Chemistry 192
Recitation Session Questions
March 26, 2018
Solutions

1. At 298 K the equilibrium constant for the gas-phase reaction

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

is $K_P = 0.323$ and the enthalpies of formation of N_2O_4 and NO_2 are respectively $\Delta_{f,m}H^\circ(N_2O_4) = 9.16$ kJ mol^{-1} and $\Delta_{f,m}H^\circ(NO_2) = 33.2$ kJ mol^{-1}. Calculate K_P at 350 K.
Answer:

$$\Delta_{r,m}H^\circ = 2\Delta_{f,m}H^\circ(NO_{2(g)}) - \Delta_{f,m}H^\circ(N_2O_{4(g)}) = 2(33.2\text{ kJ mol}^{-1}) - 9.16\text{ kJ mol}^{-1} = 57.2\text{ kJ mol}^{-1}$$

$$\ln\frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{K_p(350)}{0.323} = \frac{57200\text{ J mol}^{-1}}{8.3144\text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298\text{ K}} - \frac{1}{350\text{ K}}\right)$$

$$K_P(350) = 9.97$$

2.

Substance	$\Delta_{f,m}H^\circ$ kJ mol^{-1}	$\Delta_{f,m}G^\circ$ kJ mol^{-1}
$PbSO_{4(s)}$	-920	-813.3
$Pb^{2+}_{(aq)}$	0.92	-24.2
$SO^{2-}_{4(aq)}$	-909.3	-744.5

Given the table of thermodynamic data above valid at 298 K, calculate the temperature at which the solubility of lead sulfate in water is 2.0×10^{-4} M.
Answer:

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$K_{sp}(T) = (2.0 \times 10^{-4})^2 = 4.0 \times 10^{-8}$$

$$\Delta_{r,m}H^\circ = \Delta_{f,m}H^\circ(Pb^{2+}_{(aq)}) + \Delta_{f,m}H^\circ(SO^{2-}_{4(aq)}) - \Delta_{f,m}H^\circ(PbSO_{4(s)})$$

$$= 0.92 \text{ kJ mol}^{-1} - 909.3 \text{ kJ mol}^{-1} + 920 \text{ kJ mol}^{-1} = 17.9 \text{ kJ mol}^{-1}$$

$$\Delta_{r,m}G^\circ = \Delta_{f,m}G^\circ(\mathrm{Pb}^{2+}_{(aq)}) + \Delta_{f,m}G^\circ(\mathrm{SO}^{2-}_{4(aq)}) - \Delta_{f,m}G^\circ(\mathrm{PbSO}_{4(s)})$$

$$= -24.4 \text{ kJ mol}^{-1} - 744.5 \text{ kJ mol}^{-1} + 813.3 \text{ kJ mol}^{-1} = 44.6 \text{ kJ mol}^{-1}$$

$$K_{sp}(298) = \exp\left(-\frac{44600 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right) = 1.5 \times 10^{-8}$$

$$\ln \frac{4.0 \times 10^{-8}}{1.5 \times 10^{-8}} = \frac{17900 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298 \text{ K}} - \frac{1}{T}\right) \quad T = 345 \text{ K}$$

3. At 298 K the pH of a magnesium hydroxide solution is 10.51 and at 370 K the pH of $\mathrm{Mg(OH)_2}$ in water is 10.49. Calculate $\Delta_{r,m}H^\circ$, $\Delta_{r,m}G^\circ$ and $\Delta_{r,m}S^\circ$ for the reaction

$$\mathrm{Mg(OH)}_{2(s)} \longrightarrow \mathrm{Mg}^{2+}_{2(aq)} + 2\mathrm{OH}^-_{(aq)}$$

Answer:
At 298 K

$$\text{pOH} = 14.00 - \text{pH} = 3.49 \quad [\mathrm{OH^-}] = 3.2 \times 10^{-4} \text{ M}$$

$$K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (1.6 \times 10^{-4})(3.2 \times 10^{-4})^2 = 1.7 \times 10^{-11}$$

At 370 K

$$\text{pOH} = 14.00 - \text{pH} = 3.51 \quad [\mathrm{OH^-}] = 3.1 \times 10^{-4} \text{ M}$$

$$K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (1.5 \times 10^{-4})(3.1 \times 10^{-4})^2 = 1.5 \times 10^{-11}$$

$$\ln \frac{1.5 \times 10^{-11}}{1.7 \times 10^{-11}} = \frac{\Delta_{r,m}H^\circ}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298 \text{ K}} - \frac{1}{370 \text{ K}}\right) \quad \Delta_{r,m}H^\circ = -1590 \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^\circ = -RT\ln K = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})\ln(1.7 \times 10^{-11}) = 61400 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^\circ = \frac{\Delta_{r,m}H^\circ - \Delta_{r,m}G^\circ}{T} = \frac{-1590 \text{ J mol}^{-1} - 61400 \text{ J mol}^{-1}}{298 \text{ K}} = -211 \text{ J mol}^{-1}\text{K}^{-1}$$