture of N_2O_4 and NO_2 at 15 °C and 1.013 bar is 3.62 g L^{-1}, and the density at 75 °C and 1.013 bar is 1.84 g L^{-1}. What is the enthalpy change of the reaction $N_2O_4(g) = 2NO_2(g)$?

SOLUTION

At 15 °C
$$M = \frac{RT}{P} \frac{g}{V} = \frac{(0.08314)(288)(3.62)}{1.013} = 85.57 \text{ g mol}^{-1}$$

$$\xi = \frac{M_1 - M_2}{M_2} = \frac{92.01 - 85.57}{85.57} = 0.0753$$

$$K = \frac{4\xi^2 P}{1 - \xi^2} = \frac{4(0.0753)^2(1.013)}{1 - 0.0753^2} = 0.0231$$

At 75 °C

$$M = \frac{(0.08314)(348)(1.84)}{1.013} = 52.55 \text{ g mol}^{-1}$$

$$\xi = \frac{92.01 - 52.55}{52.55} = 0.751 \qquad K = 5.24$$

$$\Delta_r H = \frac{RT_1 T_2}{(T_2 - T_1)} \ln \frac{K_2}{K_1} = \frac{(8.314)(288)(348)}{60} \ln \frac{5.24}{0.0231}$$

$$= 75 \text{ kJ mol}^{-1}$$

5.25   Calculate K_c for the reaction in problem 5.19 at 1000 K and describe what it is equal to.

SOLUTION

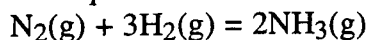$$K_c = K_P \left(\frac{P^o}{c^o RT}\right)^{\Sigma v_i}$$

$$= 0.36 \frac{1 \text{ bar}}{(1 \text{ L mol}^{-1})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(238 \text{ K})}$$

$$= 0.0145$$

$$= \frac{\left(\frac{[C_2H_4]}{c^o}\right)\left(\frac{[H_2]}{c^o}\right)}{\frac{[C_2H_6]}{c^o}}$$

where [ ] indicates concentrations in moles per liter and $c^o = 1$ mol L^{-1}.

*5.26   The equilibrium constant for the reaction
$$N_2(g) + 3H_2(g) = 2NH_3(g)$$
is 35.0 at 400 K when partial pressures are expressed in bars. Assume the gases are ideal. (a) What is the equilibrium volume when 0.25 mol N_2 is mixed with 0.75 mol H_2 at a temperature of 400 K and a pressure of 1 bar? (b) What is the equilibrium composition and equilibrium pressure if this mixture is held at a constant volume of 33.26 L at 400 K?

SOLUTION

(a)

	N_2	+	$3H_2$	=	$2NH_3$
initial	0.25		0.75		0
equil.	0.25 - ξ		0.75 - 3ξ	2ξ	total = 1 - 2ξ

$$K_P = \frac{(2\xi)^2(1 - 2\xi)^2}{(0.25 - \xi)(0.75 - 3\xi)^3} = 35.0$$

The method of successive approximations or the use of an equation solver yields $\xi = 0.1652$.

$P(N_2)/P^o = (0.25 - \xi)/(1 - 2\xi) = 0.1266$

$P(H_2)/P^o = 3(0.1266) = 0.3798$

$P(NH_3)/P^o = 2\xi/(1 - 2\xi) = 0.493$

Since the total pressure is 1 bar, these numbers also give the equilibrium mole fractions.

$V = (1 - 2\xi)RT/P$

$= (0.6696 \text{ mol})(0.8314 \text{ L bar K}^{-1} \text{ mol}^{-1})(400 \text{ K})/(1 \text{ bar})$

$= 22.27 \text{ L}$

When *Mathematica*™ is used to calculate the extent of reaction, four solutions are obtained; two of them are not satisfactory because they are imaginary and one is 0.334 mol, which is impossible because the extent of reaction has to be less than 0.25 mol. The fourth solution is correct.

(b)   In order to calculate the equilibrium composition at constant volume, it is convenient to use K_c.

$K_c = (P^o/c^oRT)^{\Sigma v_i} K_P$

$$= \left[\frac{1 \text{ bar}}{(1 \text{ mol L}^{-1})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(400 \text{ K})}\right]^{-2} 35.0$$

$= 3.871 \times 10^4$

$K_c = [c(NH_3)/c^o]^2/[c(N_2)/c^o][c(H_2)/c^o]^3$

$= (2\xi)^2 \, 33.26^2/(0.25 - \xi)(0.75 - 3\xi)^3$

$= 3.871 \times 10^4$

The method of successive approximation or the use of an equation solver yields $\xi = 0.151$.

$n(N_2) = 0.25 - \xi = 0.0990$
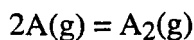
$n(H_2) = 0.75 - 3\xi = 0.2970$

$n(NH_3) = 2\xi = 0.302$

$n(\text{total}) = 0.698$

$P = \dfrac{(0.698 \text{ mol})RT}{33.26 \text{ L}} = 0.698 \text{ bar}$

5.27   Show that to a first approximation the equation of state of a gas that dimerizes to a small extent is given by

$$\frac{P\bar{V}}{RT} = 1 - K_c/\bar{V}$$

SOLUTION

$2A(g) = A_2(g)$

$K_c = [A_2]/[A]^2 = n_{A_2}V/n_A^2$

assuming an ideal gas mixture.

$n_0 = $ Total number of moles of A $= n_A + 2n_{A_2} = n_A + 2K_c n_A^2/V$ (a)

This can be solved for n_A using the quadratic formula for $ax^2 + bx + c = 0$:

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

This yields

$n_A = n_0(1 - 2K_c n_0/V)$ (b)

when the approximation $(1 + x)^{1/2} = 1 + x/2 - x^2/8 + \ldots$ is used.

The gas law indicates that

$$\frac{PV}{RT} = n_A + n_{A_2} = n_A + K_c n_A^2/V = n_A(1 + K_c n_A/V)$$ (c)

Substituting equation b in equation c yields

$$\frac{PV}{RT} = n_0(1 - 2K_c n_0/V)(1 + K_c n_A/V)$$ (d)

Since n_A is just a little smaller than n_0, it can be replaced by n_0 in a term that is small compared to unity. Thus equation d can be written as

$$\frac{PV}{RT} = n_0(1 - 2K_c/\bar{V})(1 + K_c/\bar{V})$$ (e)

When this is multiplied out ignoring higher order terms and the n_0 is moved to the left-hand side of the equation, we obtain

$$\frac{P\bar{V}}{RT} = 1 - K_c/\bar{V}$$

5.28   Water vapor is passed over coal (assumed to be pure graphite in this problem) at 1000 K. Assuming that the only reaction occurring is the water gas reaction
C(graphite) + H_2O(g) = CO(g) + H_2(g) $K = 2.52$
calculate the equilibrium pressures of H_2O, CO, and H_2 at a total pressure of 1 bar. [Actually the water gas shift reaction
CO(g) + H_2O(g) = CO_2(g) + H_2(g)
occurs in addition, but it is considerably more complicated to take this additional reaction into account.]

SOLUTION

$$K = \frac{(P_{CO}/P^o)(P_{H_2}/P^o)}{(P_{H_2O}/P^o)} = \frac{x^2}{y} = \frac{x^2}{1 - 2x} = 2.52$$

$2x + y = 1$ $x^2 = 2.52 - 5.04x$

$x^2 + 5.04x - 2.52 = 0$

$$x = \frac{-5.04 \pm \sqrt{5.04^2 + 4(2.52)}}{2} = 0.458$$

$$= \frac{P_{CO}}{P^o} = \frac{P_{H_2}}{P^o}$$

$$1 - 2x = 0.084 = \frac{P_{H_2O}}{P^o}$$

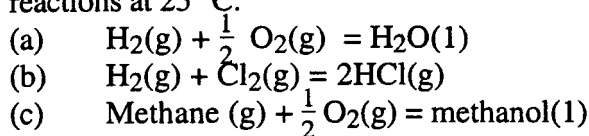$P_{H_2O} = 0.084$ bar $\qquad P_{CO} = 0.458$ bar $\qquad P_{H_2} = 0.458$ bar

5.29 What is the standard change in entropy for the dissociation of molecular oxygen at 298.15 K and 1000 K? Use Appendix C.3.

SOLUTION

$O_2(g) = 2 O(g)$
$\qquad \Delta_r S(298.15 \text{ K}) = 2(161.058) - 205.147$
$\qquad\qquad\qquad = 116.969 \text{ J K}^{-1} \text{ mol}^{-1}$
$\qquad \Delta_r S(1000 \text{ K}) = 2(186.790) - 243.578$
$\qquad\qquad\qquad = 130.002 \text{ J K}^{-1} \text{ mol}^{-1}$

5.30 Using molar entropies from Appendix C.2, calculate $\Delta_r S^o$ for the following reactions at 25 °C.
(a) $H_2(g) + \frac{1}{2} O_2(g) = H_2O(1)$
(b) $H_2(g) + Cl_2(g) = 2HCl(g)$
(c)   Methane (g) $+ \frac{1}{2} O_2(g) = $ methanol(1)

SOLUTION

(a) $\Delta_r S^o = 69.91 - 130.68 - \frac{1}{2}(205.13) = -163.34 \text{ J K}^{-1} \text{ mol}^{-1}$

(b) $\Delta_r S^o = 2(186.908) - 130.684 - 223.066 = 20.066 \text{ J K}^{-1} \text{ mol}^{-1}$

(c) $\Delta_r S^o = 126.8 - 186.264 - \frac{1}{2}(205.138) = -162.0 \text{ J K}^{-1} \text{ mol}^{-1}$

5.31 What is $\Delta_r S^o$ (298 K) for
$\qquad\qquad H_2O(1) = H^+(ao) + OH^-(ao)$
Why is this change negative and not positive?

SOLUTION

$\Delta_r S^o = -10.75 - 69.92 = -80.67 \text{ J K}^{-1} \text{ mol}^{-1}$
The ions polarize neighboring water molecules and attract them. For this reason the product state is more ordered than the reactant state.

5.32 Mercuric oxide dissociates according to the reaction $2HgO(s) = 2Hg(g) + O_2(g)$. At 420 °C the dissociation pressure is 5.16×10^4 Pa, and at 450 °C it is 10.8×10^4 Pa. Calculate (a) the equilibrium constants, and (b) the enthalpy of dissociation per mole of HgO.

SOLUTION

(a) $P_{Hg} = 2P_{O_2}$ $P_{Hg} = \frac{2}{3}P$ $P_{O_2} = \frac{1}{3}P$

$K_{420} = P_{Hg}^2 P_{O_2} = \left(\frac{2}{3}\right)^2 \left(\frac{1}{3}\right) P^3$

$\quad = \left(\frac{4}{27}\right)\left(\frac{5.16 \times 10^4 \text{ Pa}}{1.013 \times 10^5 \text{ Pa}}\right)^3 = 0.0196$

$K_{450} = \left(\frac{4}{27}\right)\left(\frac{10.8 \times 10^4 \text{ Pa}}{1.013 \times 10^5 \text{ Pa}}\right)^3 = 0.1794$

(b) $\Delta_r H^o = \dfrac{RT_1 T_2}{T_2 - T_1} \ln \dfrac{K_2}{K_1}$

$\quad = \dfrac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(693 \text{ K})(723 \text{ K})}{30K} \ln \dfrac{0.1794}{0.0196}$

$\quad = 308 \text{ kJ mol}^{-1}$ for the reaction as written

$\quad = 154 \text{ kJ mol}^{-1}$ of HgO(s)

5.33   The decomposition of silver oxide is represented by
$2Ag_2O(s) = 4Ag(s) + O_2(g)$
Using data from Appendix C.2 and assuming $\Delta_r C_p = 0$ calculate the temperature at
which the equilibrium pressure of O_2 is 0.2 bar. This temperature is of interest
because Ag_2O will decompose to yield Ag at temperatures above this value if it is in
contact with air.

SOLUTION

$\Delta_r H^o = -2(-31.05) = 62.10 \text{ kJ mol}^{-1}$

$\Delta_r S^o = 4(42.55) + 205.138 - 2(121.3) = 132.7 \text{ J K}^{-1} \text{ mol}^{-1}$
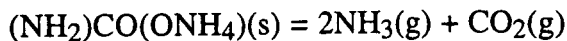
$\Delta_r G = \Delta G^o + RT \ln P_{O_2}$

$0 = \Delta H^o - T\Delta S^o + RT \ln 0.2$

$\Delta_r H^o = T(\Delta S^o - R \ln 0.2)$

$T = \dfrac{\Delta_r H^o}{\Delta_r S^o - R \ln 0.2} = \dfrac{62100 \text{ J mol}^{-1}}{(132.7 - 8.314 \ln 0.2) \text{ J K}^{-1} \text{ mol}^{-1}}$

$\quad = 425 \text{ K}$

5.34   The dissociation of ammonium carbamate takes place according to the reaction
$(NH_2)CO(ONH_4)(s) = 2NH_3(g) + CO_2(g)$
When an excess of ammonium carbamate is placed in a previously evacuated vessel,
the partial pressure generated by NH_3 is twice the partial pressure of the CO_2, and
the partial pressure of $(NH_2)CO(ONH_4)$ is negligible in comparison. Show that

$$K = \left(\frac{P_{NH_3}}{P^o}\right)^2 \left(\frac{P_{CO_2}}{P^o}\right) = \frac{4}{27}\left(\frac{P}{P^o}\right)^3$$

where P is the total pressure.

SOLUTION

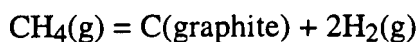$P = P_{NH_3} + P_{CO_2} = 3P_{CO_2}$ since $P_{NH_3} = 2P_{CO_2}$

$P_{CO_2} = \dfrac{P}{3}$ $\qquad\qquad$ $P_{NH_3} = \dfrac{2}{3}P$

$K = \left(\dfrac{P_{NH_3}}{P^o}\right)^2\left(\dfrac{P_{CO_2}}{P^o}\right) = \left(\dfrac{2}{3}\dfrac{P}{P^o}\right)^2\left(\dfrac{1}{3}\dfrac{P}{P^o}\right) = \dfrac{4}{27}\left(\dfrac{P}{P^o}\right)^3$

5.35   At 1000 K methane at 1 bar is in the presence of hydrogen. In the presence of a sufficiently high partial pressure of hydrogen, methane does not decompose to form graphite and hydrogen. What is this partial pressure?
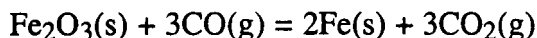
SOLUTION

$CH_4(g) = C(graphite) + 2H_2(g)$

$\Delta G^o = - RT \ln K = - 19.46 \text{ kJ mol}^{-1}$

$K = 10.39 = \dfrac{\left(\dfrac{P_{H_2}}{P^o}\right)^2}{\dfrac{P_{CH_4}}{P^o}}$

$P_{H_2} = P^o[(10.39)(1)]^{1/2} = 3.2 \text{ bar}$

5.36   For the reaction

$Fe_2O_3(s) + 3CO(g) = 2Fe(s) + 3CO_2(g)$

the following values of K are known.

$t/°C$	250	1000
K	100	0.0721

At 1120 °C for the reaction $2CO_2(g) = 2CO(g) + O_2(g)$, $K = 1.4 \times 10^{-12}$. What equilibrium partial pressure of O_2 would have to be supplied to a vessel at 1120 °C containing solid Fe_2O_3 just to prevent the formation of Fe?

SOLUTION

$\ln\left(\dfrac{K_2}{K_1}\right) = \dfrac{\Delta_r H^o(T_2 - T_1)}{RT_1T_2}$

$\Delta_r H^o = \dfrac{(8.314)(523)(1273) \ln (0.0721/100)}{(750)}$

$\qquad = -53.4 \text{ k J mol}^{-1}$

$\ln\left(\dfrac{K_{1393}}{K_{1273}}\right) = \dfrac{(53\,400)(120)}{8.314\,(1393)(1273)}$

SOLUTION

$P = P_{NH_3} + P_{CO_2} = 3P_{CO_2}$ since $P_{NH_3} = 2P_{CO_2}$

$P_{CO_2} = \dfrac{P}{3}$ $\qquad$ $P_{NH_3} = \dfrac{2}{3}P$

$K = \left(\dfrac{P_{NH_3}}{P^o}\right)^2\left(\dfrac{P_{CO_2}}{P^o}\right) = \left(\dfrac{2}{3}\dfrac{P}{P^o}\right)^2\left(\dfrac{1}{3}\dfrac{P}{P^o}\right) = \dfrac{4}{27}\left(\dfrac{P}{P^o}\right)^3$

5.35 At 1000 K methane at 1 bar is in the presence of hydrogen. In the presence of a sufficiently high partial pressure of hydrogen, methane does not decompose to form graphite and hydrogen. What is this partial pressure?
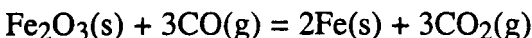
SOLUTION

$CH_4(g) = C(graphite) + 2H_2(g)$

$\Delta G^o = -RT \ln K = -19.46$ kJ mol^{-1}

$K = 10.39 = \dfrac{\left(\dfrac{P_{H_2}}{P^o}\right)^2}{\dfrac{P_{CH_4}}{P^o}}$

$P_{H_2} = P^o[(10.39)(1)]^{1/2} = 3.2$ bar

5.36 For the reaction

$Fe_2O_3(s) + 3CO(g) = 2Fe(s) + 3CO_2(g)$

the following values of K are known.

$t/^\circ C$	250	1000
K	100	0.0721

At 1120 °C for the reaction $2CO_2(g) = 2CO(g) + O_2(g)$, $K = 1.4 \times 10^{-12}$. What equilibrium partial pressure of O_2 would have to be supplied to a vessel at 1120 °C containing solid Fe_2O_3 just to prevent the formation of Fe?

SOLUTION

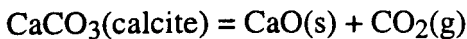$\ln\left(\dfrac{K_2}{K_1}\right) = \dfrac{\Delta_r H^o(T_2 - T_1)}{RT_1T_2}$

$\Delta_r H^o = \dfrac{(8.314)(523)(1273) \ln (0.0721/100)}{(750)}$

$\qquad = -53.4$ k J mol^{-1}

$\ln\left(\dfrac{K_{1393}}{K_{1273}}\right) = \dfrac{(53\,400)(120)}{8.314\,(1393)(1273)}$

5.39   Calculate the partial pressure of $CO_2(g)$ over $CaCO_3$(calcite) - CaO(s) at 500 °C using the equation in Example 5.11 and data in Appendix C.3.

SOLUTION

$CaCO_3$(calcite) $= CaO(s) + CO_2(g)$

$\Delta_r H^o = - 635.09 + (- 393.51) - (- 1206.92) = 178.32$ kJ mol^{-1}

$\Delta_r C_P^o = 42.80 + 37.11 - 81.88 = - 1.97$ J K^{-1} mol^{-1}

$\Delta_r S^o = 39.75 + 213.74 - 92.9 = 160.6$ J K^{-1} mol^{-1}

Substituting in the equation in Example 5.11,

$$\ln K_{773} = - \frac{178\ 320}{(8.314)(773.15)} + \frac{160.6}{8.314} + \frac{1.97}{8.314}(1 - \frac{298.15}{773.15} - \ln \frac{773.19}{298.15})$$

$$K_{773} = \frac{P_{CO_2}}{P^o} = 20 \times 10^{-5}$$

Table 5.1 gives $\frac{P_{CO_2}}{P^o} = 9.2 \times 10^{-5}$ bar

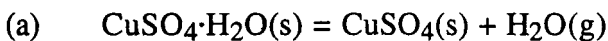5.40   The NBS Tables contain the following data at 298 K:

	$\Delta_f H^o$/kJ mol^{-1}	$\Delta_f G^o$/kJ mol^{-1}
$CuSO_4(s)$	-771.36	-661.8
$CuSO_4 \cdot H_2O(s)$	-1085.83	-918.11
$CuSO_4 \cdot 3H_2O(s)$	-1684.31	-1399.96
$H_2O(g)$	-241.818	-228.572

(a) What is the equilibrium partial pressure of H_2O over a mixture of $CuSO_4(s)$ and $CuSO_4 \cdot H_2O(s)$ at 25 °C?
(b) What is the equilibrium partial pressure of H_2O over a mixture of $CuSO_4 \cdot H_2O(s)$ and $CuSO_4 \cdot 3H_2O(s)$ at 25 °C?
(c) What are the answers to (a) and (b) if the temperature is 100 °C and ΔC_P^o is assumed to be zero?

SOLUTION

(a) $CuSO_4 \cdot H_2O(s) = CuSO_4(s) + H_2O(g)$
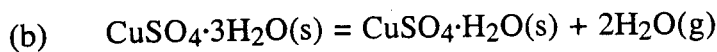 $\Delta G^o = - 228.572 - 661.8 + 918.11$
          $= 27.7$ kJ mol^{-1}

$$K = \exp\left(\frac{- \Delta G^o}{RT}\right) = 1.4 \times 10^{-5} = \frac{P_{H_2O}}{P^o}$$

$P_{H_2O} = 1.4 \times 10^{-5}$ bar

(b) $CuSO_4 \cdot 3H_2O(s) = CuSO_4 \cdot H_2O(s) + 2H_2O(g)$
$\Delta G^o = 2(-228.572) - 918.11 + 1399.46$

$\qquad = -24.71 \text{ kJ mol}^{-1}$

$$P_{H_2O} = \exp\left[\frac{-24\,710}{(2)(8.314)(298)}\right]$$

$\qquad = 6.83 \times 10^{-3} \text{ bar}$

(c)   For the first reaction
$$\ln \frac{K_{100}}{1.4 \times 10^{-5}} = \frac{72\,650(75)}{8.314(298)(373)}$$

$\Delta H^o = -241.818 - 771.36 + 1085.83 = 72.65 \text{ kJ mol}^{-1}$

$$\ln \frac{K_{100}}{1.4 \times 10^{-5}} = 5.896$$

$K_{100} = 363.6(1.4 \times 10^{-5}) = 0.0051 \text{ bar}$

For the second reaction
$\Delta H^o \quad = 2(-241.818) - 1085.83 + 1684.31$

$\qquad = 114.84 \text{ kJ mol}^{-1}$
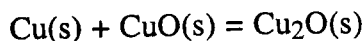
$$\ln \frac{K_{100}}{4.7 \times 10^{-5}} = \frac{114\,840(75)}{8.314(298)(373)} = 9.32$$

$K_{100} = 0.52 \text{ bar}^2 = P_{H_2O}^2$

$P_{H_2O} = 0.72 \text{ bar}$

5.41   One micromole of CuO(s) and 0.1 μmole of Cu(s) are placed in a 1 L container at 1000 K. Determine the identity and quantity of each phase present at equilibrium if $\Delta_f G^o$ of CuO is -66.66 kJ mol^{-1} and that of Cu_2O is -77.94 kJ mol^{-1} at 1000 K. (From H. F. Franzen, *J. Chem. Ed.* **65**, 146 (1988).)

SOLUTION

$Cu(s) + CuO(s) = Cu_2O(s)$
$\Delta_r G^o = -77.94 - (-66.66) = -11.28 \text{ kJ mol}^{-1}$

Therefore, this reaction goes to completion to the right. The two solids are in equilibrium with $O_2(g)$.

$2CuO(s) = Cu_2O(s) + \frac{1}{2} O_2(g)$
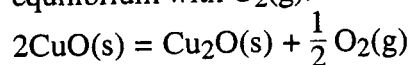
$\Delta_r G^o = -77.94 - 2(-66.66) = 55.38 \text{ kJ mol}^{-1} = -RT \ln P_{O_2}^{1/2}$

$$P_{O_2} = \exp\left[-\frac{2(55\,380)}{(8.314)(1000)}\right] = 1.64 \times 10^{-6}$$

The amount of $O_2(g)$ at equilibrium is

$$n_{O_2} = \frac{PV}{RT} = \frac{(1.64 \times 10^{-6})(1)}{(0.08314)(1000)} = 1.97 \times 10^{-8} \text{ mol}$$

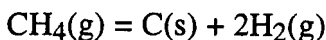Thus the amounts at equilibrium are essentially

$n_{CuO} = 0.9 - 4(0.02) = 0.82 \ \mu mol$

$n_{Cu_2O} = 0.1 + 2(0.02) = 0.14 \ \mu mol$

$n_{O_2} = 0.02 \ \mu mol$

5.42   For the heterogeneous reaction

$CH_4(g) = C(s) + 2H_2(g)$

derive the expression for the extent of reaction in terms of the equilibrium constant and the applied pressure, where the extent of reaction when graphite is in equilibrium with the gas mixture. Is this the same expression (equation 5.33) that was obtained for the reaction $N_2O_4(g) = 2NO_2(g)$?

SOLUTION

$CH_4(g) \ = \ C(s) + \ 2H_2(g)$

$1-\xi \quad \xi \quad 2\xi$

$$\frac{1-\xi}{1+\xi}P \qquad\qquad \frac{2\xi}{1+\xi}P$$

$$K = \frac{4\xi^2(P/P^o)}{1-\xi^2}$$
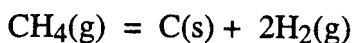
$$\xi = \left(\frac{K}{4(P/P^o)+K}\right)^{1/2}$$

This is the same as equation 5.33, but it only applies when graphite is in equilibrium with the gas.

5.43   Calculate the equilibrium extent of the reaction $N_2O_4(g) = 2NO_2(g)$ at 298.15 K and a total pressure of 1 bar if the $N_2O_4(g)$ is mixed with an equal volume of $N_2(g)$ before the reaction occurs. As shown by Example 5.3, $K = 0.143$. Do you expect the same equilibrium extent of reaction as in example? If not do you expect a larger or smaller equilibrium extent of reaction?

SOLUTION

If there is initially 1 mol of N_2O_4, the total amount of gas at equilibrium is $2 + \xi$. Thus the expression for the equilibrium constant is

$$K = \frac{4\xi^2(P/P^o)}{(2+\xi)(1-\xi)}$$

where P is the total pressure. When the total pressure is 1 bar, the equilibrium extent of reaction obtained by solving this quadratic equation with the formula

$$\xi = \frac{-b\pm(b^2 - 4ac)^{1/2}}{2a}$$

is 0.249.

This equilibrium extent of reaction is smaller than that in Example 5.3 because the partial pressure of $N_2O_4(g)$ plus $NO_2(g)$ is larger than 0.5 bar. The partial pressure of $N_2(g)$ was initially 0.5 bar, but it is less than this in the equilibrium mixture because of the expansion of the reaction mixture during the reaction at a constant pressure of 1 bar.

5.44 (a) A system contains $CO(g)$, $CO_2(g)$, $H_2(g)$, and $H_2O(g)$. How many chemical reactions are required to describe chemical changes in this system? Give an example. (b) If solid carbon is present in the system in addition, how many independent chemical reactions are there? Give a suitable set.

SOLUTION

(a)

	CO	CO₂	H₂	H₂O
C	1	1	0	0
O	1	2	0	2
H	0	0	2	2

To perform a Gaussian elimination, subtract the first row from the second, and divide the third row by 2.
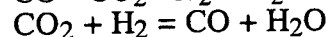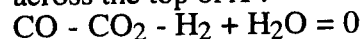
1	1	0	0
0	1	0	1
0	0	1	1

Subtract the second row from the first.

1	0	0	-1
0	1	0	1
0	0	1	1

The rank of the A matrix is 3, and so the number of independent reactions is
$R = N - \text{rank } A = 4 - 3 = 1$
where N is the number of species.
The stoichiometric numbers for a suitable reaction is obtained by changing the sign of the numbers in the last column, and extending the vector with a 1; that is, 1, -1, -1, 1. These are the stoichiometric numbers for the species across the top of A .
$CO - CO_2 - H_2 + H_2O = 0$
$CO_2 + H_2 = CO + H_2O$

(b)

	CO	CO₂	H₂	H₂O	C
C	1	1	0	0	1
O	1	2	0	1	0
H	0	0	2	2	0

Subtract the first row from the second and divide the third row by 2.

1	1	0	0	1
0	1	0	1	-1
0	0	1	1	0

Subtract the second row from the first

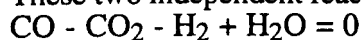| 1	0	0	-1	2
0	1	0	1	-1
0	0	1	1	0

Rank $A = 3$ and $R = N - \text{rank } A = 5 - 3 = 2$. To obtain a suitable set of reactions, change the signs in the last two columns and put an identity
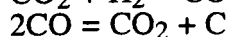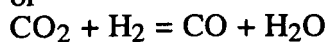
matrix at the bottom.

$$
\begin{array}{cc}
1 & -2 \\
-1 & 1 \\
-1 & 0 \\
1 & 0 \\
0 & 1
\end{array}
$$

These two independent reactions are

$CO - CO_2 - H_2 + H_2O = 0$

$-2CO + CO_2 + C = 0$

or

$CO_2 + H_2 = CO + H_2O$

$2CO = CO_2 + C$

*5.45 For a closed system containing C_2H_2, H_2, C_6H_6, and $C_{10}H_8$, use a Gaussian elimination to obtain a set of independent chemical reactions. Perform the matrix multiplication to verify $Av = 0$.

SOLUTION

$$
\begin{array}{c|cccc}
 & C_2H_2 & H_2 & C_6H_6 & C_{10}H_8 \\
C & 2 & 0 & 6 & 10 \\
H & 2 & 2 & 6 & 8
\end{array}
$$

$$
\begin{array}{cccc}
1 & 0 & 3 & 5 \\
1 & 1 & 3 & 4
\end{array}
$$

$$
\begin{array}{cccc}
1 & 0 & 3 & 5 \\
0 & 1 & 0 & -1
\end{array}
$$

$$
v = \begin{array}{c|cc}
C_2H_2 & -3 & -5 \\
H_2 & 0 & 1 \\
C_6H_6 & 1 & 0 \\
C_{10}H_8 & 0 & 1
\end{array}
$$

$3C_2H_2 = C_6H_6$

$5C_2H_2 = C_{10}H_8 + H_2$
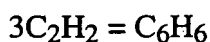
$$
\begin{bmatrix} 2 & 0 & 6 & 10 \\ 2 & 2 & 6 & 8 \end{bmatrix}
\begin{bmatrix} -3 & -5 \\ 0 & 1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix}
=
\begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}
$$

5.46 The reaction $A + B = C$ is at equilibrium at a specified T and P. Derive the fundamental equation for G in terms of components by eliminating μ_C.

SOLUTION

The fundamental equation for G is

$dG = - SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C$ (1)

When the reaction is at equilibrium,

$\mu_A + \mu_B = \mu_C$ (2)

Eliminating μ_C from equation 1 yields

$$dG = - SdT + VdP + \mu_A(dn_A + dn_C) + \mu_B(dn_B + dn_C) \qquad (3)$$

This equation is written in terms of 2 components rather than 3 species because $C = N - R = 3 - 1 = 2$. The two components can be referred to as the A,C pseudoisomer group with amount

$$n_I' = n_A + n_C \qquad (4)$$

and the B component with amount

$$n_B' = n_B + n_C \qquad (5)$$

Thus at chemical equilibrium the fundamental equation can be written as

$$dG = - SdT + VdP + \mu_A dn_I' + \mu_B dn_B' \qquad (6)$$

Note that the chemical potentials of the components are the same as the chemical potentials of two of the species.

*5.47 The article C. A. L. Figueiras, J. of Chem. Educ., 69, 276 (1992) illustrates an interesting problem you can get into in trying to balance a chemical equation. Consider the following reaction without stoichiometric numbers:

$$ClO_3^- + Cl^- + H^+ = ClO_2 + Cl_2 + H_2O$$
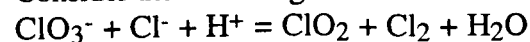
There is actually an infinite number of ways to balance this equation. The following steps in unraveling this puzzle can be carried out using a personal computer with a program like *Mathematica* ™, which can do matrix operations. Write the conservation matrix A and determine the number of components. How many independent reactions are there for this system of six species? What are the stoichiometric numbers for a set of independent reactions? These steps show that chemical change in this system is represented by two chemical reactions, not one.

SOLUTION

The conservation matrix A for this system is

	ClO_3^-	Cl^-	H^+	H_2O	ClO_2	Cl_2
H	0	0	1	2	0	0
O	3	0	0	1	2	0
Cl	1	1	0	0	1	2
charge	-3	-1	+1	0	0	0

Row reduction of this matrix yields

	ClO_3^-	Cl^-	H^+	H_2O	ClO_2	Cl_2
ClO_3^-	1	0	0	0	5/6	1/3
Cl^-	0	1	0	0	1/6	5/3
H^+	0	0	1	0	1	2
H_2O	0	0	0	1	-1/2	-1

This indicates that there are 4 components. Thus $R = N_s - C = 6 - 4 = 2$. The last two columns with changed signs and augmented by a 2x2 unit matrix at the bottom give the stoichiometric numbers of two independent reactions. Another way to obtain a set of independent reactions is to calculate the null space of the A matrix. The null space v is

	ClO_3^-	Cl^-	H^+	H_2O	ClO_2	Cl_2
rx 1	-1	-5	-6	3	0	3
rx 2	-5	-1	-5	3	6	0

5.48 A chemical reaction system contains three species: C_2H_4 (ethylene), C_3H_6 (propene), and C_4H_8 (butene). (a) Write the A matrix. (b) Row reduce the A matrix, (c) How many components are there? (d) Derive a set of independent reactions from the A matrix.

SOLUTION

(a)
$$A = \begin{array}{ccc} C_2H_4 & C_3H_6 & C_4H_8 \\ 2 & 3 & 4 \\ 4 & 6 & 8 \end{array}$$

(b) Multiplying the first row by 2 and subtracting it from the second row, and dividing by 2 yields
$$A = \begin{array}{ccc} 1 & 3/2 & 2 \\ 0 & 0 & 0 \end{array}$$

(c) There is one component because there is one independent row.

(d) Taking the last two columns, changing the sign, and appending a 2x2 matrix below it yields

$$v = \begin{array}{ccc} & rx\ 1 & rx\ 2 \\ C_2H_4 & -3/2 & -2 \\ C_3H_6 & 1 & 0 \\ C_4H_8 & 0 & 1 \end{array}$$

Thus two independent reactions are

rx 1: $1.5C_2H_4 = C_3H_6$
rx 2: $2C_2H_4 = C_4H_8$
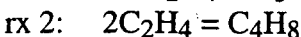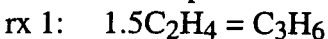
If the columns in the A matrix are put in another order, a different set of independent reactions will be obtained, but they will also be suitable.

5.49 How many degrees of freedom are there for the following systems, and how might they be chosen?

(a) $CuSO_4 \cdot 5H_2O(cr)$ in equilibrium with $CuSO_4(cr)$ and $H_2O(g)$.

(b) N_2O_4 in equilibrium with NO_2 in the gas phase.

(c) CO_2, CO, H_2O, and H_2 in chemical equilibrium in the gas phase.

(d) The system described in (c) is made up with stoichiometric amounts of CO and H_2.

SOLUTION

(a) $C = N_s - R = 3 - 1 = 2$

$$F = C - p + 2 = 2 - 3 + 2 = 1$$

Only the temperature or pressure may be fixed.

(b) $C = N_s - R = 2 - 1 = 1$

$$F = C - p + 2 = 1 - 1 + 2 = 2$$

Temperature and pressure may be fixed.

(c) $C = N_s - R = 4 - 1 = 3$

$$F = C - p + 2 = 3 - 1 + 2 = 4$$

Temperature, pressure, and two mole fractions may be fixed.

(d) $C = N_s - R - s = 4 - 1 - 2 = 1$

$$F = C - p + 2 = 1 - 1 + 2 = 2$$

Only temperature and pressure may be fixed if $n_c(C)/n_c(H)$ and $n_c(C)/n_c(O)$ are both fixed.

5.50   Graphite is in equilibrium with gaseous H_2O, CO, CO_2, H_2, and CH_4. How many degrees of freedom are there? What degrees of freedom might be chosen for an equilibrium calculation?

SOLUTION

$C = N_s - R = 6 - 3 = 3$

$F = C - p + 2 = 3 - 2 + 2 = 3$

The degrees of freedom chosen might be T, P, $n_c(H)/n_c(O)$.

5.51   A gaseous system contains CO, CO_2, H_2, H_2O, and C_6H_6 in chemical equilibrium. (a) How many components are there? (b) How many independent reactions? (c) How many degrees of freedom are there?

SOLUTION

(a)

	CO	CO₂	H₂	H₂O	C₆H₆
C	1	1	0	0	6
O	1	2	0	1	0
H	0	0	2	2	6

Subtract the first row from the second and divide the third row by 2 to obtain

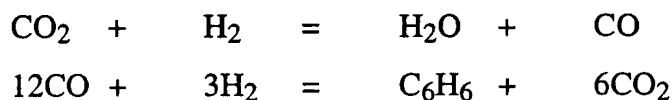| 1	1	0	0	6
0	1	0	1	-6
0	0	1	1	3

Subtract the second row from the first to obtain

$$
\begin{array}{ccccc}
1 & 0 & 0 & -1 & 12 \\
0 & 1 & 0 & 1 & -6 \\
0 & 0 & 1 & 1 & 3
\end{array}
$$

The rank of this matrix is 3, and so there are 3 independent components.

(b) The stoichiometric numbers of 2 independent reactions are given by the last 2 columns.

$$CO_2 \; + \; H_2 \; = \; H_2O \; + \; CO$$

$$12CO \; + \; 3H_2 \; = \; C_6H_6 \; + \; 6CO_2$$

If the species are arranged in a different order in the matrix, a different pair of independent equations will be obtained.

(c) $F = C - p + 2 = 3 - 1 + 2 = 4$

These four degrees of freedom can be taken to be T, P, $n_c(C)/n_c(O)$ and $n_c(C)/n_c(H)$. Alternatively, the mole fractions of 2 species and the temperature and pressure may be specified. The two equilibrium constant expressions provide two relations between 5 mole fractions, 4 of which are independent since $\Sigma y_i = 1$. If 2 mole fractions are known, the other two can be calculated from the two simultaneous equations.

5.52   0.696

5.53   0.0166

5.54   0.351 bar

    3.74 bar

5.56   0.803, 1.84

5.57 $K = (2\xi)^2(4 - 2\xi)^2/(1 - \xi)(3 - 2\xi)^3(P/P^o)^2$

5.58   26.3

5.59   (a) 3.81×10^{-2}, (b) 0.348

5.60   (a) 0.0788, (b) 0.0565

5.61   0.0273, 0.0861

5.62   0.465, 0.494, 0.041. The pressure has no effect.

5.65   (a) 16.69 kJ mol^{-1}, (b) 0.787 bar

5.66 1.84×10^6

5.67 30.1 bar

5.68 (a) 0.5000, 0.4363, 0.0637

(b) 0.5481, 0.3946, 0.0574

(c) When additional N_2 is added, the equilibrium shifts so that the mole fraction of N_2 is reduced below what it otherwise would have been.

5.69 (a) Yield of CH_4 will increase. (b) Yield of CH_4 will decrease. (c) Mole fraction CH_4 computed without including N_2 will increase.

5.70 (a) No, (b) 0.286

5.71 (a) 0.0050 bar, (b) 0.0220 bar

5.73 225.1 kJ mol^{-1}

5.74 (a) 0.1852, 0.3775, 0.6284, (b) 60.7 kJ mol^{-1}, (c) 0.320, (d) 0.371

5.76 $K_P = 0.0024$, $K_c = 4.15$

5.77 - 5.082, 0.070 J K^{-1} mol^{-1}

5.78 98.752, 113.526, 122.521 J K^{-1} mol^{-1}

5.79 (a) - 33.0, (b) - 77.4 J K^{-1} mol^{-1}

5.80 56.6 J K^{-1} mol^{-1}

5.81 Hydrogen dissolves as atoms.

5.82 Fe_2O_3

5.83 7.56 bar

5.84 16.06 kJ mol^{-}

5.85 (a) 6.66 x 10^{-3}, (b) 12.1 kJ mol^{-}

5.86 (a) 57.3 kJ mol^{-1}, (b) 5.82 kJ mol^{-1}, (c) 154.7 J K^{-1} mol^{-}

5.87 - 14.8 kJ mol^{-1}

5.88 $K_1 = 2.5$, $K_2 = 0.61$, $K_3 = 0.35$, $y_{CH_4} = 0.27$, $y_{CO} = 0.27$, $y_{H_2O} = 0.46$

5.89 Two, for example, $2C_2H_6 = 2CH_4 + C_2H_4$

5.91 (a) $F = N - R - p + 2 = 3 - 2 - 1 + 2 = 2$. T and P can be chosen.

(b) $F = 3 - 2 - 1 + 2 = 2$. T and P can be chosen.