4. CHEMICAL EQUILIBRIUM

## Equilibrium Constants

### 4.1. \(2A \rightleftharpoons Y + 2Z\)

<table>
<thead>
<tr>
<th>Initial amounts:</th>
<th>2A</th>
<th>(\rightleftharpoons)</th>
<th>Y</th>
<th>+</th>
<th>2Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>mol</td>
<td></td>
</tr>
<tr>
<td>Amounts at equilibrium:</td>
<td>1</td>
<td>1.5</td>
<td>3.0</td>
<td>mol</td>
<td></td>
</tr>
<tr>
<td>Concentrations at equilibrium:</td>
<td>(\frac{1}{5})</td>
<td>(\frac{1.5}{5})</td>
<td>(\frac{3.0}{5})</td>
<td>mol dm(^{-3})</td>
<td></td>
</tr>
</tbody>
</table>

\[
K_c = \frac{(\frac{1.5}{5})(\frac{3.0}{5})^2}{(\frac{1}{5})^2} \text{ mol dm}^{-3} = \frac{(1.5)(3)^2}{(5)} \text{ mol dm}^{-3}
\]

\[
= 2.7 \text{ mol dm}^{-3}
\]

### 4.2. \(A + B \rightleftharpoons Y + Z\)

<table>
<thead>
<tr>
<th>Initial amounts:</th>
<th>A</th>
<th>+</th>
<th>B</th>
<th>(\rightleftharpoons)</th>
<th>Y</th>
<th>+</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amounts at equilibrium:</td>
<td>(x - 2)</td>
<td>1</td>
<td>2</td>
<td>2 mol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{2 \times 2}{(x - 2) \times 1} = 0.1; \quad x - 2 = 40
\]

\[
x = 42
\]

Thus, initially there must be 42 mol of A.

### 4.3. \(A + 2B \rightleftharpoons Z\)

<table>
<thead>
<tr>
<th>Initial amounts:</th>
<th>A</th>
<th>+</th>
<th>2B</th>
<th>(\rightleftharpoons)</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>4</td>
<td>0</td>
<td>0 mol</td>
<td></td>
</tr>
<tr>
<td>Amounts at equilibrium:</td>
<td>(x - 1)</td>
<td>2</td>
<td>1</td>
<td>mol</td>
<td></td>
</tr>
<tr>
<td>Concentrations at equilibrium:</td>
<td>(\frac{x - 1}{5})</td>
<td>(\frac{2}{5})</td>
<td>(\frac{1}{5})</td>
<td>mol dm(^{-3})</td>
<td></td>
</tr>
</tbody>
</table>
\[ \frac{1}{5} \frac{1}{[(x-1)/5]^2} \frac{(2/5)^2}{25} = 0.25 = \frac{25}{4(x-1)} \]

Thus, initially there must be 26 mol of A.

4.4. Two moles of \( \text{SO}_3(\text{g}) \) produce 3 mol of product; thus \( \Sigma \nu = +1 \text{ mol} \). Then, from Eq. 4.26,

\[
K_p = K_c (RT)^{+1} = (0.0271 \text{ mol dm}^{-3}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 1100 \text{ K})
\]

\[ = 247.8 \text{ J dm}^{-3} = 2.478 	imes 10^5 \text{ J m}^{-3} \]

\[ = 2.478 	imes 10^5 \text{ Pa} = 2.48 \text{ bar} \]

4.5. Initial amounts:

<table>
<thead>
<tr>
<th>( \text{I}_2 )</th>
<th>( \text{I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0061 mol</td>
<td>0 mol</td>
</tr>
</tbody>
</table>

Equilibrium amounts:

\[
\frac{0.0061(1 - 0.0274)}{0.0061 \times 2 \times 0.0274} = 5.93 \times 10^{-3} = 3.3428 \times 10^{-4} \text{ mol} \]

\[
K_c = \frac{(3.3428\times10^4/0.5)^2}{5.93\times10^4/0.5} \text{ mol dm}^{-3} = 3.77 \times 10^{-5} \text{ mol dm}^{-3} \]

\[ K_p = 3.77 \times 10^{-5} \text{ mol dm}^{-3} \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 900 \text{ K}) \]

\[ = 0.282 \text{ Pa} = 2.82 \times 10^{-6} \text{ bar} \]

4.6. Addition of \( \text{N}_2 \) at constant \textit{volume} and temperature necessarily requires the equilibrium to shift to the \textit{right}.

\[
K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{n_{\text{NH}_3}^2 V^2}{n_{\text{N}_2} n_{\text{H}_2}^3} \]

If \( n_{\text{N}_2} \) is increased at constant \( V \), the equilibrium must shift so as to produce more ammonia. If the \textit{pressure} (as well as the temperature) is held constant, however, addition of \( \text{N}_2 \) requires that \( V \) is increased. If the proportional increase in \( V^2 \) is greater than the increase in \( n_{\text{N}_2} \), the equilibrium will shift to the \textit{left} when \( \text{N}_2 \) is added.

The volume \( V \) is proportional to \( n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3} \), and \( V^2 \) is proportional to

\[
(n_{\text{N}_2} + n_{\text{H}_2} + n_{\text{NH}_3})^2 \]

If \( n_{\text{N}_2} \) is very much larger than \( n_{\text{H}_2} + n_{\text{NH}_3} \), \( V^2 \) will increase approximately with \( n_{\text{N}_2}^2 \) and therefore increases more strongly than \( n_{\text{N}_2} \). If \( n_{\text{N}_2} \) is not much larger than \( n_{\text{H}_2} + n_{\text{NH}_3} \), an increase in \( n_{\text{N}_2} \) will have a relatively smaller effect on \( V^2 \). The increase in ammonia dissociation when \( \text{N}_2 \) is added is therefore expected when \( \text{N}_2 \) is in excess, but not otherwise.
On the other hand, \( n_3 H_2 \) appears in the equilibrium expression; this varies more strongly than \( V^2 \), and added \( H_2 \) therefore cannot lead to the dissociation of ammonia.

### 4.7. Suppose that in 1 dm\(^3\) there are

\[
x \text{ mol of } N_2O_4
\]
\[
y \text{ mol of } NO_2
\]

Pressure = 0.597 bar = \((x + y)RT/V\)

\[
= \frac{(x + y)\text{mol} \times 0.0831 \text{ bar dm}^3 \text{K}^{-1} \text{mol}^{-1} \times 298.15 \text{K}}{1 \text{ dm}^3}
\]

Therefore, \( x + y = 0.02408 \) (1)

Density = 1.477 g dm\(^{-3}\) = \(\frac{92.02x + 46.01y}{1 \text{ dm}^3}\) g

Therefore, \( 2x + y = 0.03210 \) (2)

From Eqs. (1) and (2), we get \( x = 0.00802; \quad y = 0.0161 \)

\[
N_2O_4(g) \rightleftharpoons 2NO_2(g)
\]

\[
P(1-\alpha) = 2P\alpha
\]

Since partial pressures are proportional to the number of moles of each species present, \( x \propto P(1-\alpha) \) and \( y \propto 2P\alpha \), which means that

\[
\frac{y}{x} = \frac{2P\alpha}{P(1-\alpha)}
\]

from which we get

\[
\alpha = \frac{y}{(2x + y)} = 0.500.
\]

\[
K_c = \frac{(0.01286)^2}{0.00962} = 0.0322 \text{ mol dm}^{-3}
\]

\[
K_P = K_cRT \quad \text{(from Eq. 4.26, with } \Sigma\nu = 1) \]

\[
= 0.0322 \text{ mol dm}^{-3} \times 0.083145 \times 298.15 \text{ dm}^3 \text{ bar} \text{ mol}^{-1}
\]

\[
= 0.798 \text{ bar}
\]

\[
K_x = K_P^{-1} \quad \text{(from Eq. 4.32)}
\]

\[
= K_P \quad \text{(1 bar)}^{-1} = 0.798
\]

Addition of He produces no effect, since concentrations, partial pressures, and mole fractions remain unchanged.

### 4.8. 1.10 g NOBr = \(\frac{1.10 \text{ g NOBr}}{14.01 \text{ g mol}^{-1} \text{ N} + 16.00 \text{ g mol}^{-1} \text{ O} + 79.91 \text{ g mol}^{-1} \text{ Br}} = 0.010 \text{ mol NOBr} \)

If \( \alpha \) is the degree of dissociation,
\[ n_{\text{NOBr}} = 0.01 \ (1 - \alpha) \text{ mol}; \quad n_{\text{NO}} = 0.01 \ \alpha \text{ mol} \]
\[ n_{\text{Br}_2} = 0.005 \ \alpha \text{ mol} \]

Total amount, \( n = 0.01 + 0.005 \ \alpha \text{ mol} \)

\[
\frac{PV}{RT} = \frac{0.355 \text{ bar} \times 1 \text{ dm}^3}{0.0831 \times 298.15 \text{ bar} \text{ dm}^3 \text{ mol}^{-1}} = 0.0143 \text{ mol} 
\]

\( \alpha = 0.861; \quad n = 0.0143 \)
\[ n_{\text{NOBr}} = 1.39 \times 10^{-3} \text{ mol}; \quad n_{\text{NO}} = 8.61 \times 10^{-3} \text{ mol} \]
\[ n_{\text{Br}_2} = 4.305 \times 10^{-3} \text{ mol} \]

\[
K_c = \frac{(8.61 \times 10^{-3} \text{ mol dm}^{-3})^2 \ (4.305 \times 10^{-3} \text{ mol dm}^{-3})}{(1.39 \times 10^{-3} \text{ mol dm}^{-3})^2} = 0.165 \text{ mol dm}^{-3} 
\]

\[
K_p = K_c RT \quad \text{(from Eq. 4.26)} 
\]
\[
= 0.165 \text{ mol dm}^{-3} \times 0.0831 \times 298.15 \text{ dm}^3 \text{ atm mol}^{-1} = 4.09 \text{ bar} 
\]

\[
K_x = K_p (0.355 \text{ bar})^{-1} \quad \text{(from Eq. 4.32)} = 11.5 
\]

4.9. Suppose that, if there were no dissociation, the partial pressure of \( \text{COCl}_2 \) was \( P \); then the actual partial pressures are

\[
\text{COCl}_2(g) \underset{\rightarrow}{\xrightarrow{\leftarrow}} \text{CO}(g) + \text{Cl}_2(g) 
\]

\[
P(1 - \alpha) \quad P\alpha \quad P\alpha 
\]

With \( \alpha = 6.30 \times 10^{-5} \)

\[
P = \frac{2 \text{ bar}}{1 + (6.3 \times 10^{-5})} \approx 2 \text{ bar} 
\]

\[
K_p = \frac{(2 \times 6.3 \times 10^{-5})^2}{2[1 - (6.3 \times 10^{-5})]} \approx 2 \times (6.3 \times 10^{-5})^2 \text{ bar} 
\]
\[
= 7.94 \times 10^{-9} \text{ bar} 
\]

\[
K_c = K_p(RT)^{-1} \quad \text{(from Eq. 4.26)} 
\]
\[
= 7.94 \times 10^{-9} \text{ bar} \times (0.0831 \times 373.15 \text{ dm}^3 \text{ bar} \text{ mol}^{-1})^{-1} 
\]
\[
= 2.56 \times 10^{-10} \text{ mol dm}^{-3} 
\]

\[
K_x = K_pP^{-1} \quad \text{(from Eq. 4.32)} = 7.94 \times 10^{-9} \text{ bar} \ (2 \text{ bar})^{-1} = 3.97 \times 10^{-9} 
\]
4.10. \[ H_2 + I_2 \rightarrow 2HI \]

<table>
<thead>
<tr>
<th>Initially:</th>
<th>H₂</th>
<th>+</th>
<th>I₂</th>
<th>→</th>
<th>2HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

At equilibrium:

| 1 - \( \frac{x}{2} \) | 3 - \( \frac{x}{2} \) | \( x \) |

After addition of 2 mol H₂:

| 3 - \( x \) | 3 - \( x \) | 2\( x \) |

\[ K = \frac{x^2}{(1 - \frac{x}{2})(3 - \frac{x}{2})} = \frac{4x^2}{(3 - x)^2} \]

\[ x = \frac{3}{2} \]

\[ K = \frac{4(3/2)^2}{(3/2)^2} = 4 \]

4.11. 12.7 g iodine = 0.05 mol I₂

When all of the solid iodine has just gone, the iodine pressure is 0.10 atm. The consumption of 0.05 mol I₂ leads to the formation of 0.10 mol HI, which exerts a pressure of

\[ P_{HI} = \frac{0.1 \text{ mol} \times 0.0831 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 313.15 \text{ K}}{10 \text{ dm}^3} = 0.260 \text{ bar} \]

Then, if \( P_{H_2} \) is the partial pressure of H₂ after equilibrium is established,

\[ \frac{(0.260 \text{ bar})^2}{P_{H_2} \times 0.10 \text{ bar}} = 20 \]

\[ P_{H_2} = 0.0338 \text{ bar} \]

\[ n_{H_2} = \frac{0.0338 \text{ bar} \times 10 \text{ dm}^3}{0.0831 \times 313.15 \text{ bar dm}^3 \text{ mol}^{-1}} = 0.0130 \text{ mol} \]

Thus, 0.0130 mol of H₂ is produced in the equilibrium mixture, and 0.05 mol of H₂ is required to remove the 0.05 mol of I₂. Therefore, 0.065 mol of H₂ must be added.

4.12. Assuming that we start with one mole of N₂O₄(g),

\[ N_2O_4(g) \rightleftharpoons 2NO_2(g) \]

\[ 1- \alpha \]

\[ 2\alpha \]

We obtain \((1+\alpha)\) moles of gas at equilibrium. Therefore, equilibrium partial pressures are

\[ P_{N_2O_4} = \frac{1-\alpha}{1+\alpha} P; \quad P_{NO_2} = \frac{2\alpha}{1+\alpha} P, \]

and
\[ K_p = \frac{4\alpha^2}{1-\alpha^2} P; \quad K_c = K_p (RT)^{-1}; \quad K_x = K_p / P. \]

Therefore, at 0.597 bar,

\[ K_P = 1.08 \text{ bar}, \quad K_c = 4.35 \times 10^{-2} \text{ mol dm}^{-3}, \quad K_x = 1.81, \]

and at 6.18 bar,

\[ K_P = 1.45 \text{ bar}, \quad K_c = 5.84 \times 10^{-2} \text{ mol dm}^{-3}, \quad K_x = 0.234. \]

4.13. Rewriting the reaction in terms of one mole of HCl, we get

\[ \text{HCl(g)} + \frac{1}{4} \text{O}_2(g) \rightleftharpoons \frac{1}{2} \text{Cl}_2(g) + \frac{1}{2} \text{H}_2\text{O}(g) \]

\[ (1-y) \quad P_{\text{O}_2} \quad y/2 \quad y/2 \]

From examining the equation above, it is possible to establish the following relationships:

\[ \frac{x_{\text{Cl}_2}}{x_{\text{HCl}}} = \frac{y}{2(1-y)}; \quad \frac{x_{\text{H}_2\text{O}}}{x_{\text{Cl}_2}} = 1. \]

It is important to remember that the same ratios hold for partial pressures also. Now,

\[ K_p = \frac{P_{\text{Cl}_2}^{1/2} \times P_{\text{H}_2\text{O}}^{1/2}}{P_{\text{HCl}} \times P_{\text{O}_2}^{1/4}} = \frac{P_{\text{Cl}_2}}{P_{\text{HCl}} \times P_{\text{O}_2}^{1/4}} = \frac{y}{2(1-y)} \times \frac{1}{P_{\text{O}_2}^{1/4}}. \]

4.14. Assuming ideal behavior, the partial pressure of oxygen is 0.51 bar. Therefore,

\[ K_p = \frac{0.76}{2(1-0.76)} \times \frac{1}{0.51^{0.25}} = 1.87 \text{ bar}^{-1/4}. \]

4.15. Since no reactants are initially present, we write

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons \text{HI}(g) \]

\[ x \quad x \quad n-2x \]

where \( n \) is the initial amount of HI: \( n = 10.0 \text{ g}/(127.912 \text{ g mol}^{-1}) = 7.8179 \times 10^{-2} \text{ mol}. \)

Since \( K_p = 65.0 = \frac{(n-2x)^2}{x^2}, \) or \( \sqrt{65} = \frac{n-2x}{x}, \) we can solve for \( x. \) The solution is \( x = 7.7695 \times 10^{-3} \text{ mol}. \) Therefore, the equilibrium mole fractions are \( x_{\text{H}_2} = x_{\text{I}_2} = x/n = 9.94 \times 10^{-2}; \ x_{\text{HI}} = (n-2x)/n = 0.801. \)
Equilibrium Constants and Gibbs Energy Changes

4.16. a. \( \Delta G^0 / J \text{ mol}^{-1} = -8.3145 \times 283.15 \ln (2.19 \times 10^{-3}) \)
\( \Delta G^0 = 14417 \text{ J mol}^{-1} = 14.42 \text{ kJ mol}^{-1} \)

b. \((\text{C}_6\text{H}_5\text{COOH})_2 \rightleftharpoons 2\text{C}_6\text{H}_5\text{COOH}\)

Initially:
- \((\text{C}_6\text{H}_5\text{COOH})_2\): 0 mol dm\(^{-3}\)
- \(2\text{C}_6\text{H}_5\text{COOH}\): 0.1 mol dm\(^{-3}\)

At equilibrium:
- \((\text{C}_6\text{H}_5\text{COOH})_2\): \(x\) mol dm\(^{-3}\)
- \(2\text{C}_6\text{H}_5\text{COOH}\): \(0.1 - 2x\) mol dm\(^{-3}\)

\[
\frac{(0.1 - 2x)^2}{x} = 2.19 \times 10^{-3}
\]
\[
4x^2 - 0.40219x + 0.01 = 0
\]
\[
x = \frac{0.40219 \pm \sqrt{0.00176}}{8} = \frac{0.40219 \pm 0.04195}{8}
\]
\[
= 0.0555 \text{ or } 0.04503 \text{ mol}
\]

Only the second answer is possible, and this leads to
- Dimer: 0.045 mol dm\(^{-3}\)
- Monomer: 0.01 mol dm\(^{-3}\)

4.17. \(K_P\) at 3000 K = \(\frac{(0.4)^2 \times 0.2}{(0.6)^2}\) = 0.0889 atm
\(\Delta G^0 / J \text{ mol}^{-1} = -8.3145 \times 3000 \ln 0.0889\)
\(\Delta G^0 = 60370 \text{ J mol}^{-1} = 60.4 \text{ kJ mol}^{-1}\)

4.18. a. \(\ln K_c = -\frac{2930}{8.3145 \times 310.15} = -1.136;\) \(K_c = 0.321\)

b. \(\ln K_c = +\frac{15500}{8.3145 \times 310.15} = 6.01;\) \(K_c = 408\)

c. \(K_c = 0.321 \times 408 = 130.9\)
\(\Delta G^0 = 2.93 - 15.5 = -12.6 \text{ kJ mol}^{-1}\)

4.19. a. \(\Delta G^0 = \Delta G^0_{\text{Products}} - \Delta G^0_{\text{Reactants}} = 2(-16.63) - 0 - (3 \times 0) = -33.26 \text{ kJ mol}^{-1}\)
\(K_P = \exp(-\Delta G^0/RT) = 6.71 \times 10^5 \text{ bar}^{-2}\)

b. \(\Delta G^0 = -32.82 - 209.20 = -242.02 \text{ kJ mol}^{-1}\)
\(K_P = 2.5 \times 10^{42} \text{ bar}^{-2}\)

c. \(\Delta G^0 = -32.82 - 68.15 = -100.97 \text{ kJ mol}^{-1}\)
\(K_P = 4.9 \times 10^{17} \text{ bar}^{-1}\)
d. \[ \Delta G^\circ = -32.82 + (2 \times 50.72) = 68.62 \text{ kJ mol}^{-1} \]
\[ K_P = 9.5 \times 10^{-13} \]

4.20. 

<table>
<thead>
<tr>
<th>( K_P )</th>
<th>( \Sigma v )</th>
<th>( K_c = K_P (RT)^{-\Sigma v} )</th>
<th>( K_x = K_P P^{-\Sigma v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. ( 6.71 \times 10^5 \text{ bar}^{-2} )</td>
<td>-2</td>
<td>1091.9 (mol dm(^{-3}))(^{-2} )</td>
<td>6.71 \times 10^5</td>
</tr>
<tr>
<td>b. ( 2.5 \times 10^{42} \text{ bar}^{-2} )</td>
<td>-2</td>
<td>4.0682 \times 10^{39} (mol dm(^{-3}))(^{-2} )</td>
<td>2.5 \times 10^{42}</td>
</tr>
<tr>
<td>c. ( 4.9 \times 10^{17} \text{ bar}^{-1} )</td>
<td>-1</td>
<td>1.9766 \times 10^{16} (mol dm(^{-3}))(^{-1} )</td>
<td>4.9 \times 10^{17}</td>
</tr>
<tr>
<td>d. ( 9.5 \times 10^{-13} )</td>
<td>0</td>
<td>9.5 \times 10^{-13}</td>
<td>9.5 \times 10^{-13}</td>
</tr>
</tbody>
</table>

4.21. 

a. \[ \Delta G^\circ = -RT \ln K \]
\[ = -8.3145 \times 298.15 \ln 10^{-5} \]
\[ = 28.540 \text{ J mol}^{-1} = 28.5 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ = \Delta G^\circ + T \Delta S^\circ = 28.540 - 298.15 \times 41.8 \]
\[ = 16.077 \text{ J mol}^{-1} = 16.1 \text{ kJ mol}^{-1} \]

b. 

\[
\begin{array}{ccc}
\text{CO} & + & \text{H}_2\text{O} & \rightleftharpoons & \text{CO}_2 & + & \text{H}_2 \\
\text{Initially:} & 2 & 2 & 0 & 0 \text{ mol} \\
\text{At equilibrium:} & 2 - x & 2 - x & x & x \text{ mol} \\
\end{array}
\]
\[ K_P = K_c = \frac{x^2}{(2-x)^2} = 1.00 \times 10^{-5} \]

(Note that the total volume cancels out and so need not be considered.)
\[ \frac{x}{2-x} = 3.16 \times 10^{-3}; \quad x = 6.30 \times 10^{-3} \]

The amounts are therefore
1.994 mol (CO); 1.994 mol (H\(_2\)O)
6.30 \times 10^{-3} mol (CO\(_2\)); 6.30 \times 10^{-3} mol (H\(_2\))

4.22. For reaction (1)
\[ K_1 = \exp(-23\ 800/8.3145 \times 310.15) \]
\[ = 9.81 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \]

For reaction (2)
\[ K_2 = \exp(31\ 000/8.3145 \times 310.15) = 1.66 \times 10^5 \text{ mol dm}^{-3} \]

For the coupled reaction (3)
\[ K_3 = K_1K_2 = 16.3 \]

4.23. \[ K_1 = \frac{2.9}{90.9} = 0.0319 \quad K_2 = \frac{6.2}{2.9} = 2.138 \]

\[ K(\text{overall}) = K_1K_2 = 0.0682 \]

\[ \Delta G^\circ = -RT \ln K = 8.3145 \times 298.15 \ln 0.0682 \]

\[ = -6656.8 \text{ J mol}^{-1} = -6.66 \text{ kJ mol}^{-1} \]

4.24. Let the solubility be \( c \) moles per dm\(^3\). Then

\[ \text{Cr(OH)}_3(s) \rightleftharpoons \text{Cr}^{3+} + 3\text{OH}^- \]

\[ c \quad 3c \]

Then the value of the solubility product is \( K_{sp} = c(3c)^3 = 27c^4 \). Therefore,

\[ c = \left( \frac{K_{sp}}{27} \right)^{1/4} = 3.2 \times 10^{-8} \text{ mol dm}^{-3}. \]

### Temperature Dependence of Equilibrium Constants

4.25. a. Zero

b. \( \Delta G^\circ = 0; \quad \Delta H^\circ > 0; \quad \therefore \Delta S^\circ > 0 \)

c. \[ K_c = K_p(RT)^{\Sigma \nu} = (0.0831 \times 298.15)^{-1} \]

\[ = 0.0404 \text{ mol dm}^{-3} \]

\[ \Delta G^\circ = -8.3145 \times 298.15 \ln 0.0404 = 7955 \text{ J mol}^{-1} \]

\[ = 7.96 \text{ kJ mol}^{-1} \]

d. \( K_p > 1 \text{ bar} \)

e. \( \Delta G^\circ < 0 \)

4.26. a. Yes

b. Yes

c. \( \Delta S^\circ > 0 \)

4.27. a. \( \Delta G^\circ = -32.82 - 68.15 = -100.97 \text{ kJ mol}^{-1} \)

\[ \Delta H^\circ = -84.68 - 52.26 = -136.94 \text{ kJ mol}^{-1} \]

\[ \Delta S^\circ = \frac{-136.940 + 100.970}{298.15} = -120.6 \text{ J K}^{-1} \text{ mol}^{-1} \]

Standard state is 1 bar
b. \( \ln \left( \frac{K_P}{\text{bar}^{-1}} \right) = -\frac{\Delta G^\circ}{RT} = \frac{+100 \, 970}{8.3145 \times 298.15} = 40.73 \)

\( K_P = 4.89 \times 10^{17} \, \text{bar}^{-1} \)

c. \( K_c = K_P (RT) = 4.89 \times 10^{17} \times 0.0831 \times 298.15 = 1.21 \times 10^{19} \, \text{dm}^3 \, \text{mol}^{-1} \)

d. \( \Delta G^\circ = -RT \ln K_c = -8.3145 \times 298.15 \ln (1.21 \times 10^{19}) = -108,925 \, \text{J} \, \text{mol}^{-1} = -108.9 \, \text{kJ} \, \text{mol}^{-1} \)

e. \( \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-136,940 + 108,925}{298.15} = -93.96 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} \)

f. \( \Delta G^\circ(100 \, ^\circ\text{C}) = \Delta H^\circ - T\Delta S^\circ = -136,940 + (373.15 \times 120.6) = -91,938 \, \text{J} \, \text{mol}^{-1} \)

\( \ln \left( \frac{K_P}{\text{bar}^{-1}} \right) = \frac{-\Delta G^\circ}{RT} = \frac{91,938}{8.3145 \times 373.15} = 29.63 \)

\( K_P(100 \, ^\circ\text{C}) = 7.38 \times 10^{12} \, \text{bar}^{-1} \)

4.28. a. \( 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) \)

\( \Delta_f G^\circ = 2 \Delta_f G^\circ_{\text{H}_2\text{O}} - 2 \Delta_f G^\circ_{\text{H}_2} - \Delta_f G^\circ_{\text{O}_2} = 2(-228.57) - 2(0) - 0 = -457.14 \, \text{kJ} \, \text{mol}^{-1} \)

\( \Delta_f H^\circ = 2 \Delta_f H^\circ_{\text{H}_2\text{O}} - 2 \Delta_f H^\circ_{\text{H}_2} - \Delta_f H^\circ_{\text{O}_2} = 2(-241.82) - 2(0) - 0 = -483.64 \, \text{kJ} \, \text{mol}^{-1} \)

\( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \frac{-457.14 - (-483.64)}{298.15} = -0.0888 \, \text{kJ} \, \text{mol}^{-1} = -88.88 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} \)

b. \( \Delta G^\circ = -RT \ln K_P \)

\( \ln \left( \frac{K_P}{\text{bar}^{-1}} \right) = \frac{457 \, 140 \, \text{J} \, \text{mol}^{-1}}{8.3145 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} \times 298.15 \, \text{K}} = 184.4 \)

\( K_P = 1.222 \times 10^{80} \, \text{bar}^{-1} \)

c. \( \Delta G(2000 \, ^\circ\text{C})/\text{kJ} \, \text{mol}^{-1} = \Delta_f H^\circ - 2273.15 \Delta_f S^\circ \)

\( = -483.64 - 2273.15 (-0.0888) = -281.6 \, \text{kJ} \, \text{mol}^{-1} \)

\( \ln \left( \frac{K_P}{\text{bar}^{-1}} \right) = \frac{281 \, 600}{8.3145 \times 2273.15} = 14.90 \)

\( K_P = 2.96 \times 10^{6} \, \text{bar}^{-1} \)
CHAPTER 4

4.29. \( \Delta r G^\circ = 2 \Delta f G^\circ(O_3, g) - 3 \Delta f G^\circ(O_2, g) \)

\[ = 2(163.2) - 3(0) = 326.4 \text{ kJ mol}^{-1}. \]

\( K = \exp(-\Delta r G^\circ/RT) = \exp[-326400/(8.3145 \times 400)] \)

\[ = 3.371 \times 10^{-43}. \]

4.30. a. \( \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-20100 + 31000}{310.15} \)

\[ = 35.1 \text{ J K}^{-1} \text{ mol}^{-1}. \]

b. \( \ln K_c = \frac{31000}{8.3145 \times 310.15} = 12.02 \)

\( K_c = 1.66 \times 10^5 \text{ mol dm}^{-3} \)

c. \( \Delta G^\circ(25^\circ C) = -20100 - (298.15 \times 35.1) \)

\[ = -30570 \text{ J mol}^{-1}. \]

\( \ln K_c = \frac{30570}{8.3145 \times 298.15} = 12.33 \)

\( K_c = 2.27 \times 10^5 \text{ mol dm}^{-3} \)

4.31. a. \( \Delta H^\circ = -165.98 + 146.44 = -19.54 \text{ kJ mol}^{-1} \)

\( \Delta S^\circ = 306.4 - 349.0 = -42.6 \text{ J K}^{-1} \text{ mol}^{-1} \)

\( \Delta G^\circ = -19540 + (42.6 \times 298.15) \)

\[ = -6839 \text{ J mol}^{-1} = -6.84 \text{ kJ mol}^{-1}. \]

b. \( \ln K_P = \frac{6839}{8.3145 \times 298.15} = 2.759; \quad K_P = 15.78 \)

If partial pressure of neopentane = \( x \) bar, partial pressure of \( n \)-pentane = \( (1 - x) \) bar

\[ \frac{x}{1 - x} = 15.78 \]

\[ x = 15.78 - 15.78x; \quad x = 0.940 \]

\[ 1 - x = 0.060 \]

Thus \( P(\text{neopentane}) = 0.940 \) bar and \( P(\text{\( n \)-pentane}) = 0.060 \) bar.

4.32. a. Slope of plot of \( \ln K_c \) against \( 1/T \) is

\[ \frac{\ln 3}{\left( \frac{1}{313.15} - \frac{1}{298.15} \right)} = \frac{1.0986}{1.607 \times 10^{-4}} = -6836 \]

From Eq. 4.73,

\( \Delta H^\circ = 6836 \times 8.3145 = 56840 \text{ J mol}^{-1} \)
4.33. a. Slope of plot of $\ln K_c$ against $1/T$ is

$$\frac{-\ln 1.45}{298.15 - 303.15} = -\frac{0.372}{5.532 \times 10^{-5}} = -6724.6 \, K$$

$$\Delta H^\circ = 6724.6 \times 8.3145 = 55 \, 910 \, J \, mol^{-1}$$

$$= 55.9 \, kJ \, mol^{-1}$$

At $25^\circ C$, $\Delta G^\circ = -RT \ln 1.00 \times 10^{-14}$

$$= -8.3145 \times 298.15 \times (-32.236)$$

$$= 79 \, 912 \, J \, mol^{-1}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{55 \, 910 - 79 \, 912}{298.15}$$

$$= -80.5 \, J \, K^{-1} \, mol^{-1}$$

b. The difference between the reciprocals of the absolute temperatures corresponding to $25^\circ C$ and $37^\circ C$ is

$$3.3540 \times 10^{-3} - 3.2242 \times 10^{-3} = 1.298 \times 10^{-4}$$

The slope of the plot $\ln K_w$ against $1/T$ was $-6724.6 \, K$, and in going from $25^\circ C$ to $37^\circ C$ $\ln K_w$ is thus increased by

$$6724.6 \times 1.298 \times 10^{-4} = 0.873$$

At $25^\circ C$, $\ln K_w$ is $-32.244$ and at $37^\circ C$ it is therefore

$$-32.244 + 0.873 = -31.371$$

$K_w$ at $37^\circ C$ is therefore $2.38 \times 10^{-14}$ mol$^2$ dm$^{-6}$.

4.34. a. At $400 \, ^\circ C$,

$$\log_{10}(K_P/bar) = 7.55 - \frac{4844}{673.15} = 0.354$$

$$K_P = 2.259 \, bar$$

$$\Delta G^\circ/kJ \, mol^{-1} = -8.3145 \times 673.15 \ln 2.259$$

$$\Delta G^\circ = -4549 \, J \, mol^{-1} = -4.55 \, kJ \, mol^{-1}$$

From Figure 4.2 (b),

$$\Delta H^\circ = 4844 \times 8.3145 \times 2.303 \, J \, mol^{-1}$$

$$= 92 \, 750 \, J \, mol^{-1}$$

$$= 92.75 \, kJ \, mol^{-1}$$

$$\Delta S^\circ = \frac{92 \, 800 + 4549}{673.15} \, J \, K^{-1} \, mol^{-1}$$
= 144.6 J K⁻¹ mol⁻¹

b. \[ K_c = 2.259 \times (0.0831 \times 673.15)^{-1} \]
\[ = 0.0404 \text{ mol dm}^{-3} \]
\[ \Delta G^o/\text{kJ mol}^{-1} = -8.3145 \times 673.15 \ln 0.0404 \]
\[ \Delta G^o = 17,960 \text{ J mol}^{-1} = 17.96 \text{ kJ mol}^{-1} \]

c. \[ \text{I}_2 + \text{cyclopentene} \rightleftharpoons 2\text{HI} + \text{cyclopentadiene} \]
\[ 0.1-x \quad 0.1-x \quad 2x \quad x \]
\[ \frac{4x^3}{(0.1-x)^2} = 0.0404 \]

For a very approximate solution, neglect \( x \) in comparison with 0.1:
\[ 4x^3 = 0.0404 \times (0.1)^2 = 4.04 \times 10^{-4} \]
\[ x^3 = 1.01 \times 10^{-4} \]
\[ x = 0.0466 \]

For a better solution, calculate \( 4x^3/(0.1-x)^2 \) at various \( x \) values:

<table>
<thead>
<tr>
<th>( x )</th>
<th>0.0466</th>
<th>0.04</th>
<th>0.03</th>
<th>0.0350</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{4x^3}{(0.1-x)^2} )</td>
<td>0.1419</td>
<td>0.0711</td>
<td>0.022</td>
<td>0.0406</td>
</tr>
</tbody>
</table>

\[ x = 0.0350 \]

Final concentrations are
\[ [\text{I}_2] = 0.0650 \text{ M}; \]
\[ [\text{cyclopentene}] = 0.0650 \text{ M}; \]
\[ [\text{HI}] = 0.0700 \text{ M}; \]
\[ [\text{cyclopentadiene}] = 0.0350 \text{ M} \]

4.35. \( \Delta H^o = -283.66 + 110.53 = -173.13 \text{ kJ mol}^{-1} \)
\[ \Delta G^o = -166.27 + 137.17 = -29.10 \text{ kJ mol}^{-1} \]
\[ \Delta S^o = \frac{-173.130 + 29.10}{298.15} = -483.1 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ \ln K_P = \frac{29.10}{8.3145 \times 298.15} = 11.74 \]
\[ K_P = 1.25 \times 10^5 \text{ bar}^{-3} \]

4.36. \( \Delta H^o = -207.4 + 104.6 = -102.8 \text{ kJ mol}^{-1} \)
\[ \Delta G^o = -111.3 + 37.2 = -74.1 \text{ kJ mol}^{-1} \]
\[ \Delta S^o = \frac{-102.800 + 74.100}{298.15} = -96.3 \text{ J K}^{-1} \text{ mol}^{-1} \]
4.37. a. \( K_c = \frac{95}{5} = 19 \)
\( \Delta G^\circ /J \text{ mol}^{-1} = -8.3145 \times 298.15 \ln 19 \)
\( \Delta G^\circ = -7299 \text{ J mol}^{-1} = -7.30 \text{ kJ mol}^{-1} \)
b. \( \Delta G/J \text{ mol}^{-1} = -7299 + 8.3145 \times 298.15 \ln \frac{10^{-4}}{10^{-2}} \)
\( \Delta G = (-7299 - 11416) \text{ J mol}^{-1} = -18714 \text{ J mol}^{-1} \)
\( = -18.7 \text{ kJ mol}^{-1} \)
The reaction will therefore go from left to right.

4.38. a. \( \Delta H^\circ = -110.53 - 241.82 + 393.51 = 41.16 \text{ kJ mol}^{-1} \)
\( \Delta G^\circ = -137.17 - 228.57 + 394.36 = 28.62 \text{ kJ mol}^{-1} \)
\( \Delta S^\circ = \frac{41\,160 - 28\,620}{298.15} = 42.06 \text{ J K}^{-1} \text{ mol}^{-1} \)
b. \( \ln K_P = -\frac{28\,620}{8.3145 \times 298.15} = -11.55 \)
\( K_P = 9.68 \times 10^{-6} \)
c. From the data in Table 2.1,
\( \Delta d = 28.41 + 30.54 - 44.22 - 27.28 \)
\( = -12.55 \text{ J K}^{-1} \text{ mol}^{-1} \)
\( \Delta e = 10^{-3}(4.10 + 10.29 - 8.79 - 3.26) \)
\( = 2.34 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1} \)
\( \Delta f = 10^4(-4.6 + 0 + 86.2 - 5.0) \)
\( = 76.6 \times 10^4 \text{ J K}^{-1} \text{ mol}^{-1} \)
Then, from Eq. 2.52,
\( \Delta H^\circ /J \text{ mol}^{-1} = 41\,160 - 12.55[(T/K) - 298.15] + 1.17 \times 10^{-3}[(T/K)^2 - 298.15^2] - 
\[76.6 \times 10^4 \left(\frac{1}{T/K} - \frac{1}{298.15}\right)\] 
\( = 47\,367 - 12.55(T/K) + 1.17 \times 10^{-3}(T/K)^2 - 76.6 \times 10^4/(T/K) \)
d. \( \ln K = \int \frac{\Delta H^\circ}{RT^2} \, dT \)
\( = \frac{1}{8.3145} \left[ \frac{47\,367}{(T/K)^2} - \frac{12.55}{T/K} + 1.17 \times 10^{-3} - \frac{76.6 \times 10^4}{(T/K)^3} \right] d(T/K) \)
\( = \frac{1}{8.3145} \left[ -\frac{47\,367}{(T/K)} - 12.55 \ln (T/K) + 1.17 \times 10^{-3} (T/K) + \frac{38.3 \times 10^4}{(T/K)^2} \right] + l \)
\[= \frac{5697}{T/K} - 1.51 \ln \left(\frac{T}{K}\right) + 1.41 \times 10^{-4} \left(\frac{T}{K}\right) + \frac{4.61 \times 10^4}{(T/K)^2} + I\]

I is obtained from the fact that at 298.15, \(\ln K = -11.55\)

\[I = -11.55 + 19.11 + 8.60 - 0.042 - 0.519 = 15.60\]

\[\ln K = 15.60 - \frac{5697}{1000} - 1.51 \ln 1000 + 0.141 + \frac{4.61 \times 10^4}{1000^2}\]

\[= -0.34\]

\(K_P (1000 \text{ K}) = 0.71\)

4.39. Partial pressures at 1395 K are:

\[
\text{CO: } 0.000 \text{ atm; } \text{CO}_2: (1 - 0.000 140) \text{ atm; } \text{O}_2: 0.000 070 \text{ atm}
\]

\[K_P = \frac{(0.000 140)^2 \times 0.000 070}{(0.9999)^2} = 1.372 \times 10^{-12} \text{ atm} = 1.39 \times 10^{-12} \text{ bar}\]

At 1443 K,

\[K_P = \frac{(0.000 250)^2 \times 0.000 125}{(0.99975)^2} = 7.814 \times 10^{-12} \text{ atm} = 7.92 \times 10^{-12} \text{ bar}\]

At 1498 K,

\[K_P = \frac{(0.000 471)^2 \times 0.000 2355}{(0.999 529)^2} = 5.227 \times 10^{-11} \text{ atm} = 5.30 \times 10^{-11} \text{ bar}\]

Then

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(10^{12}K_P/\text{atm})</th>
<th>(10^4/(T/K))</th>
<th>(\ln(10^{12}K_P/\text{atm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1395</td>
<td>1.372</td>
<td>7.168</td>
<td>0.3163</td>
</tr>
<tr>
<td>1443</td>
<td>7.814</td>
<td>6.930</td>
<td>2.0559</td>
</tr>
<tr>
<td>1498</td>
<td>52.27</td>
<td>6.676</td>
<td>3.956</td>
</tr>
</tbody>
</table>

From a plot of \(\ln (K_P/\text{atm})\) against \(1/(T/K)\),

slope = \(-7.39 \times 10^4 \text{ K}\) and \(\Delta H^0 = -R \times \text{slope} = 609 \text{ kJ mol}^{-1}\).

\(\Delta G^0(1395 \text{ K}) = -8.3145 \times 1395 \ln (1.372 \times 10^{-12})\)

\[= 316.8 \text{ kJ mol}^{-1}\]

\(\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = 209 \text{ J K}^{-1} \text{ mol}^{-1}\)

(standard state 1 atm)
4.40. Suppose that there are present $x$ mol of $I_2$ and $y$ mol of $I$:

$$x + \frac{y}{2} = 1.958 \times 10^{-3}$$

$$P = \frac{(x+y) \text{ mol } RT}{V}$$

At 800° C

$$\frac{558.0}{760.0} \text{ atm} = \frac{(x+y) 0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}}{249.8 \times 10^{-3} \text{ dm}^3} \times 1073.15 \text{ K}$$

$$x + y = 2.0829 \times 10^{-3}$$

$$\frac{y}{2} = 0.1249 \times 10^{-3}; \quad y = 2.498 \times 10^{-4}$$

$$x = 1.833 \times 10^{-3}$$

Degree of dissociation,

$$\alpha = 1 - \frac{x}{1.958 \times 10^{-3}} = 1 - \frac{1.833 \times 10^{-3}}{1.958 \times 10^{-3}} = 0.0638$$

At 1000° C, $x + y = 2.3535 \times 10^{-3}$

$$\frac{y}{2} = 3.955 \times 10^{-4}; \quad y = 7.91 \times 10^{-4}$$

$$x = 1.5625 \times 10^{-3}; \quad \alpha = 0.202$$

At 1200° C, $x + y = 2.7715 \times 10^{-3}$

$$\frac{y}{2} = 8.135 \times 10^{-4}; \quad y = 1.627 \times 10^{-3}$$

$$x = 1.1445 \times 10^{-3}; \quad \alpha = 0.415$$

a. $\alpha = 0.0638, 0.202, 0.415$ at the three temperatures

b. At 800 °C,

$$K_c = \frac{(2.498 \times 10^{-4} \text{ mol})^2}{1.833 \times 10^{-3} \text{ mol} \times 0.2498 \text{ dm}^3}$$

$$= 1.363 \times 10^{-4} \text{ mol dm}^{-3}$$

At 1000 °C,

$$K_c = \frac{(7.91 \times 10^{-4})^2}{1.5625 \times 10^{-3} \times 0.2498}$$

$$= 16.0 \times 10^{-4} \text{ mol dm}^{-3}$$

At 1200 °C,

$$K_c = \frac{(1.627 \times 10^{-3})^2}{1.1445 \times 10^{-3} \times 0.2498}$$

$$= 92.59 \times 10^{-4} \text{ mol dm}^{-3}$$
c. \( K_P = K_c (RT)^\Sigma_v \)  
\[ = K_c RT \text{ since } \Sigma_v = 1 \]

At 800 °C, \( K_P \)
\[ = 1.363 \times 10^{-4} \text{ mol dm}^{-3} \times 100 \text{ dm}^{-3} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 1073.15 \text{ K} \]
\[ = 1.216 \text{ kPa} = 9.12 \text{ Torr} = 0.0122 \text{ bar} \]

At 1000 °C, \( K_P = 16.97 \text{ kPa} \)

At 1200 °C, \( K_P = 113.4 \text{ kPa} \)

d. \[
\begin{array}{cccc}
T/K & 10^4 K_c/\text{mol dm}^{-3} & 10^4/(T/K) & \ln 10^4 K_c/\text{mol dm}^{-3} \\
1073.15 & 1.363 & 9.318 & 0.310 \\
1273.15 & 16.03 & 7.855 & 2.774 \\
1473.15 & 92.59 & 6.788 & 4.528 \\
\end{array}
\]
Slope of a plot of \( \ln(K_c/\text{mol dm}^{-3}) \) against \( 1/(T/K) \) is \(-1.67 \times 10^4 \text{ K}^{-1} \).

\[
\Delta U^\circ = 139 \text{ kJ mol}^{-1} \\
\Delta H^\circ = \Delta U^\circ + RT = 139000 + (8.3145 \times 1273.15) \\
\quad = 149586 \text{ J mol}^{-1} = 150 \text{ kJ mol}^{-1} \\
\]

e. At 1000 °C, \( K_P = 16.97 \text{ kPa} = 0.169 \text{ bar} \).

\[
\Delta G^\circ = -(8.3145 \times 1273.15 \text{ J mol}^{-1}) \ln(0.169/\text{bar}) \\
\quad = 18819 \text{ J mol}^{-1} \\
\quad = 18.8 \text{ kJ mol}^{-1} \\
\text{(standard state: 1 bar)} \\
\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = 103.0 \text{ J K}^{-1} \text{ mol}^{-1} \\
\]

4.41. \( \Delta G^\circ = -RT \ln K^\circ = -8.3145 \times 300 \ln 5.7 \times 10^{-3} \)
\[ = 12889 \text{ J mol}^{-1} = 12.9 \text{ kJ mol}^{-1} \]

Slope of plot \[ \frac{\ln (5.7 \times 10^{-3}/7.8 \times 10^{-4})}{(1/300) - (1/340)} = \frac{1.989}{3.922 \times 10^{-4}} \]
\[ = 5071 \text{ K} \]

\( \Delta H^\circ = -8.3145 \times 5071 = -42160 \text{ J mol}^{-1} = -42.16 \text{ kJ mol}^{-1} \)

\( \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = -183 \text{ J K}^{-1} \text{ mol}^{-1} \)

4.42. \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -85200 + 300 \times 170.2 \)
\[ = -34140 \text{ J mol}^{-1} \]
\[ K_c = \exp\left(\frac{34.140}{8.3145 \times 300}\right) \]
\[ = 8.8 \times 10^5 \]
The equilibrium constant is equal to unity when \( \Delta G^\circ \) is equal to zero.
\[ 0 = -85.200 + T \times 170.2 \]
\[ T = 500.6 \text{ K} \]

4.43. \( \Delta G^\circ = -8.3145 \times 310.15 \times \ln 1.66 \times 10^5 \)
\[ = -30.996 \text{ J mol}^{-1} \]
\[ \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-20.100 + 31.996}{310.15} \]
\[ = 35.13 = 35.1 \text{ J K}^{-1} \text{ mol}^{-1} \]
At 25 °C, \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -20.100 - (298.15 \times 35.1) \)
\[ = -30.565 \text{ J mol}^{-1} \]
\[ = -8.3145 \times 298.15 \ln K_c \]
\[ \ln K_c = \frac{30.565}{8.3145 \times 298.15} = 12.33 \]
\[ K_c = 2.26 \times 10^5 \text{ mol dm}^{-3} \]

4.44. \( \Delta G^\circ = -8.3145 \times 300 \times \ln 7.2 \times 10^{-5} \)
\[ = 23.793 \text{ J mol}^{-1} \]
\[ \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{40.000 - 23.793}{300} \]
\[ = 54.02 \text{ J K}^{-1} \text{ (standard state: 1 mol dm}^{-3}) \]
The equilibrium constant is unity when \( \Delta G^\circ \) is zero:
\[ 0 = \Delta H^\circ - T\Delta S^\circ \]
\[ T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{40.000}{54.02} \]
\[ = 740 \text{ K} \]

4.45. \( \Delta G^\circ = -RT \ln K_c = -8.3145 \times 300 \ln (4.5 \times 10^4) \)
\[ = -26.725 \text{ J mol}^{-1} \]
\[ \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-40.200 + 26.725}{300} \]
\[ = -44.9 \text{ J K}^{-1} \text{ mol}^{-1} \]
The equilibrium constant is unity when \( \Delta G^\circ = 0 \).
ΔG° = 0 = –40 200 + (44.9 × T)

T = 895 K

4.46. For the equilibrium

Br₂(l) = Br₂(g)

the vapor pressures are the equilibrium constants. The corresponding ΔG° values (standard state: 1 bar) are

ΔG°(331.35 K) = –RT ln 1 = 0

ΔG°(282.45 K) = – 8.3145 × 282.45 (J mol⁻¹) ln 0.1334

= 4730.7 J mol⁻¹

We can therefore set up two simultaneous equations:

0 = ΔH° – (331.35 K) ΔS°

4730.7 J mol⁻¹ = ΔH° – (282.45 K) ΔS°

Subtraction gives

ΔS° = 4730.7 J mol⁻¹/48.9 K = 96.74 J K⁻¹ mol⁻¹

ΔH° = 96.74 J K⁻¹ mol⁻¹ × 331.35 K = 32 055 J mol⁻¹

At 25°C,

ΔG° = 32 055 – (96.74 × 298.15) J mol⁻¹

= 3212 J mol⁻¹

The vapor pressure at 25°C is the corresponding equilibrium constant:

P = K_p = exp(–3212/8.3145 × 298.15)

= 0.274 bar

4.47. For the reaction, ΔG° = 2 × 162.3 = 324.6 kJ mol⁻¹

Then

K_p = exp(–ΔG° /RT) = exp(–324 600/8.3145 × 298.15)

= 1.36 × 10⁻⁵⁷ bar⁻¹ (The unit arises from the standard state of 1 bar.)

Σν for the reaction is 2 – 3 = –1. From Eq. 4.26,

K_c = K_p (RT)⁻Σν

= 1.36 × 10⁻⁵⁷ bar⁻¹ (8.3145 × 298.15 J)

= 3.37 × 10⁻⁵⁹ m³ mol⁻¹ (since J Pa⁻¹ = m³)

= 3.37 × 10⁻⁵⁶ dm³ mol⁻¹

From Eq. 4.32,
\[ K_x = K_P P^{-\Sigma r} \] so that at 2 bar pressure,
\[ K_x = 1.36 \times 10^{-57} \text{ bar}^{-1} \times 2 \text{ bar} = 2.72 \times 10^{-57} \]

This equilibrium constant (Eq. 4.31) is \( x(O_3)^2/x(O_2)^3 \), and since it is so small, \( x(O_2) \) is almost exactly unity. Thus
\[ x(O_3)^2 = 2.72 \times 10^{-57} \]

and
\[ x(O_3) = 5.22 \times 10^{-29} \]

4.48. At 500 K, by Eq. 2.46,
\[ \Delta H^\circ = \Delta H^\circ(300 \text{ K}) + \Delta C_P(500 - 300) \]
\[ = -9600 -(7.11 \times 200) = -11022 \text{ J mol}^{-1} \]

For the entropy change at 500 K, the corresponding equation is
\[ \Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \int_{T_1}^{T_2} \frac{T \Delta C_P}{T} \, dT \]
\[ = \Delta S^\circ(T_1) + \Delta C_P \ln \left( \frac{T_2}{T_1} \right) \]

At 500 K, \( \Delta S^\circ \) is therefore
\[ \Delta S^\circ = 22.18 - 7.11 \ln(500/300) = 18.55 \text{ J K}^{-1} \text{ mol}^{-1} \]

Therefore
\[ \Delta G^\circ = -11022 - 18.55 \times 500 = -20297 \text{ J mol}^{-1} \]

The equilibrium constant \( K_P \) is therefore
\[ \exp(20297/8.3145 \times 500) = 131.9 \]

Since the reaction involves no change in the number of molecules, \( K_c \) and \( K_x \) also have this value (see Eqs. 4.26 and 4.32), and they are not affected by the pressure.

Let the mole fraction of HI be \( x \); then the mole fractions of H\(_2\) and I\(_2\) are both \( (1 - x)/2 \), and the expression for \( K_x \) is therefore
\[ K_x = 4x^2/(1 - x)^2 = 131.9 \]

Taking square roots
\[ 11.48 = 2x/(1 - x) \]

whence \( x = 0.85 \)

Pressure has no effect on the above values.

4.49. Values of \( \Delta G^\circ \) and of \( K = \exp(-\Delta G^\circ/RT)^\mu \) are

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \theta )/°C</th>
<th>( T/K )</th>
<th>( \Delta G^\circ/kJ \text{ mol}^{-1} )</th>
<th>( K )</th>
</tr>
</thead>
</table>

Binding to Protein Molecules

4.50. If the concentration of M is \([M]\), that of sites occupied and unoccupied is \(n[M]\). The association reactions may be formulated in terms of the sites, \(S\),

\[
S + A \rightleftharpoons SA
\]

\[
K_s = \frac{[SA]}{[S][A]}
\]

where \([S]\) is the concentration of unoccupied sites and \([SA]\) is the concentration of occupied sites. The total concentration of sites, \(n[M]\), is

\[
n[M] = [S] + [SA] = [SA] \left\{ \frac{1}{K_s[A]} + 1 \right\}
\]

The average number of occupied sites per molecule is the total concentration of occupied sites divided by the total concentration of M:

\[
\bar{\nu} = \frac{[SA]}{[M]} = \frac{n}{K_s[A] + 1} = \frac{nK_s[A]}{1 + K_s[A]}
\]

4.51. The total concentration of the molecule M is

\[
[M]_0 = [M] + [MA] + [MA_2] + \ldots + [MA_n]
\]

The total concentration of occupied sites is the total concentration of bound A molecules:

\[
[A]_b = [MA] + 2[MA_2] + \ldots + n[MA_n]
\]

Expressing every term in terms of \([A]\):

\[
[M]_0 = [M]\{1 + K_1[A] + K_1K_2[A]^2 + \ldots + (K_1K_2 \ldots K_n)[A]^n\}
\]

\[
[A]_b = [M]\{K_1[A] + 2K_1K_2[A]^2 + \ldots + n(K_1K_2 \ldots K_n)[A]^n\}
\]

Thus

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0 \text{ when } T = 317.6 \text{ and } K = 44.4^\circ C
\]

At this temperature there will be equal concentrations of P and D.
CHEMICAL EQUILIBRIUM

\[ \bar{v} = \frac{[A]_0}{[M]_0} = \frac{K_1[A] + 2K_1K_2[A]^2 + \ldots + n(K_1K_2 \ldots K_n)[A]^n}{1 + K_1[A] + K_1K_2[A]^2 + \ldots + (K_1K_2 \ldots K_n)[A]^n} \]

4.52. With \( K_1 = nK_s, K_2 = (n-1)K_s/2, \) and so on, the preceding equation becomes

\[ \bar{v} = \frac{nK_1[A] + n(n-1)K_2^2[A]^2 + \ldots + nK_n^n[A]^n}{1 + nK_1[A] + n(n-1)K_2^2[A]^2 + \ldots + K_n^n[A]^n} \]

\[ = \frac{nK_1[A]}{1 + nK_1[A] + n(n-1)K_2^2[A]^2 + \ldots + K_n^n[A]^n} \]

The coefficients are the binomial coefficients,

\[ \bar{v} = \frac{nK_1[A](1 + K_s[A])^{n-1}}{(1 + K_s[A])^n} \]

\[ = \frac{nK_1[A]}{1 + K_s[A]} \]

which are the expressions obtained in Problem 49. To test the equation, plot \( 1/\bar{v} \) against \( 1/[A] \):

\[ \frac{1}{\bar{v}} = \frac{1}{n} + \frac{1}{nK_s[A]} \]

One of the intercepts is \( 1/n \). Alternatively, plot \( \bar{v} \) against \( \bar{v}/[A] \):

\[ \bar{v} = n - \frac{\bar{v}}{K_s[A]} \]

4.53. If \( K_n \) is very much larger than \( K_1, K_2, \) and so on, the equation obtained in Problem 51 reduces as follows:

\[ \bar{v} = \frac{n(K_1K_2 \ldots K_n)[A]^n}{1 + (K_1K_2 \ldots K_n)[A]^n} = \frac{nK[A]^n}{1 + K[A]^n} \]

where \( K = K_1K_2 \ldots K_n \) is the overall equilibrium constant for the binding of \( n \) molecules:

\[ nA + M \rightleftharpoons MA_n \]

The fraction of sites occupied, \( \theta \), is \( \bar{v}/n \):

\[ \theta = \frac{K[A]^n}{1 + K[A]^n} \]

or

\[ \frac{\theta}{1-\theta} = K[A]^n \]
The slope of a plot of $\ln \left( \frac{\theta}{1 - \theta} \right)$ against $[A]$ is thus $n$. If the sites are identical and independent (Problem 50), the slope is 1. Intermediate behavior can give nonlinear plots; the maximum slope of a Hill plot cannot be greater than $n$. 