CHAPTER 8

Practice Exercises

8.1 28 J K^{-1}

8.3 $3.94 \times 10^2 \text{ kJ mol}^{-1}$

8.5 $2.5H_2(g) + \frac{2.5}{2}O_2(g) \square\ 2.5H_2O(g)$ $\Delta_r H\ = (-241.8 \text{ kJ}) \times 2.5 = -604.5 \text{ kJ}$

8.7 $Na(s) + \frac{1}{2}H_2(g) + C(s) + \frac{3}{2}O_2(g)\ \square\ NaHCO_3(s)$ $\square_f H^\oplus = -947.7 \text{ kJ mol}^{-1}$

8.9   Heat produced $=$ $507 \text{ mole} \times 5450.5 \text{ kJ mol}^{-1}$ $=$ $2.76 \times 10^6 \text{ kJ}$

8.11   (a) ΔS should be negative since there are fewer gaseous molecules on the right hand side of the equation than on the left hand side of the equation.
        (b) ΔS should be negative since there are fewer gaseous molecules on the right hand side of the equation than on the left hand side of the equation.

8.13   (a) $\Delta_r S^\oplus = -229 \text{ J mol}^{-1} \text{ K}^{-1}$
        (b) $\Delta_r S^\oplus = -120.9 \text{ J mol}^{-1} \text{ K}^{-1}$

8.15   (a) $\Delta_r G^\oplus = -69.70 \text{ kJ}$
        (b) $\Delta_r G^\oplus = -120.1 \text{ kJ}$

8.17 $T_b = \dfrac{60.7 \times 10^3 \text{ J mol}^{-1}}{99 \text{ J mol}^{-1} \text{ K}^{-1}} = 6.1 \times 10^2 \text{ K}$

Review Questions

8.1   The word 'thermodynamics' comes from the Greek words for 'heat' and 'powerful'.

8.3   An isolated system cannot exchange either mass or energy with its surroundings, whereas a closed system can exchange energy with its surroundings.

8.5   The energy depends directly on the specific heat, so the material with the higher specific heat requires the higher energy input for a given rise in temperature.

8.7   A substance with a high specific heat needs more energy to undergo a particular temperature rise. A substance with a high specific heat has a greater capacity to hold   energy and not undergo an increase in T. Therefore, a substance with a low specific heat capacity experiences the larger increase in temperature when it absorbs 100 J.

8.9   Since the amount of heat is related to the change in temperature by the equation:

$$q = C\Delta T$$

if the temperature increases by a factor of 10, the amount of heat must also increase by a factor of 10.

8.11   If object A has twice the specific heat and twice the mass of object B, and the same amount of heat is applied to both objects, the temperature change of A will be one quarter the temperature change in B.

8.13 $w = -p\Delta V$

8.15 $\Delta U = U_{final} - U_{initial}$

8.17   A state function is a thermodynamic quantity whose value is determined only by the state of the system currently and is not determined by the prior condition or history of the system. A change in a state function is the same regardless of the path that is used to arrive at the final state from the initial state. That is, changes in state function quantities are path–independent. In the statement of the first law, only ΔU is a state function; q and w are not.

8.19 $\Delta H = \Delta U + p\Delta V$

8.21 $\Delta U = q + w = 28\ J - 45\ J = -17\ J$

8.23 $H = U + pV$

8.25 $\Delta H < 0$ for an exothermic change.

8.27   A coefficient signifies the actual number of moles involved.

8.29 ΔH is a state function.

8.31 $\Delta_r H^\circ = $ [Sum of $\Delta_f H^\circ$ of all the products] – [Sum of $\Delta_f H^\circ$ of all the reactants]

8.33   Entropy is a measure of the number of equivalent ways in which energy can be distributed throughout a system.

8.35   The statistical probability of a system in a given state, relative to all the other states, is the same regardless of how the system was formed.

8.37   The entropy of the universe increases when a spontaneous event occurs.

8.39   A spontaneous event occurs when ΔG is negative. Since $\Delta G = \Delta H - T\Delta S$, even if the entropy is negative for a process, the enthalpy, ΔH may be sufficiently negative at a given temperature to allow the overall change in free energy to be negative.

8.41   The entropy of a mixture must be higher than that of two separate pure materials because the mixture is guaranteed to have a higher degree of disorder. A mixture is more disordered than either of its two separate components. Only a pure substance can have an entropy of zero and then only at 0 K.

8.43   No, glass is an amorphous solid that is a mixture of different substances, so it is not a perfect crystalline solid and does not have an entropy value of 0 at 0 K.

8.45   Spontaneous: a ball rolling down a hill; water draining out of a sink; a coin falling to the floor after it has been dropped; sugar dissolving in a cup of coffee; lemonade going flat after taking the top off the bottle.
        Nonspontaneous: boiling water to make a cup of coffee; lifting the groceries up the steps; squeezing toothpaste out of the tube; tying your shoelace; peeling a banana.

8.47   The ammonium and nitrate atoms are in a highly ordered geometry in the crystalline NH_4NO_3 sample. When NH_4NO_3 dissolves, the NH_4^+ and NO_3^- ions become randomly dispersed throughout the solvent. The increase in disorder that accompanies the dissolution of the solid is responsible for the process being favourable, or spontaneous, in spite of the fact that the enthalpy change is endothermic.

8.49   (a)   A change is spontaneous at all temperatures only if ΔH is negative and ΔS is positive.
        (b)   A change is spontaneous at low temperatures but not at high temperatures only if ΔH is negative and ΔS is negative.
        (c)   A change is spontaneous at high temperatures but not at low temperatures only if ΔH is positive and ΔS is positive.

8.51   By itself, it is not possible for a reaction to proceed in reverse, but if the reaction is coupled to another process which can put energy into the reaction to reverse it, it can occur.

8.53   A thermodynamically reversible process is one in which the driving force of the process is nearly completely balanced by an opposing force. This situation is somewhat esoteric, since no process can be proceed in a completely reversible manner. Nevertheless, the closer one comes to reversibility, the more efficient the system becomes as a source of the maximum amount of useful work that can be achieved from the process.

8.55   A truly reversible process would take forever to complete. Thus, if we can observe an event happening, it cannot be a truly reversible one.

Review Problems

8.57 $\Delta U = q + w$
        $-1455 \text{ J} = 812 \text{ J} + w$
        $w = -2267 \text{ J}$

8.59 $q = cm\Delta T$

        $= 4.184 \text{ J g}^{-1} \text{ K}^{-1} \times (1.0 \times 10^3 \text{ g}) \times (99 - 25) \text{ K}$
        $= 3.1 \times 10^5 \text{ J} = 3.1 \times 10^2 \text{ kJ}$

8.61 $(22 + 21.5) \, ^{\circ}\text{C} = 43 \, ^{\circ}\text{C}$

8.63   (a) $q = cm\Delta T$

= 4.184 J g^{-1} K^{-1} × 200 g × (26.50 – 25.00) K
= 1.26 × 10^3 J

(b)   As the water gained 1.26 × 10^3 J, the metal must have lost the same amount of heat, namely 1.26 × 10^3 J.

(c) $q = cm\Delta T$, therefore

$$m = \frac{q}{c\Delta T} = \frac{1.26 \times 10^3 \text{ J}}{0.387 \text{ J g}^{-1} \text{ K}^{-1} \times (120 - 26.50)\text{ K}} = 34.8 \text{ g}$$

8.65 $q = cm\Delta T$

= 4.18 J g^{-1} K^{-1} × 4.54 × 10^3 g × (58.65 – 60.25) K
= – 3.04 × 10^4 J = –30.4 kJ
The negative sign shows that heat left the system.

8.67 $\Delta_r H = \dfrac{-3.8 \times 10^3 \text{ J}}{0.072 \text{ mol}} = -53 \text{ kJ mol}^{-1}$

8.69   (a) $q = C\Delta T$ = 97.1 kJ K^{-1} × (27.282 – 25.000) K = 2.22 × 10^2 kJ = 2.22 × 10^5 J

(b)   The rise in temperature means that the reaction is exothermic. 1.00 mole of propane was burned, and constant pressure conditions apply, so $q = \Delta H$. Therefore, on a mole basis:

$$\Delta_r H = \frac{-2.22 \times 10^2 \text{ kJ}}{1.00 \text{ mol}} = -2.22 \times 10^2 \text{ kJ mol}^{-1}$$

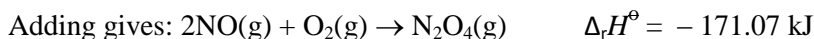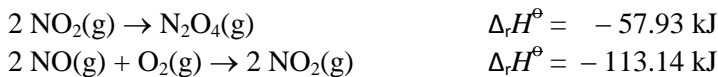8.71   (a)   Multiply the given equation and the value of $\Delta_r H^\ominus$ by the fraction $\frac{2}{3}$.

2 CO(g) + O$_2$(g) → 2 CO$_2$(g), $\Delta_r H^\ominus$ = – 566 kJ
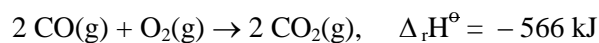
(b)   To determine $\Delta rH^\ominus$ for the formation of 1 mole of CO$_2$, multiply the original $\Delta_r H$ by $\frac{1}{3}$, which gives – 283 kJ mol^{-1}.
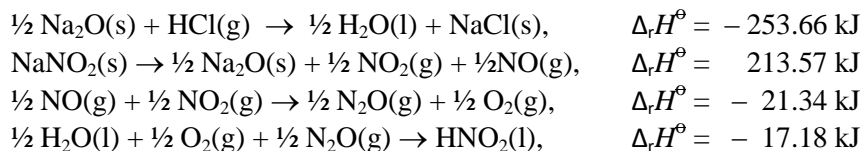
8.73   4Al(s) + 2Fe$_2$O$_3$(s) → 2Al$_2$O$_3$(s) + 4Fe(s) $\Delta_r H^\ominus$ = – 1708 kJ
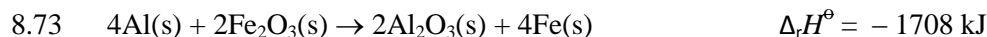
8.75   6.54 g of Mg, $\Delta_r H^\ominus$ = –602 kJ mol^{-1} × 2.69 × 10^{-1} mol = –162 kJ.

8.77   Since NO$_2$ does not appear in the desired overall reaction, the two steps need to be manipulated to remove it by cancellation. Add the second equation to the reverse of the first, remembering to change the sign of the first equation:

2 NO$_2$(g) → N$_2$O$_4$(g) $\Delta_r H^\ominus$ = – 57.93 kJ
2 NO(g) + O$_2$(g) → 2 NO$_2$(g) $\Delta_r H^\ominus$ = – 113.14 kJ

Adding gives: 2NO(g) + O$_2$(g) → N$_2$O$_4$(g) $\Delta_r H^\ominus$ = – 171.07 kJ

8.79   If we label the four given thermochemical equations consecutively, 1, 2, 3, and 4, then the sum is made in the following way: divide equation 3 by two and reverse all the other equations (1, 2, and 4), while also dividing each by two:
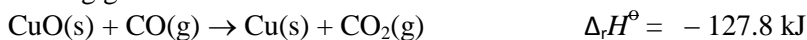
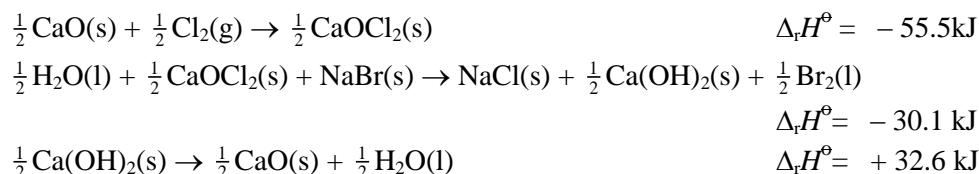½ $Na_2O(s)$ + $HCl(g)$ → ½ $H_2O(l)$ + $NaCl(s)$, $\Delta_r H^\circ$ = − 253.66 kJ
$NaNO_2(s)$ → ½ $Na_2O(s)$ + ½ $NO_2(g)$ + ½$NO(g)$, $\Delta_r H^\circ$ =   213.57 kJ
½ $NO(g)$ + ½ $NO_2(g)$ → ½ $N_2O(g)$ + ½ $O_2(g)$, $\Delta_r H^\circ$ = − 21.34 kJ
½ $H_2O(l)$ + ½ $O_2(g)$ + ½ $N_2O(g)$ → $HNO_2(l)$, $\Delta_r H^\circ$ = − 17.18 kJ

Adding gives:
$HCl(g)$ + $NaNO_2(s)$ → $NaCl(s)$ + $HNO_2(l)$ $\Delta_r H^\circ$ = − 78.61 kJ

8.81   Reverse the second equation and then divide each by two before adding:

$CO(g)$ + ½ $O_2(g)$ → $CO_2(g)$ $\Delta_r H^\circ$ = − 283.0 kJ
$CuO(s)$ → $Cu(s)$ + ½ $O_2(g)$ $\Delta_r H^\circ$ =   155.2 kJ

Adding gives:
$CuO(s)$ + $CO(g)$ → $Cu(s)$ + $CO_2(g)$ $\Delta_r H^\circ$ = − 127.8 kJ

8.83   Multiply all three equations by ½ and add them :

$\frac{1}{2} CaO(s)$ + $\frac{1}{2} Cl_2(g)$ → $\frac{1}{2} CaOCl_2(s)$ $\Delta_r H^\circ$ = − 55.5kJ
$\frac{1}{2} H_2O(l)$ + $\frac{1}{2} CaOCl_2(s)$ + $NaBr(s)$ → $NaCl(s)$ + $\frac{1}{2} Ca(OH)_2(s)$ + $\frac{1}{2} Br_2(l)$
                                            $\Delta_r H^\circ$ = − 30.1 kJ
$\frac{1}{2} Ca(OH)_2(s)$ → $\frac{1}{2} CaO(s)$ + $\frac{1}{2} H_2O(l)$ $\Delta_r H^\circ$ = + 32.6 kJ

Adding gives:
$\frac{1}{2} Cl_2(g)$ + $NaBr(s)$ → $NaCl(s)$ + $\frac{1}{2} Br_2(l)$ $\Delta_r H^\circ$ = − 53.0 kJ
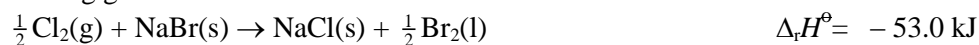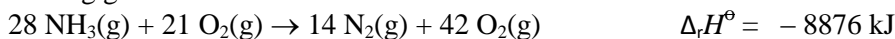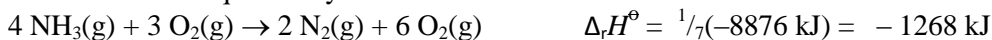
8.85   We need to eliminate NO_2 from the two given equations by multiplying the first equation by three and the second equation by two and adding :
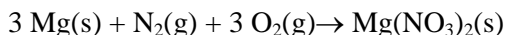
12 $NH_3(g)$ + 21 $O_2(g)$ → 12 $NO_2(g)$ + 18 $H_2O(g)$ $\Delta_r H^\circ$ = − 3396 kJ
12 $NO_2(g)$ + 16 $NH_3(g)$ → 14 $N_2(g)$ + 24 $H_2O(g)$ $\Delta_r H^\circ$ = − 5480 kJ

Adding gives:
28 $NH_3(g)$ + 21 $O_2(g)$ → 14 $N_2(g)$ + 42 $O_2(g)$ $\Delta_r H^\circ$ = − 8876 kJ
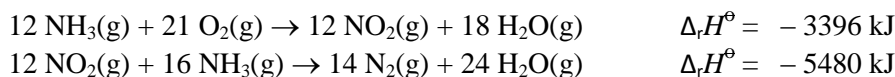
Now divide this equation by 7 to obtain:
4 $NH_3(g)$ + 3 $O_2(g)$ → 2 $N_2(g)$ + 6 $O_2(g)$ $\Delta_r H^\circ$ = $^1/_7$(−8876 kJ) = − 1268 kJ

8.87   The equation we need is:

$$3\ Mg(s) + N_2(g) + 3\ O_2(g) \rightarrow Mg(NO_3)_2(s)$$

Reverse all three reactions and multiply the third equation by three:

$Mg_3N_2(s) + 6\ MgO(s) \rightarrow 8\ Mg(s) + Mg(NO_3)_2(s)$	$\Delta_r H^\ominus =\ \ + 3884\ kJ$
$3\ Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$	$\Delta_r H^\ominus =\ \ - 463\ kJ$
$6\ Mg(s) + 3\ O_2(g) \rightarrow Mg(NO_3)_2(s)$	$\Delta_r H^\ominus =\ \ - 3609\ kJ$

Adding gives:

$Mg(s) + N_2(g) + 3\ O_2(g) \rightarrow Mg(NO_3)_2(s)$	$\Delta_r H^\ominus =\ \ - 188\ kJ$
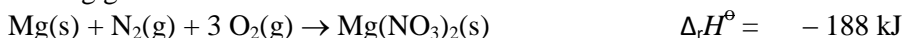
8.89 Only (b) and (f) are consistent with $\Delta_f H^\ominus$ since 1 mole of product is formed from the elements in their respective standard states.

8.91   (a) $\Delta_r H^\ominus = \Delta_f H^\ominus [O_2(g)] + 2\Delta_f H^\ominus [H_2O(l)] - 2\Delta_f H^\ominus [H_2O_2(l)]$

$$\Delta_r H^\ominus = 0\ kJ\ mol^{-1} + 2\ mol \times (-285.9\ kJ\ mol^{-1}) - 2\ mol \times (-187.6\ kJ\ mol^{-1})$$
$$=\ -196.6\ kJ$$

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus [H_2O(l)] + \Delta_f H^\ominus [NaCl(s)] - \Delta_f H^\ominus [HCl(g)] - \Delta_f H^\ominus [NaOH(s)]$
$$= 1\ mol \times (-285.9\ kJ\ mol^{-1}) + 1\ mol \times (-411.0\ kJ\ mol^{-1})$$
$$-\ 1\ mol \times (-92.30\ kJ\ mol^{-1}) - 1\ mol \times (-426.8\ kJ\ mol^{-1})$$
$$=\ -177.8\ kJ$$

(c) $\Delta_r H^\ominus = \Delta_f H^\ominus [HCl(g)] + \Delta_f H^\ominus [CH_3Cl(g)] - \Delta_f H^\ominus [CH_4(g)] - \Delta_f H^\ominus [Cl_2(g)]$
$$= 1\ mol \times (-92.30\ kJ\ mol^{-1}) + 1\ mol \times (-82.0\ kJ\ mol^{-1})$$
$$-\ 1\ mol \times (-74.848\ kJ\ mol^{-1}) - 1\ mol \times (0.0\ kJ\ mol^{-1})$$
$$=\ -99.5\ kJ$$

(d) $\Delta_r H^\ominus = \Delta_f H^\ominus [H_2O(l)] + \Delta_f H^\ominus [CO(NH_2)_2(s)] - 2\Delta_f H^\ominus [NH_3(g)] -$
$$\Delta_f H^\ominus [CO_2(g)]$$
$$= 1\ mol \times (-285.9\ kJ\ mol^{-1}) + 1\ mol \times (-333.19\ kJ\ mol^{-1})$$
$$-\ 2\ mol \times (-46.19\ kJ\ mol^{-1}) - 1\ mol \times (-393.5\ kJ\ mol^{-1})$$
$$=\ -133.2\ kJ$$

8.93 $C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O$ $\Delta H^\ominus = -5.65 \times 10^3\ kJ\ mol^{-1}$
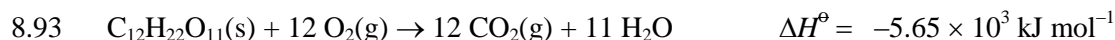
$\Delta_r H^\ominus = \square\square\square\square$ sum$(\Delta_f H^\ominus(products)) -$ sum$(\Delta_f H^\ominus(reactants))$
$= [12\ \Delta_f H^\ominus (CO_2(g)) + 11\ \Delta_f H^\ominus (H_2O)] - [\Delta_f H^\ominus(C_{12}H_{22}O_{11}(s)) + 12\Delta_f H^\ominus (O_2(g))]$

Rearranging and noting that $\Delta_f H^\ominus O_2(g) = 0$, we obtain:
$\Delta_f H^\ominus [C_{12}H_{22}O_{11}(s)] = 12\Delta_f H^\ominus (CO_2(g)) + 11\Delta_f H^\ominus(H_2O(l)) - \Delta_r H^\ominus$
$= 12\ mol \times (-393\ kJ\ mol^{-1}) + 11\ mol \times (-285.9\ kJ\ mol^{-1}) - 1\ mol \times (-5.65 \times 10^3\ kJ)$
$=\ -2.22 \times 10^3\ kJ\ mol^{-1}$

8.95   The atomisation enthalpy of $NH_3(g)$ is the enthalpy change for the reaction:

$NH_3(g) \rightarrow N(g) + 3H(g)$

This process involves breaking 3 N—H bonds, each of which has an average bond enthalpy of 388 kJ mol^{-1}. Therefore, the atomisation enthalpy, $\Delta_{at}H^{\ominus}$ of NH_3 is given by: $\Delta_{at}H^{\ominus}$ (NH_3,g) = 3 × 388 kJ mol^{-1} = 1164 kJ mol^{-1}

8.97   C=C bond enthalpy = 2252.62 kJ mol^{-1} – 1648 kJ mol^{-1} = 605 kJ mol^{-1}

8.99   average H—S bond enthalpy = 732.91 kJ mol^{-1} /2 = 366 kJ mol^{-1}

8.101   The percentage difference between this value and the measured value of – 718.4 kJ mol^{-1} is approximately 0.6%

8.103 ΔfHo ($CCl4(g)$)
= ΔfHo (2) + ΔfHo (3) + ΔrHo(4)]
= [716.67 + 485.88 + –1352] kJ mol–1
= –149 kJ mol–1

8.105   Not necessarily. The carbon–carbon bonds in benzene have a formal bond order of 1.5. As tabulated values of carbon–carbon bonds generally only refer to either single or double bonds, it is likely that use of these values will not give an accurate answer.

8.107   (a)   negative – since the number of moles of gaseous material decreases.
         (b)   negative – since the number of moles of gaseous material decreases.
         (c)   negative – since the number of moles of gas decreases.
         (d)   positive – since a gas appears where there formerly was none.
         (e)   positive – since the number of moles of gaseous material increases.
         (f)   negative – since the number of moles of gaseous material decreases.
         (g)   negative – since the number of moles of gas decreases.
         (h)   negative – since a solid is the only product.

8.109   (a) $\Delta_fS^{\ominus} = -52.8$ J K^{-1} or –52.8 J mol^{-1} K^{-1}
         (b) $\Delta_fS^{\ominus} = -74.0$ J K^{-1} or –74.0 J mol^{-1} K^{-1}
         (c) $\Delta_fS^{\ominus} = -90.1$ J K^{-1} or –90.1 J mol^{-1} K^{-1}
         (d) $\Delta_fS^{\ominus} = -318$ J K^{-1} or –318 J mol^{-1} K^{-1}
         (e) $\Delta_fS^{\ominus} = -868.8$ J K^{-1} or –868.8 J mol^{-1} K^{-1}
         (f) $\Delta_fS^{\ominus} = -313.1$ J K^{-1} or –313.1 J mol^{-1} K^{-1}
         (g) $\Delta_fS^{\ominus} = -261.7$ J K^{-1} or –261.7 J mol^{-1} K^{-1}
         (h) $\Delta_fS^{\ominus} = -298$ J K^{-1} or –298 J mol^{-1} K^{-1}
         (i) $\Delta_fS^{\ominus} = -469$ J K^{-1} or –469 J mol^{-1} K^{-1}
         (j) $\Delta_fS^{\ominus} = -373.9$ J K^{-1} or –373.9 J mol^{-1} K^{-1}

8.111 $\Delta_rS^{\ominus} = \{S^{\ominus} [CH_3COOH(l)] + S^{\ominus}[H_2O(l)]\} - \{S^{\ominus} [C_2H_5OH(l)] + S^{\ominus}[O_2(g)]\}$

= {1 mol × (160 J mol^{-1} K^{-1}) + 1 mol × (69.96 J mol^{-1} K^{-1})}
                         – {1 mol × (161 J mol^{-1} K^{-1}) + 1 mol × (205.0 J mol^{-1} K^{-1})}
= –136 J K^{-1}

8.113   (a) $\Delta_r G^\ominus = -82.3$ kJ
      (b) $\Delta_r G^\ominus = -8.8$ kJ
      (c) $\Delta_r G^\ominus = +70.7$ kJ
      (d) $\Delta_r G^\ominus = -14.3$ kJ
      (e) $\Delta_r G^\ominus = -715.3$ kJ
      (f) $\Delta_r G^\ominus = -184.1$ kJ
      (g) $\Delta_r G^\ominus = 0.5$ kJ
      (h) $\Delta_r G^\ominus = 8.6$ kJ
      (i) $\Delta_r G^\ominus = -530.8$ kJ
      (j) $\Delta_r G^\ominus = -91.9$ kJ

8.115 $\Delta_r G^\ominus = \quad +0.16$ kJ

8.117   1,299.8 kJ

8.119 $T = \dfrac{\Delta H}{\Delta S} = \dfrac{31.4 \times 10^3 \text{ J mol}^{-1}}{94.2 \text{ J mol}^{-1} \text{ K}^{-1}} = 333$ K

8.121 $\Delta S = \dfrac{\Delta H}{T} = \dfrac{31.9 \times 10^3 \text{ J mol}^{-1}}{329.2 \text{ K}} = 96.9 \text{ J mol}^{-1} \text{ K}^{-1}$

8.123   (a) $\Delta_r G^\ominus = -84.5$ kJ

          Therefore this reaction is spontaneous under standard conditions at 25 $^\circ$C

      (b) $\Delta_r G^\ominus = -144$ kJ

          Therefore this reaction is spontaneous under standard conditions at 25 $^\circ$C

      (c) $\Delta_r G^\ominus = 835.4$ kJ

          Therefore this reaction is not spontaneous under standard conditions at 25 $^\circ$C

      (d) $\Delta_r G^\ominus = 68.7$ kJ

          Therefore this reaction is not spontaneous under standard conditions at 25 $^\circ$C

8.125   No work can be done inside a bomb calorimeter, as it is a constant volume device.

      The value of $\Delta_r G^\ominus$ is the maximum work that can be done under standard conditions. We apply
      $\Delta_r G^\ominus \equiv \Delta_r H^\ominus - T \Delta_r S^\ominus$ to determine this.

      $\Delta_r H^\ominus = (\text{sum}(\Delta_f H^\ominus \text{ (products)})) - (\text{sum}(\Delta_f H^\ominus \text{ (reactants)}))$
      $\Delta_r H^\ominus = [8\Delta_f H^\ominus (CO_2(g)) + 10\Delta_f H^\ominus (H_2O(g))] - [2\Delta_f H^\ominus (C_4H_{10}(g)) + 13\Delta_f H^\ominus (O_2(g))]$
      $\Delta_r H^\ominus = \{8 \text{ mol} \times (-393.5 \text{ kJ mol}^{-1}) + 5 \text{ mol} \times (-241.8 \text{ kJ mol}^{-1})\}$
                                 $- \{2 \text{ mol} \times (-126 \text{ kJ mol}^{-1}) + 13 \text{ mol} \times (0 \text{ kJ mol}^{-1})\}$
      $\Delta_r H^\ominus = -4.11 \times 10^3$ kJ

      $\Delta_r S^\ominus = \{8 S^\ominus [CO_2(g)] + 10 S^\ominus [H_2O(g)]\} - \{2 S^\ominus [C_4H_{10}(g)] + 13 S^\ominus [O_2(g)]\}$
      $\Delta_r S^\ominus = \{8 \text{ mol} \times (213.6 \text{ J mol}^{-1} \text{ K}^{-1}) + 10 \text{ mol} \times (188.7 \text{ J mol}^{-1} \text{ K}^{-1})\}$
                      $- \{2 \text{ mol} \times (310.2 \text{ J mol}^{-1} \text{ K}^{-1}) + 13 \text{ mol} \times (205.0 \text{ J mol}^{-1} \text{ K}^{-1})\}$
      $\Delta_r S^\ominus = 310.4 \text{ J K}^{-1}$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$
$$= -4.11 \times 10^6 \text{ J} - (298 \text{ K} \times 310.4 \text{ J K}^{-1})$$
$$= -4.20 \times 10^6 \text{ J}$$
$$= -4.20 \times 10^3 \text{ kJ}$$

This is the maximum work that can be obtained from this reaction under these conditions.

8.127   For the first expansion:

$$p_i V_i = p_f V_f$$

$$4 \times 10^5 \text{ Pa} \times 5.00 \times 10^{-3} \text{ m}^3 = 2 \times 10^5 \text{ Pa} \times V_f$$

$$V_f = \frac{4 \times 10^5 \text{ Pa} \times 5.00 \times 10^{-3} \text{ m}^3}{2 \times 10^5 \text{ Pa}} = 1 \times 10^{-2} \text{ m}^3.$$

$$w = -p\Delta V$$
$$= -2 \times 10^5 \text{ Pa} \times (1 \times 10^{-2} - 5.00 \times 10^{-3}) \text{ m}^3$$
$$= -1.0 \times 10^3 \text{ Pa m}^3 = -1.0 \times 10^3 \text{ J}$$

For the second expansion:
$$p_i V_i = p_f V_f$$

$$2 \times 10^5 \text{ Pa} \times 5.00 \times 10^{-3} \text{ m}^3 = 1 \times 10^5 \text{ Pa} \times V_f$$

$$V_f = \frac{2 \times 10^5 \text{ Pa} \times 1 \times 10^{-2} \text{ m}^3}{1 \times 10^5 \text{ Pa}} = 2 \times 10^{-2} \text{ m}^3$$

$$w = -p\Delta V$$
$$= -1 \times 10^5 \text{ Pa} \times (2 \times 10^{-2} - 1 \times 10^{-2}) \text{ m}^3$$
$$= -1.0 \times 10^3 \text{ Pa m}^3 = -1.0 \times 10^3 \text{ J}$$

Therefore, the total work done in the 2-stage process is:
$(-1.0 \times 10^3 \text{ J} + -1.0 \times 10^3 \text{ J}) = -2.0 \times 10^3 \text{ J}.$

This compares with -1.5×10^3 J of work done in the single stage process and demonstrates that work is not a state function – it is path-dependent.

Additional Exercises

8.129 $x = 28.8\ ^{\circ}C$

8.131 $\Delta_r H^{\ominus} = 3\Delta_f H^{\ominus}\ [CO_2(g)] + 4\Delta_f H^{\ominus}\ [Fe(s)] - 2\Delta_f H^{\ominus}\ [Fe_2O_3(s)] - 3\Delta_f H^{\ominus}\ [C(s)]$

$= 3\ mol \times (-393.5\ kJ\ mol^{-1}) + 4\ mol \times (0\ kJ\ mol^{-1})$
$\quad\quad\quad - 2\ mol \times (-822.2\ kJ\ mol^{-1}) - 3\ mol \times (0\ kJ\ mol^{-1})$
$=\quad 463.9\ kJ$

This reaction is endothermic.

8.133 $\Delta_r H^{\ominus} = [\Delta_f H^{\ominus}\ (CO_2(g)) + \Delta_f H^{\ominus}\ (Fe(s))] - [\Delta_f H^{\ominus}\ (FeO(s)) + \Delta_f H^{\ominus}\ (CO(g))]$

Rearranging and remembering that $\Delta_f H^{\circ}(Fe(s)) = 0$:
$\Delta_f H^{\ominus}\ (FeO(s)) = \Delta_f H^{\ominus}\ (CO_2(g)) - \Delta_f H^{\ominus}\ (CO(g)) - \Delta_r H^{\ominus}$
$\Delta_f H^{\ominus} = -393.5\ kJ - (-110.5\ kJ) - (-16.8\ kJ) =\quad -266.2\ kJ$

8.135 $\Delta_f H^{\ominus}\ [H_2NCH_2COOH] =\quad -528.3\ kJ\ mol^{-1}$

8.137 $LiOH(aq) + HCl(aq) \rightarrow LiCl(aq) + H_2O(l)\quad\quad\quad \Delta_r H^{\ominus} =\ -53.9\ kJ$

8.139 $8.30 \times 10^{-2}\ mol \times -5.65 \times 10^3\ kJ\ mol^{-1} =\ -4.69 \times 10^2\ kJ$

8.141   The net reaction is:
$3\ CuS(s) + 3\ Cu(s) \rightarrow 3\ Cu_2S(s)\quad\quad\quad\quad \Delta_r H^{\ominus} =\ -79\ kJ$

Divide by 3 to obtain:
$CuS(s) + Cu(s) \rightarrow Cu_2S(s)\quad\quad\quad\quad\quad \Delta_r H^{\ominus} =\ -26\ kJ\ mol^{-1}$
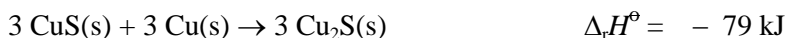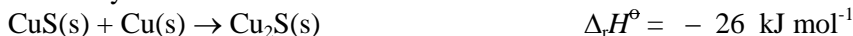
8.143 $Cl_2(g)$ and $Br_2(g)$ molecules resemble each other in shape and are chemically similar.   Therefore, the product molecule $BrCl(g)$ resembles both $Cl_2(g)$ and $Br_2(g)$ in shape, and this leads to a small $\Delta_r S^{\ominus}$.

8.145   (a) $H_2C_2O_4(s) + \frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)\quad\quad\quad \Delta_c H^{\ominus} = -246.05\ kJ$

(b) $H_2(g) + 2C(s) + 2O_2(g) \rightarrow H_2C_2O_4(s)\quad\quad\quad \Delta_f H^{\ominus} = ?$

(c) $\Delta_f H^{\ominus}\ (H_2C_2O_4(s)) =\ -826.9\ kJ\ mol^{-1}$

(d)   For the formation reaction in (b) above:
$\Delta_f S^{\ominus} = S^{\ominus}\ (H_2C_2O_4(s)) - [S^{\ominus}\ (H_2(g)) + 2S^{\ominus}\ (C(s)) + 2S^{\ominus}\ (O_2(g))]$
$= 1\ mol \times (120.1\ J\ mol^{-1}\ K^{-1}) - [1\ mol \times (130.6\ J\ mol^{-1}\ K^{-1}) + 2\ mol$
$\quad\quad\quad\quad \times (5.69\ J\ mol^{-1}\ K^{-1}) + 2\ mol \times (205.0\ J\ mol^{-1}\ K^{-1})]$
$=\ -431.9\ J\ K^{-1}$

For the combustion reaction in (a) above:
$\Delta_c S^{\ominus} = 2S^{\ominus}\ (CO_2(g)) + S^{\ominus}\ (H_2O(l)) - [S^{\ominus}\ (H_2C_2O_4(s)) + \frac{1}{2}S^{\ominus}\ (O_2(g))]$

$= 2 \text{ mol} \times (213.6 \text{ J mol}^{-1} \text{ K}^{-1}) + 1 \text{ mol} \times (69.96 \text{ J mol}^{-1} \text{ K}^{-1})$
$\quad - [\, 1 \text{ mol} \times (120.1 \text{ J mol}^{-1} \text{ K}^{-1}) + \frac{1}{2} \text{ mol} \times (205.0 \text{ J mol}^{-1} \text{ K}^{-1})]$
$= 274.6 \text{ J K}^{-1}$

(e) $\Delta_f G^{\ominus} = \Delta_f H^{\ominus} - T\Delta_f S^{\ominus}$
$= -826.9 \times 10^3 \text{ J} - (298 \text{ K} \times -431.9 \text{ J K}^{-1}) = -6.98 \times 10^5 \text{ J} = -6.98 \times 10^2 \text{ kJ}.$
As this is a formation reaction, it refers to the formation of 1 mole of product, so $\Delta_f G^{\ominus} = -6.98 \times 10^2 \text{ kJ mol}^{-1}$

For the combustion reaction:
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$= -246.05 \times 10^3 \text{ J} - (298 \text{ K} \times 274.6 \text{ J K}^{-1})$
$= -3.28 \times 10^5 \text{ J} = -3.28 \times 10^2 \text{ kJ}$

As this is for the combustion of 1 mole of oxalic acid:
$\Delta_c G^{\ominus} = -3.28 \times 10^2 \text{ kJ mol}^{-1}$

8.147   No real thermodynamic process occurs without the evolution of waste heat. The combustion of either petrol or diesel is used to do work in the engine, but there is always waste heat evolved, which is why cooling systems are required.

8.149   The reaction is:

$N_2(g) \rightarrow 2N(g)$
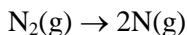
and for this:
$\Delta_r H^{\ominus} = 2\Delta_f H^{\ominus} [N(g)] - \Delta_f H^{\ominus} [N_2(g)]$

Since the enthalpy of formation of molecular nitrogen is zero, the enthalpy change for this reaction and consequently, the bond enthalpy of a nitrogen molecule, is twice the enthalpy of formation of atomic nitrogen.
Bond enthalpy $(N_2) = 2 \text{ mol} \times 472.68 \text{ kJ mol}^{-1} = 945.36 \text{ kJ}$

A similar argument applies for oxygen and therefore:

Bond enthalpy $(O_2) = 2 \text{ mol} \times 249.17 \text{ kJ mol}^{-1} = 498.34 \text{ kJ}$

8.151   (a) $2 N_2(g) + 4 H_2(g) + 3 O_2(g) \rightarrow 2 NH_4NO_3 (s)$
Standard states for reactants are the pure gases at 10^5 Pa pressure and 298 K temperature.
Standard state for ammonium nitrate is the pure solid at 298 K.

(b) $NH_3(g) + HNO_3(l) \rightarrow NH_4NO_3(s)$
$\Delta_r H^o$ = [sum $\Delta_f H^o$ (products)] - [sum $\Delta_f H^o$ (reactants)]
From Table 8.2: $\Delta_f H^o \; NH_4NO_3 = -356.56 \text{ kJ mol}^{-1}$
$\Delta_f H^o \; NH_3 = -46.19 \text{ kJ mol}^{-1}$
$\Delta_f H^o \; HNO_3 = -173.2 \text{ kJ mol}^{-1}$
Thus $\Delta_r H^o = -365.56 - (-46.19 - 173.2) = -145.46 \text{ kJ mol}^{-1}$

(c) NH_4NO_3 (s) → N_2O (g) + 2 H_2O (g)
        Δ_rH^o = [sum Δ_fH^o (products)] - [sum Δ_fH^o (reactants)]
        From Table 8.2: Δ_fH^o N_2O = + 81.57 kJ mol^{-1}
                       Δ_fH^o H_2O (g) = -241.8 kJ mol^{-1}
        Thus Δ_rH^o = 81.57 + 2 (-241.8) - (-365.56) = -36.4 kJ mol^{-1}

(d) NH_4NO_3 (s) → N_2(g) + 2 H_2O (g) + ½ O_2 (g)
        Δ_rH^o = [sum Δ_fH^o (products)] - [sum Δ_fH^o (reactants)]
        Thus Δ_rH^o = 2 (-241.8) - (-365.56) = -118 kJ mol^{-1}
        molar mass of NH_4NO_3 = 80 g mol^{-1}
        so, n(NH_4NO_3) = 106/80 = 1.25 x 10^4 mol
        so, heat evolved = 118 x 1.25 x 10^4 = 1.5 x 10^6 J

(e)   Heat gained by water q = c m ΔT
        so 1.5 x 10^6 = 4.18 x 100 x 1000 x ΔT
        so ΔT = 1.5 x 10^6/4.18 x 10^5 = 3.6^o
        so final temperature of the water is 25.0 + 3.6 = 28.6 ^{o}C.

CHAPTER 9

Practice Exercises

9.1   (a) $K_c = \dfrac{[H_2O]^2}{[H_2]^2[O_2]}$

       (b) $K_c = \dfrac{[CO_2][H_2O]^2}{[CH_4][O_2]^2}$

9.3   Use the equation $K_p = K_c(RT)^{\Delta n_g}$. For this reaction, $\Delta n_g = 3 - 2 = 1$, so

       $K_p = K_c(RT)^{\Delta n_g} = (7.3 \times 10^{34})(0.0821)(298) = 1.8 \times 10^{36}$

9.5   Since the starting equation has been reversed and divided by two, we invert the equilibrium constant and then take the square root: $K_c = 1.2 \times 10^{-13}$.

9.7   Reaction (b) proceeds furthest to completion, since it has the largest value of K_c.

9.9 $\Delta G^\ominus = (\text{sum }\Delta G_f^\ominus[\text{products}]) - (\text{sum }\Delta G_f^\ominus[\text{reactants}])$
        $\Delta G^\ominus = 2\Delta G_f^\ominus[SO_3(g)] - \{2\Delta G_f^\ominus[SO_2(g)] + \Delta G_f^\ominus[O_2(g)]\}$
        $\Delta G^\ominus = 2\text{ mol} \times (-370.4 \text{ kJ mol}^{-1}) - \{2\text{ mol} \times (-300.4 \text{ kJ mol}^{-1}) + (0.0 \text{ kJ mol}^{-1})\}$
        $\Delta G^\ominus = -140.0 \text{ kJ mol}^{-1}$
        Since the sign of $\Delta G^\ominus$ is negative, the reaction is spontaneous.

9.11   Since ΔG is negative, the forward reaction is spontaneous and the reaction proceeds to the right.

9.13 $K_p = 0.26$

9.15   (a)   The equilibrium shifts to the right, decreasing the concentration of Cl_2 at equilibrium and consuming some of the added PCl_3. The value of K_p is unchanged.

       (b)   The equilibrium shifts to the left, consuming some of the added PCl_5 and increasing the amount of Cl_2 at equilibrium. The value of K_p is unchanged.

       (c)   For any exothermic equilibrium, an increase in temperature causes the equilibrium to shift to the left, in order to remove energy in response to the stress. This equilibrium is shifted to the left, increasing the partial pressures of Cl_2 and PCl_3 at the new position of equilibrium. K_p is given by:

$$K_p = \frac{p_{PCl_5}}{p_{PCl_3} \times p_{Cl_2}}$$

In this system, an increase in temperature (which causes an increase in the equilibrium concentrations of both PCl_3 and Cl_2 and a decrease in the equilibrium concentration of PCl_5) causes an increase in the denominator of the above expression as well as a decrease in the numerator of the above expression. Both of these changes decrease the value of K_p.

(d)   Decreasing the container volume for a gaseous system produces an increase in partial pressures for all gaseous reactants and products. In order to lower the increase in partial pressures, the equilibrium shifts so as to favour the reaction side having the smaller number of gaseous molecules, in this case to the right. This shift decreases the amount of Cl_2 and PCl_3 at equilibrium and increases the amount of PCl_5 at equilibrium. This increases the magnitude of the numerator and decreases the magnitude of the denominator in the above expression for K_p, causing it to increase.
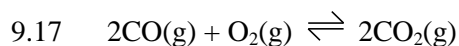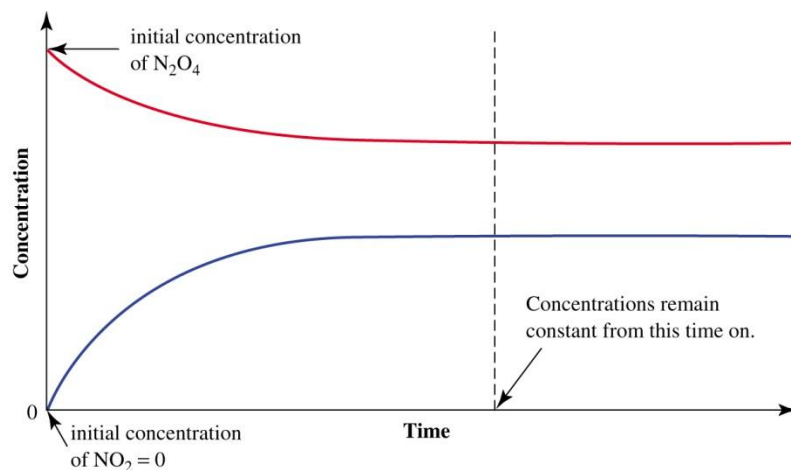
9.17 $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
From the stoichiometry of the reaction we see that for every mol of O_2 that is used, twice as much CO reacts and twice as much CO_2 is produced. Consequently, if the $[O_2]$ decreases by 0.030 mol L^{-1}, the $[CO]$ decreases by 0.060 mol L^{-1} and $[CO_2]$ increases by 0.060 mol L^{-1}.

9.19 $[H_2] = [I_2] = 0.200 - 0.156 = 0.044$ M, $[HI] = 2(0.156) = 0.312$ M.

Review Questions

9.1

9.3 $$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The reaction quotient, Q_c, is the value of this expression with defined concentrations of reactants and products. Note that the expression can also be written in terms of partial pressures of reactants and products as Q_p.
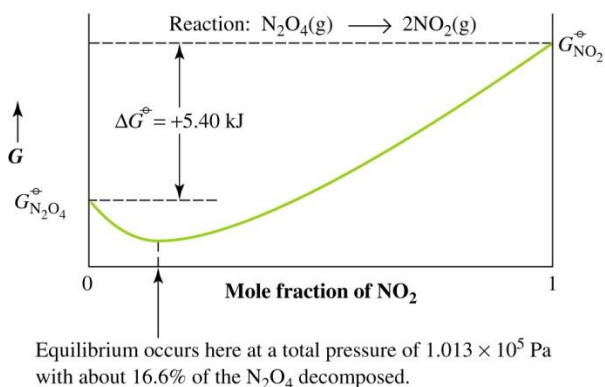
9.5 The equilibrium constant expression is derived from the chemical equation. By convention, the concentrations of the products are always written into the numerator and the concentrations of the reactants are written into the denominator of the equilibrium constant expression.

9.7 The increasing tendency to go to completion is: (a) < (c) < (b), based on the relative magnitudes of K_c.

9.9 The proportionality constant between p_i and the molar concentration of the gas i, c_i, is RT.

9.11 These concentrations are omitted because they are constants that are incorporated into the numerical values of equilibrium constants. These concentrations are constant because as a solid or liquid loses (or gains) mass, it loses (or gains) a volume proportional to the mass.

9.13

Reaction: $N_2O_4(g) \longrightarrow 2NO_2(g)$

$G_{NO_2}^{\ominus}$

$\Delta G^{\ominus} = +5.40$ kJ

G

$G_{N_2O_4}^{\ominus}$

Mole fraction of NO$_2$

Equilibrium occurs here at a total pressure of 1.013×10^5 Pa with about 16.6% of the N_2O_4 decomposed.

9.15 From the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, we see that if $\Delta S^{\ominus}$ is negative, then as the temperature is increased, the $T\Delta S^{\ominus}$ term becomes larger and more negative. This has the effect of making $\Delta G^{\ominus}$ more positive and therefore less product is present at equilibrium.

9.17 $\Delta G^{\ominus} = -RT \ln K$

9.19 The natural log of 1 is zero so $\Delta G^{\ominus} = 0$.

9.21 (a) Increasing [CO] instantaneously decreases the value of Q by increasing the value of the bottom line of the equilibrium quotient expression. Therefore, the system shifts to the right to consume some of the added CO, thereby increasing the value of Q.

(b) Decreasing [H$_2$] instantaneously increases the value of Q by decreasing the value of the bottom line of the equilibrium quotient expression. Therefore, the system shifts to the left to form H$_2$, thereby decreasing the value of Q.

(c)   Since $c = \dfrac{n}{V}$, the equilibrium quotient expression becomes:

$$Q_c = \frac{\dfrac{\left(n_{CH_3OH}\right)}{V}}{\dfrac{\left(n_{CO}\right)}{V}\dfrac{\left(n_{H_2}\right)^2}{V^2}} = \frac{\left(n_{CH_3OH}\right)V^{-1}}{\left(n_{CO}\right)V^{-1}\times\left(n_{H_2}\right)^2 V^{-2}} = \frac{\left(n_{CH_3OH}\right)}{\left(n_{CO}\right)\left(n_{H_2}\right)^2}\times\frac{V^{-1}}{V^{-3}}$$

$$= \frac{\left(n_{CH_3OH}\right)}{\left(n_{CO}\right)\left(n_{H_2}\right)^2}\times V^2$$

Q is proportional to V^2 and so decreasing V instantaneously decreases the value of Q. The system therefore shifts to the right, thereby increasing the value of Q.

(d)   Adding a catalyst increases the rate of a reaction but does not change the value of either Q or K. There is no change in the system.

(e)   As the forward reaction is exothermic, the slope of the graph of ln K versus T is negative. This means that K decreases as the temperature increases. Q therefore decreases in order to maintain equilibrium and so the system shifts to the left.

9.23   The value of K can only be altered by changing the temperature as in 9.21(e) and 9.22(d).

9.25   The equilibrium constant expression for this reaction is:

$$K_c = \frac{[HNO_2]^2}{[NO][NO_2][H_2O]}$$

Since the initial concentration of HNO_2 is zero, the system shifts to the right to reach equilibrium. From the stoichiometry of the reaction, the final concentration of HNO_2 is equal to twice the change in molar concentration that NO, NO_2, and H_2O each undergo. The given data allow us to calculate the equilibrium concentrations for each of the three reactants. Values of the equilibrium concentrations for all four components are then substituted directly into the equilibrium constant expression in order to obtain the value for K_c.

For the reaction: $NO(g) + NO_2(g) + H_2O(g) \rightleftharpoons 2HNO_2(g)$

	[NO(g)]	[NO$_2$(g)]	[H$_2$O(g)]	[HNO$_2$(g)]
Initial	2.59×10^{-3}	2.59×10^{-3}	9.44×10^{-4}	0.00
Change	-2×10^{-4}	-2×10^{-4}	-2×10^{-4}	4×10^{-4}
Equilibrium	2.39×10^{-3}	2.39×10^{-3}	7.44×10^{-4}	4×10^{-4}

9.27   The concentration table is:

	[Br$_2$]	[Cl$_2$]	[BrCl]
Initial	0.6	0.4	0
Change	$-x$	$-x$	$+2x$
Equilibrium	0.6–x	0.4–x	$+2x$

$$K_c = 2 = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{(2x)^2}{(0.6 - x)(0.4 - x)}$$

This leads to the quadratic equation: $2x^2 + 2x - 0.48 = 0$, the solution of which gives $x = 0.2$. Thus, at equilibrium, [Br$_2$] = 0.4 M, [Cl$_2$] = 0.2 M and [BrCl] = 0.4 M.

These initial and equilibrium concentrations are best represented by figure D. Figures A and E are rejected because in each case, one reactant completely reacts and thus, no equilibrium is achieved. Figure C is rejected because the [BrCl]$_{equil}$ is too high. Finally, figure B represents the nature of an oscillatory reaction and not a dynamic equilibrium.

Review Problems

9.29   (a) $K_p = \dfrac{(p_{POCl_3})^2}{(p_{PCl_3})^2(pO_2)}$

(b) $K_p = \dfrac{(p_{SO_2})^2(p_{O_2})}{(p_{SO_3})^2}$

(c) $K_p = \dfrac{(p_{NO})^2(p_{H_2O})^2}{(p_{N_2H_4})(p_{O_2})^2}$

(d) $K_p = \dfrac{(p_{NO_2})^2 (p_{H_2O})^8}{(p_{N_2H_4})(p_{H_2O_2})^6}$

(e) $K_p = \dfrac{(p_{SO_2})(p_{HCl})^2}{(p_{SOCl_2})(p_{H_2O})}$

(f) $K_p = \dfrac{(p_{NCl_3})(p_{HCl})^3}{(p_{Cl_2})^3(p_{NH_3})}$

(g) $K_p = \dfrac{(p_{PCl_2Br})(p_{PClBr_2})}{(p_{PCl_3})(p_{PBr_3})}$

(h) $K_p = \dfrac{(p_{HNO_2})^2}{(p_{NO})(p_{NO_2})(p_{H_2O})}$

(i) $\quad K_p = \dfrac{(p_{HOCl})^2}{(p_{H_2O})(p_{Cl_2O})}$

(j) $\quad K_p = \dfrac{(p_{BrF_5})^2}{(p_{Br_2})(p_{F_2})^5}$

9.31   The second equation is the reverse of the first equation. We therefore take the inverse of the first equilibrium constant in order to determine the second equilibrium constant as: $K = 1 \times 10^{85}$.

9.33   (a) $\quad K_c = \dfrac{[HCl]^2}{[H_2][Cl_2]}$

(b) $\quad K_c = \dfrac{[HCl]}{[H_2]^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}}$

K_c for reaction (b) is the square root of K_c for reaction (a).

9.35   Since 1000 L equals 1 m^{-3}, $[NH_3] = 0.0376$ mol L^{-1}

9.37   (b) and (d) only. This is because the number of moles of gas Δn_g do not change. Therefore, in the equation $K_p = K_c \left(\dfrac{RT}{p^\theta} \right)^{\Delta n_g}$, the $\left(\dfrac{RT}{p^\theta} \right)^{\Delta n_g}$ term becomes equal to 1 and $K_p = K_c$

9.39 $K_p = K_c \left(\dfrac{RT}{p^\theta} \right)^{\Delta n_g}$

$1.6 \times 10^6 = K_c \left(\dfrac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 673 \text{ K}}{1.00 \times 10^5 \text{ Pa}} \right)^1 = K_c \times (5.60 \times 10^{-2})$

$K_c = 2.9 \times 10^7$

9.41 $K_p = K_c \left(\dfrac{RT}{p^\theta} \right)^{\Delta n_g}$

$K_p = (2.2 \times 10^{59}) \times \left(\dfrac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 573 \text{ K}}{1.00 \times 10^5 \text{ Pa}} \right)^{-1}$

$K_p = 4.6 \times 10^{60}$

9.43 $K_p = K_c \left(\dfrac{RT}{p^\theta} \right)^{\Delta n_g}$

$4.6 \times 10^{-2} = K_c \left(\dfrac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 668 \text{ K}}{1.00 \times 10^5 \text{ Pa}} \right)^1 = K_c \times (5.55 \times 10^{-2})$

$K_c = 8.3 \times 10^{-1}$

9.45 $\rho = \dfrac{m}{V}$, therefore $m = \rho V = 2.164$ g cm^{-3} × 12.0 cm^3 = 26.0 g

$$n_{NaCl} = \frac{m}{M} = \frac{26.0 \text{ g}}{58.44 \text{ g mol}^{-1}} = 4.45 \times 10^{-1} \text{ mol}$$

$$c = \frac{n}{V} = \frac{4.45 \times 10^{-1} \text{ mol}}{12.0 \times 10^{-3} \text{ L}} = 37.1 \text{ mol L}^{-1}$$

$\rho = \dfrac{m}{V}$, therefore $V = \dfrac{m}{\rho} = \dfrac{25.0 \text{ g}}{2.164 \text{ g cm}^{-3}} = 11.6$ cm^3

$$n_{NaCl} = \frac{m}{M} = \frac{25.0 \text{ g}}{58.44 \text{ g mol}^{-1}} = 4.28 \times 10^{-1} \text{ mol}$$

$$c = \frac{n}{V} = \frac{4.28 \times 10^{-1} \text{ mol}}{11.6 \times 10^{-3} \text{ L}} = 36.9 \text{ mol L}^{-1}$$

9.47 [HI] = $2x = 1.47 \times 10^{-12}$ M

[Cl$_2$] = $x = 7.37 \times 10^{-13}$ M

9.49 (a) $DG^\circ = \{2 \times D_fG^\circ[POCl_3(g)]\} - \{2 \times D_fG^\circ[PCl_3(g)] + 2 \times D_fG^\circ[O_2(g)]\}$
$DG^\circ = \{2 \text{ mol} \times (-1019 \text{ kJ mol}^{-1})\}$
$\qquad\qquad - \{2 \text{ mol} \times (-267.8 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (0 \text{ kJ mol}^{-1})\}$
$DG^\circ = -1502 \text{ kJ} = -1.502 \times 10^6 \text{ J}$
$-1.502 \times 10^6 \text{ J} = -RT\ln K_p = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \times \ln K_p$
$\ln K_p = 606$ therefore $K_p = 1.93 \times 10^{263}$.

(b) $DG^\circ = \{2 \times D_fG^\circ[SO_2(g)] + 1 \times D_fG^\circ[O_2(g)]\} - \{2 \times D_fG^\circ[SO_3(g)]\}$
$DG^\circ = \{2 \text{ mol} \times (-300 \text{ kJ mol}^{-1}) + 1 \text{ mol} \times (0 \text{ kJ mol}^{-1})\} - \{2 \text{ mol} \times (-370 \text{ kJ mol}^{-1})\}$
$DG^\circ = 140 \text{ kJ} = 1.40 \times 10^5 \text{ J}$
$1.40 \times 10^5 \text{ J} = -RT\ln K_p = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \times \ln K_p$
$\ln K_p = -56.5$ and $K_p = 2.90 \times 10^{-25}$

(c) $\Delta G^\ominus = \{2 \times D_fG^\ominus [NO(g)] + 2 \times D_fG^\ominus [H_2O(g)]\}$
$\qquad\qquad - \{1 \times D_fG^\ominus [N_2H_4(g)] + 2 \times D_fG^\ominus [O_2(g)]\}$
$\Delta G^\ominus = \{2 \text{ mol} \times (86.69 \text{ kJmol}^{-1}) + 2 \text{ mol} \times (-228.6 \text{ kJ mol}^{-1})\}$
$\qquad - \{1 \text{ mol} \times (149.4 \text{ kJ mol}^{-1}) + 2 \text{ mol} \times (0.0 \text{ kJ mol}^{-1})\}$
$\Delta G^\ominus = -433.2 \text{ kJ} = -4.332 \times 10^5 \text{ J}$
$-4.332 \times 10^5 \text{ J} = -RT\ln K_p = -(8.314 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K}) \times \ln K_p$
$\ln K_p = 175$ and $K_p = 1.00 \times 10^{76}$

(d) $\Delta G^\ominus = \{2 \times D_fG^\ominus [NO_2(g)] + 8 \times D_fG^\ominus [H_2O(g)]\}$

$$- \{1 \times D_fG^{\ominus} [N_2H_4(g)] + 6 \times D_fG^{\ominus} [H_2O(g)]\}$$
$$\Delta G^{\ominus} = [2 \text{ mol} \times (51.84 \text{ kJ mol}^{-1}) + 8 \text{ mol} \times (-228.6 \text{ kJ mol}^{-1})]$$
$$- [1 \text{ mol} \times (149.4 \text{ kJ mol}^{-1}) + 6 \text{ mol} \times (-228.6 \text{ kJ mol}^{-1})]$$
$$\Delta G^{\ominus} = -502.9 \text{ kJ} = -5.029 \times 10^5 \text{ J}$$
$$-5.029 \times 10^5 \text{ J} = -RT \ln K_p = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \times \ln K_p$$
$$\ln K_p = 203 \quad \therefore \ K_p = 1.45 \times 10^{88}$$

9.51 Since the value of Q_p is larger than the value of K_p, the system shifts to the left in order to reach equilibrium.

9.53 $T = 37 + 273 = 310$ K
$$\Delta G^{\ominus}_{310K} = -RT \ln K_c$$
$$-33 \times 10^3 \text{ J} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(310 \text{ K}) \times \ln K_c$$
$$\ln K_c = 13$$
$$K_c = 4.4 \times 10^5$$

9.55 $\Delta G^{\ominus}_{500} = -RT \ln K_p$
$$\Delta G^{\ominus}_{500} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(500 \text{ K}) \ln (6.25 \times 10^{-3})$$
$$\Delta G^{\ominus}_{500} = 2.11 \times 10^4 \text{ J mol}^{-1} = 21.1 \text{ kJ mol}^{-1}$$

9.57 $K_p = 1.64 \times 10^{40}$

9.59 (a)   No, as $Q_c \neq K_c$, we conclude that the system is not at equilibrium.
(b)   Since the value of the reaction quotient Q_c is larger than the value of the equilibrium constant K_c, the system shifts to the left to make Q_c smaller and hence reach equilibrium.

9.61 $[H_2] = 0.47$ M

9.63 $$K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]} = \frac{(0.180)}{(0.0148)(0.0336)} = 362$$

9.65 $$K_c = \frac{[H_2][CO]}{[CH_2O]} = \frac{(0.034)(0.034)}{0.066} = 1.8 \times 10^{-2}$$

9.67 $$K_c = \frac{(0.020)^4}{(0.010)^2 (0.041)^3} = 23$$

9.69 $x = 0.0142$ M and the individual concentrations are: $[Br_2] = [Cl_2] = 0.0250 - 0.0142 = 0.0108$ M, $[BrCl] = 2(0.0142) = 0.0284$ M.

9.71 Solving for $x = 0.0703$ M $= [NO] = [SO_3]$, $[NO_2] = [SO_2] = 0.120 - x = 0.050$ M.

Although these two systems reach different equilibrium positions, the equilibrium concentrations of the four components in each experiment give the same value for the equilibrium constant when substituted into the equilibrium constant expression.

An alternative method for solving problems where the reaction proceeds from right to left, such as this problem, is to reverse the written reaction and use this 'new' reaction as the basis for the problem. In doing this, the equilibrium constant expression and the equilibrium constant must change to reflect the 'new' reaction. As outlined in section 9.2, 'when the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original' and the 'new' equilibrium constant expression is also the reciprocal of the original. Try solving this problem using this method. Your answer should, of course, be the same.

9.73 $x = 8.9 \times 10^{-19}$ M $= [H_2] = [Cl_2]$
$[HCl] = (0.0500 - x) \approx 0.0500$ M

9.75 $[CO] = 2x = 5.0 \times 10^{-4}$ M

9.77 $[PCl_3] = (0.013 - x) \approx 0.013$ M

9.79 $[NO_2] = [SO_2] = 0.0281$ M

9.81 $[CO] = [H_2O] = 0.200 - x = 0.200$ M

Additional Exercises

9.83 (a) $p_{NO_2} = 1.88 \times 10^4$ Pa

(b) $p_{total} = p_{NO_2} + p_{N_2O_4} = 1.88 \times 10^4$ Pa $+ 2.53 \times 10^4$ Pa $= 4.41 \times 10^4$ Pa

9.85 $[NO_2] = 0.0500 - 0.00508 = 0.0449$M
$[NO] = 0.0750 - 0.00508 = 0.0699$ M
$[N_2O] = 0.0375 + 0.00508 = 0.0426$ M
$[O_2] = 0.0625 + 0.00508 = 0.0676$ M

9.87 $[NO] = 3x = 1.4 \times 10^{-8}$ M
$[N_2O] = [NO_2] = 0.010 - x = 0.010$ M

9.89 $[N_2O] = 0.0391 + 0.00228 = 0.0414$ M
$[O_2] = 0.0391 + 0.00228 = 0.0414$ M
$[NO_2] = 0.0509 - 0.00228 = 0.0486$ M

$[NO] = 0.0409 - 0.00228 = 0.0386$ M