Worksheet 11 – Answers to Critical Thinking Questions

The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

Model 1: The Equilibrium Constant

1. \[ K_c (A) = \frac{[N_2O_4(g)]}{[NO_2(g)]^2} \quad K_c (B) = \frac{[N_2O_4(g)]^{1/2}}{[NO_2(g)]} \]
   \[ K_c (C) = \frac{[NO_2(g)]^2}{[N_2O_4(g)]} \quad K_c (D) = \frac{[NO_2(g)]}{[N_2O_4(g)]^{1/2}} \]

2. (a) \[ K_c (B) = \sqrt{K_c (A)} \]
   (b) \[ K_c (A) = 1 / K_c (C) \]

3. \[ K_c (A) = 0.078, \quad K_c (B) = 0.280, \quad K_c (C) = 12.8. \]

Model 2: The Reaction Quotient

1. The reaction will shift to the right to decrease [NO_2(g)].
2. The reaction will shift to the left to increase [NO_2(g)].
3. (a) \[ [NO_2(g)] = 2.00 \text{ M and } [N_2O_4] = 0.20 \text{ M: } \frac{Q_c}{Q_c} = 0.050 \]
   (b) \[ [NO_2(g)] = 1.00 \text{ M and } [N_2O_4] = 0.20 \text{ M: } \frac{Q_c}{Q_c} = 0.20. \]
4. (a) If \( \frac{Q_c}{Q_c} < K_c \), the reaction will shift to the right.
   (b) If \( \frac{Q_c}{Q_c} > K_c \), the reaction will shift to the left.
5. For the reaction, \( \text{AgI(s)} \rightleftharpoons \text{Ag}^+(aq) + \Gamma(aq) \), the equilibrium constant, \( K_p = [\text{Ag}^+(aq)][\Gamma(aq)]. \)
   (a) From the reaction, in water [\text{Ag}^+(aq)] = [\Gamma(aq)]. Hence,
   \[ K_p = [\text{Ag}^+(aq)][\Gamma(aq)] = [\text{Ag}^+(aq)]^2 = 1.5 \times 10^{-16} \]
   \[ [\text{Ag}^+(aq)] = 1.2 \times 10^{-8} \text{ M and } [\Gamma(aq)] = 1.2 \times 10^{-8} \text{ M} \]
   (b) From (a), the solubility of AgI(s) is very low. When it is added to a solution already containing \( \Gamma(aq) \), its concentration will not be changed greatly. Hence,
   \[ [\Gamma(aq)]_{\text{equilibrium}} \approx [\Gamma(aq)] = 0.0050 \text{ M}. \]
   Using this value,
   \[ K_p = [\text{Ag}^+(aq)] \times 0.0050 = 1.5 \times 10^{-16} \]
   \[ [\text{Ag}^+(aq)] = 3.0 \times 10^{-14} \text{ M} \]
   Note that the presence of the common ion, \( \Gamma \), greatly reduces the solubility of AgI(s).
Model 3: Ellingham Diagrams

1. \[ K_p (A) = \frac{1}{(p_{O_2})^{1/2}} \quad K_p (B) = \frac{p_{CO}}{(p_{O_2})^{1/2}} \quad K_p (C) = p_{CO} \]

2. \[ K_p (A) = \ln \left[ \frac{1}{(p_{O_2})^{1/2}} \right] = -\frac{1}{2} \ln [p_{O_2}] \quad K_p (B) = \ln \left[ \frac{p_{CO}}{(p_{O_2})^{1/2}} \right] = \ln [p_{CO}] - \frac{1}{2} \ln [p_{O_2}] \]

3. \[ K_p (C) = K_p (B) / K_p (A) \quad \text{or} \quad \ln K_p (C) = \ln K_p (B) - \ln K_p (A) \]

4. As \( K_p (A) > K_p (B) \), \( \ln K_p (C) \) is negative and so \( K_p < 1 \). The extraction reaction is not favourable.

5. As \( K_p (A) < K_p (B) \), \( \ln K_p (C) \) is positive and so \( K_p > 1 \). The extraction reaction is favourable.

6. As \( K_p (A) = K_p (B) \), \( \ln K_p (C) \) is zero and so \( K_p = 1 \). The extraction reaction is an equilibrium containing a 50 : 50 mixture of reactants and products.

7. (i) \( 2C(s) + O_2(g) \Rightarrow 2CO(g) \)

   (ii) \( C(s) + O_2(g) \Rightarrow CO_2(g) \)

8. Using \( \Delta_{rxn}H^o = \Sigma m \Delta H^o \text{(products)} - \Sigma n \Delta H^o \text{(reactants)} \),

   \[ \Delta_{comb}H^o \text{ (i)} = [(2 \times -111) - (0)] \text{ kJ mol}^{-1} = -222 \text{ kJ mol}^{-1} \]
   \[ \Delta_{comb}H^o \text{ (ii)} = [(-394) - (0)] \text{ kJ mol}^{-1} = -394 \text{ kJ mol}^{-1} \]

Using \( \Delta_{rxn}S^o = \Sigma m S^o \text{(products)} - \Sigma n S^o \text{(reactants)} \),

\[ \Delta_{comb}S^o \text{ (i)} = [(2 \times 198) - (2 \times 6 + 205)] \text{ J K}^{-1} \text{ mol}^{-1} = +179 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ \Delta_{comb}S^o \text{ (ii)} = [(214) - (6 + 205)] \text{ J K}^{-1} \text{ mol}^{-1} = +3 \text{ J K}^{-1} \text{ mol}^{-1} \]

9. Using \( \Delta_{rxn}G^o = -RT \ln K_p \) and \( \Delta_{rxn}G^o = \Delta_{rxn}H^o - T \Delta_{rxn}S^o \), the value of \( \ln K_p \) for each reaction can be calculated at a number of temperatures.

   For example, at 400 K:

   (i) \[ \Delta_{rxn}G^o = \Delta_{rxn}H^o - T \Delta_{rxn}S^o = (-222 \times 10^3 \text{ J mol}^{-1}) - (400 \text{ K}) \times (+179 \text{ J K}^{-1} \text{ mol}^{-1}) \]
   \[ = -294000 \text{ J mol}^{-1} \]
   \[ \ln K_p = \Delta_{rxn}G^o / (-RT) = (-294000 \text{ J mol}^{-1}) / ((8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})) = 88 \]

   (ii) \[ \Delta_{rxn}G^o = \Delta_{rxn}H^o - T \Delta_{rxn}S^o = (-394 \times 10^3 \text{ J mol}^{-1}) - (400 \text{ K}) \times (+3 \text{ J K}^{-1} \text{ mol}^{-1}) \]
   \[ = -395000 \text{ J mol}^{-1} \]
   \[ \ln K_p = \Delta_{rxn}G^o / (-RT) = (-395000 \text{ J mol}^{-1}) / ((8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})) = 120 \]

The table below shows results for both reactions at several temperatures.

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<th>( \ln K ) (ii)</th>
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9. From the graph, the crossover point is at ~950 K. CO is the favoured product above this value.

The temperature at which both reactions are equally favoured occurs when $\Delta_{\text{rxn}}G^\circ (i) = \Delta_{\text{rxn}}G^\circ (ii)$:

$$\Delta_{\text{rxn}}H^o (i) - T\Delta_{\text{rxn}}S^o (i) = \Delta_{\text{rxn}}H^o (ii) - T\Delta_{\text{rxn}}S^o (ii)$$

$$(-222 \times 10^3 \text{ J mol}^{-1}) - T \times (+179 \text{ J K}^{-1} \text{ mol}^{-1}) = (-394 \times 10^3 \text{ J mol}^{-1}) - T \times (+4 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$T = 977 \text{ K}$$

The reaction favours CO$_2$ at lower temperatures as $\ln K (ii) > \ln K (i)$ and favours CO at higher temperatures as $\ln K (i) > \ln K (ii)$. Hence, CO is favoured when $T > 977 \text{ K}$. 