Exercise

6A.3(b) $2\ \mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}$ $\quad \Delta_r G^{\ominus} = -4.73\ \mathrm{kJ\ mol^{-1}}$

$$\begin{aligned}\Delta_r G &= \Delta_r G^{\ominus} + RT\ln Q \quad [6A.10]\\ &= \left(-4.73\ \mathrm{kJ\ mol^{-1}}\right) + \left(2.4790\ \mathrm{kJ\ mol^{-1}}\right)\times \ln Q \qquad \text{at } 298.15\ \mathrm{K}\end{aligned}$$

The above equation is used to calculate $\Delta_r G$ values at the given Q values in the following table.

Part	Q	$\ln Q$	$\Delta_r G$ / kJ mol^{-1}
(i)	0.10	−2.303	−10.44
(ii)	1.0	0	−4.73
(iii)	10	2.303	+0.979
(iv)	100	4.605	+6.69

The above equation also indicates that a plot of $\ln Q$ against $\Delta_r G$ should be linear so points ii and iii, which straddle $\Delta_r G = 0$, can be used to perform a linear interpolation to find K from our equilibrium knowledge that $\ln Q = \ln Q_{\text{equilibrium}} = \ln K$ when $\Delta_r G = 0$. Performing the linear interpolation:

$$\begin{aligned}\ln Q &= \ln Q_{\text{ii}} + \left(\frac{\ln Q_{\text{iii}} - \ln Q_{\text{ii}}}{\Delta_r G_{\text{iii}} - \Delta_r G_{\text{ii}}}\right)\times\left(\Delta_r G - \Delta_r G_{\text{ii}}\right)\\ &= 0 + \left(\frac{2.303 - 0}{0.979 - (-4.73)}\right)\times\left(\frac{\Delta_r G}{\mathrm{kJ\ mol^{-1}}} - (-4.73)\right)\\ &= 0.4034\times\left(\frac{\Delta_r G}{\mathrm{kJ\ mol^{-1}}} + 4.73\right)\end{aligned}$$

Thus,

$$\begin{aligned}\ln K &= 0.4034\times(0 + 4.73)\\ &= 1.908\end{aligned}$$

$K = e^{1.908} = \boxed{6.74}$ from a two-point interpolation

The two-point interpolation is in agreement with the result given by eqn 6A.8:

$$\begin{aligned}K &= e^{-\Delta_r G^{\ominus}/RT} \quad [6A.8]\\ &= e^{-\left(-4.73\times 10^{3}\ \mathrm{J\ mol^{-1}}\right)/\left\{\left(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\times\left(298.15\ \mathrm{K}\right)\right\}}\\ &= 6.74\end{aligned}$$

6A.4(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $T = 298.15$ K, $p = 1$ bar $= p^{\ominus}$, $\alpha = 0.201$ at equilibrium
We draw up the following equilibrium table (Example 6A.2).

	$N_2O_4(g)$	$NO_2(g)$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$
Partial pressure	$\frac{(1-\alpha)p}{1+\alpha}$	$\frac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6A.13] = \left(\prod_J \left(p_J / p^{\ominus}\right)^{\nu_J}\right)_{\text{equilibrium}} \quad \text{(perfect gas assumption)}$$

$$= \frac{\left(p_{NO_2} / p^{\ominus}\right)^2}{p_{N_2O_4} / p^{\ominus}} = \frac{p_{NO_2}{}^2}{p_{N_2O_4} p^{\ominus}} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha}\right)p^{\ominus}}$$

$$= \frac{4p}{p^{\ominus}}\left\{\frac{\alpha^2}{(1-\alpha)\times(1+\alpha)}\right\} = 4\left\{\frac{(0.201)^2}{(1-0.201)\times(1+0.201)}\right\}$$

$$= \boxed{0.168}$$

6A.6(b) $CH_4(g) + 3\ Cl_2(g) \rightleftharpoons CHCl_3(l) + 3\ HCl(g)$

(i) Using data tables of the text *Resource section* at 25°C, we find

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(CHCl_3, l) + 3\ \Delta_f G^{\ominus}(HCl, g) - \Delta_f G^{\ominus}(CH_4, g)$$

$$= (-73.66\ \text{KJ mol}^{-1}) + (3)\times(-95.30\ \text{KJ mol}^{-1}) - (-50.72\ \text{KJ mol}^{-1})$$

$$= \boxed{-308.84\,\text{kJ mol}^{-1}}$$

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(CHCl_3, l) + 3\ \Delta_f H^{\ominus}(HCl, g) - \Delta_f H^{\ominus}(CH_4, g)$$

$$= (-134.47\ \text{kJ mol}^{-1}) + (3)\times(-92.31\ \text{kJ mol}^{-1}) - (-74.81\ \text{kJ mol}^{-1})$$

$$= -336.59\ \text{kJ mol}^{-1} \quad \text{[Used in part (ii)]}$$

$$\ln K = \frac{-\Delta_r G^\ominus}{RT}[6A.14] = \frac{-\left(-308.84\times10^3\ \mathrm{J\,mol^{-1}}\right)}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\ \mathrm{K})} = 124.6$$

$$K = \mathrm{e}^{124.6} = \boxed{1.30\times10^{54}}$$

(ii) $$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\quad [6A.22]$$

$$\ln K_{50°\mathrm{C}} = \ln K_{25°\mathrm{C}} - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323.15\ \mathrm{K}}-\frac{1}{298.15\ \mathrm{K}}\right)$$

$$= \ln\left(1.30\times10^{54}\right) - \left(\frac{-336.59\times10^3\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\right)\times\left(\frac{1}{323.15\ \mathrm{K}}-\frac{1}{298.15\ \mathrm{K}}\right) = 114.\overline{1}$$

$$K_{50°\mathrm{C}} = \mathrm{e}^{114.\overline{1}} = \boxed{3.57\times10^{49}}$$

As expected, the temperature increase causes a shift to the left when the reaction is exothermic.

$$\Delta_r G^\ominus = -RT\ln K\quad [6A.14]$$

$$\Delta_r G^\ominus_{50°\mathrm{C}} = -\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)\times\left(323.15\ \mathrm{K}\right)\ln\left(3.57\times10^{49}\right) = \boxed{-307\ \mathrm{kJ\ mol^{-1}}}$$

6A.8(b) Draw up the following table for the reaction equation: A + B $\rightleftharpoons$ C + 2 D.

	A	B	C	D	Total
Initial amounts / mol	2.00	1.00	0	3.00	6.00
Stated change / mol			+0.79		
Implied change / mol	–0.79	–0.79	+0.79	+1.58	
Equilibrium amounts / mol	1.21	0.21	0.79	4.58	6.79
Mole fractions	$0.178\overline{2}$	$0.030\overline{9}$	$0.116\overline{3}$	$0.674\overline{5}$	$0.999\overline{9}$

(i) Mole fractions are given in the table.

(ii) $$K_x = \prod_J x_J^{\nu_J}$$

$$K_x = \frac{(0.116\overline{3})\times(0.674\overline{5})^2}{(0.178\overline{2})\times(0.030\overline{9})} = \boxed{9.61}$$

(iii) $p_J = x_J p$. Assuming the gases are perfect, $a_J = p_J / p^\ominus$, so

$$K = \frac{(p_C/p^\ominus)\times(p_D/p^\ominus)^2}{(p_A/p^\ominus)\times(p_B/p^\ominus)} = K_x\left(\frac{p}{p^\ominus}\right) = K_x \quad \text{when } p = 1.00\ \text{bar}$$

$$K = K_x = \boxed{9.61}$$

(iv) $$\Delta_r G^\ominus = -RT\ln K = -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})\times\ln(9.61) = \boxed{-5.61\ \mathrm{kJ\ mol^{-1}}}$$

6B.1(b) At 1120 K, $\Delta_r G^\ominus = +22\times10^3\ \mathrm{J\ mol^{-1}}$

$$\ln K_1(1120\text{K}) = -\frac{\Delta_r G^{\ominus}}{RT}\ [6\text{A}.14] = -\frac{(22\times10^3\ \text{J mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(1120\ \text{K})} = -2.3\overline{63}$$

$$K = \text{e}^{-2.3\overline{63}} = 9.\overline{41}\times10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\ [6\text{B}.4]$$

Solve for T_2 at $\ln K_2 = 0$ ($K_2 = 1$).

$$\frac{1}{T_2} = \frac{R\ \ln K_1}{\Delta_r H^{\ominus}} + \frac{1}{T_1} = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(-2.3\overline{63})}{(125\times10^3\ \text{J mol}^{-1})} + \frac{1}{1120\ \text{K}} = 7.3\bar{6}\times10^{-4}$$

$$T_2 = \boxed{1.4\times10^3\ \text{K}}$$

6B.4(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K = 1.69\times10^{-3}$ at 2300 K

Initial modes: $n_{N_2} = \dfrac{5.0\ \text{g}}{28.013\ \text{g mol}^{-1}} = 0.17\overline{85}\ \text{mol}$

Initial moles: $n_{O_2} = \dfrac{2.0\ \text{g}}{32.00\ \text{g mol}^{-1}} = 6.2\overline{50}\times10^{-2}\ \text{mol}$

	N_2	O_2	NO	Total
Initial amount/mol	$n_{N_2} = 0.17\overline{85}$	$n_{O_2} = 0.062\bar{5}$	0	$n = 0.2410$
Change/mol	$-z$	$-z$	$+2z$	0
Equilibrium amount/mol	$n_{N_2} - z$	$n_{O_2} - z$	$2z$	$n = 0.2410$
Mole fractions	$\left(n_{N_2} - z\right)/n$	$\left(n_{O_2} - z\right)/n$	$2z/n$	1

$$K = K_x\left(\frac{p}{p^{\ominus}}\right)^{\Delta\nu} = K_x \quad \text{(Because } \Delta\nu = \sum_{J}\nu_J = 0 \text{ for this reaction. See Exercise 6B.3(a) or (b))}$$

$$K = \frac{(2z)^2}{\left(n_{N_2} - z\right)\times\left(n_{O_2} - z\right)}$$

$$\left(1 - {}^{4}\!/_{K}\right)z^2 - nz + n_{N_2}n_{O_2} = 0$$

$$z = \frac{n \pm \sqrt{n^2 - 4\left(1 - {}^{4}\!/_{K}\right)n_{N_2}n_{O_2}}}{2\left(1 - {}^{4}\!/_{K}\right)}$$

$$= \frac{0.2410 \pm \sqrt{0.2410^2 - 4\left(1 - {}^{4}\!/_{1.69\times10^{-3}}\right)(0.1785)(0.0625)}}{2\left(1 - {}^{4}\!/_{1.69\times10^{-3}}\right)}$$

$$= -2.223\times10^{-3} \text{ or } 2.121\times10^{-3}$$

$$= 2.121\times10^{-3} \quad \text{because the negative value is non-physical.}$$

$$x_{NO} = \frac{2z}{n} = \frac{2(2.121\times10^{-3})}{0.24\bar{1}} = \boxed{1.8\times10^{-2}}$$

6B.7(b) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ Vapor pressures: $p_{427°C} = 608$ kPa and $p_{459°C} = 1115$ kPa

The gases originate from the dissociation of the solid alone so $p_{NH_3} = p_{HCl} = \tfrac{1}{2}p$.

(i) Equilibrium constants

$$K = \left(p_{NH_3}/p^{\ominus}\right)\times\left(p_{HCl}/p^{\ominus}\right) \quad \text{[Perfect gas assumption]}$$

$$= \left(\tfrac{1}{2}p/p^{\ominus}\right)\times\left(\tfrac{1}{2}p/p^{\ominus}\right)$$

$$= \tfrac{1}{4}\left(p/p^{\ominus}\right)^2$$

$$K_{427°C} = \tfrac{1}{4}\left(608\ \text{kPa}/100\ \text{kPa}\right)^2 = \boxed{9.24}$$

$$K_{459°C} = \tfrac{1}{4}\left(1115\ \text{kPa}/100\ \text{kPa}\right)^2 = 31.08$$

(ii) $\Delta G^{\ominus} = -RT\ln K$ [6A.14]

$$\Delta_r G^{\ominus}_{427°C} = -\left(8.3145\ \text{J K}^{-1}\text{mol}^{-1}\right)\times(700.15\ \text{K})\times\ln(9.24) = \boxed{-12.9\ \text{kJ mol}^{-1}}$$

(iii) $\ln\dfrac{K_2}{K_1} = -\dfrac{\Delta_r H^{\ominus}}{R}\left(\dfrac{1}{T_2}-\dfrac{1}{T_1}\right)$ [6B.4]

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

$$= \left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\left(\frac{1}{700.15\ \text{K}}-\frac{1}{732.15\ \text{K}}\right)^{-1}\times\ln\left(\frac{31.08}{9.24}\right)$$

$$= \boxed{162\ \text{kJ mol}^{-1}}$$

(iv) $\Delta_r S^{\ominus} = \dfrac{\Delta_r H^{\ominus}-\Delta_r G^{\ominus}}{T} = \dfrac{(162\ \text{kJ mol}^{-1})-(-12.9\ \text{kJ mol}^{-1})}{700.15\ \text{K}} = \boxed{+250\ \text{J K}^{-1}\ \text{mol}^{-1}}$