2

Internal energy

2A Internal energy

Answers to discussion questions

D2A.2 Work is done when a body is moves against an opposing force. For an infinitesimal displacement in the x-direction, $\mathrm{d}x$, against a force F along that direction the work done by the body is $F\,\mathrm{d}x$.

When the energy of a system changes as a result of a temperature difference between the system and its surroundings, the resulting energy transfer from the hotter to the cooler body is described as heat. In thermodynamic terms, both heat and work cause the internal energy of an object to change: if heat 'flows in' the internal energy of the body rises, if the body 'does work', its internal energy decreases.

If the internal energy of an object increases, this is interpreted in molecular terms as the molecules moving up to higher energy levels. If the molecules drop down to lower levels the resulting energy is available as heat or work.

D2A.4 A reversible gas expansion is one in which the direction of the process can be reversed by an infinitesimal change in the external pressure. This is achieved if the external pressure is altered so that it is only ever infinitesimally different from the pressure of the gas which is expanding or contracting. In other words, the external pressure must always match the pressure of the expanding/contracting gas.

Solutions to exercises

E2A.1(b) *The chemist's toolkit* 7 in Topic 2A gives an explanation of the equipartition theorem. The molar internal energy is given by

$$U_\mathrm{m} = \tfrac{1}{2} \times (\nu_\mathrm{t} + \nu_\mathrm{r} + 2\nu_\mathrm{v}) \times RT$$

where ν_t is the number of translational degrees of freedom, ν_r is the number of rotational degrees of freedom and ν_v is the number of vibrational degrees of freedom. As each gas molecule can move independently along the x, y and z axis, the number of translational degrees of freedom is three. All the listed molecules have three degrees of rotational freedom and none of them is expected to have any vibrational modes which are significantly excited at room temperature. Therefore, at room temperature, ozone, ethane and sulfur dioxide are all expected to have an approximate molar internal energy of

$$U_m = \tfrac{1}{2}\times(3+2+0)\times RT = 3\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\,\mathrm{K}) = \boxed{7.4\,\mathrm{kJ\,mol^{-1}}}$$

E2A.2(b) A state function is a property with a value that depends only on the current state of the system and is independent of how the state has been prepared. Volume, internal energy and density are all state functions.

E2A.3(b) The system is expanding against a constant external pressure, hence the expansion work is given by [2A.6–*40*], $w = -p_{ex}\Delta V$. The change in volume is the cross-sectional area times the linear displacement

$$\Delta V = (75\ \mathrm{cm^2})\times(25\ \mathrm{cm}) = 1875\ \mathrm{cm^3} = 1.87...\times10^{-3}\ \mathrm{m^3}$$

The external pressure is 150 kPa = 1.50×10^5 Pa, therefore the expansion work is

$$w = -(1.50\times10^5\ \mathrm{Pa})\times(1.87...\times10^{-3}\ \mathrm{m^3}) = \boxed{-281\ \mathrm{J}}$$

Note that the volume is expressed in $\mathrm{m^3}$. The relationships $1\ \mathrm{Pa} = 1\ \mathrm{kg\,m^{-1}\,s^{-2}}$ and $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$ are used to verify the units of the result.

E2A.4(b) For all cases $\Delta U = 0$, because the internal energy of a perfect gas depends on the temperature alone.

(i) The work of reversible isothermal expansion of a perfect gas is given by [2A.9–*41*]

$$\begin{aligned} w &= -nRT\ln\left(\frac{V_f}{V_i}\right) \\ &= -(2.00\ \mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(273.15\ \mathrm{K})\times\ln\left(\frac{20.0\ \mathrm{dm^3}}{5.0\ \mathrm{dm^3}}\right) \\ &= -6.3\times10^3\ \mathrm{J} = \boxed{-6.3\ \mathrm{kJ}} \end{aligned}$$

Note that the temperature is expressed in K in the above equation. Using the First Law of thermodynamics, [2A.2–*38*], gives

$$q = \Delta U - w = 0 - (-2.68\ \mathrm{kJ}) = \boxed{+2.68\ \ \mathrm{kJ}}$$

(ii) The final pressure of the expanding gas is found using the perfect gas law, [1A.4–*8*]

$$\begin{aligned} p_f &= \frac{nRT}{V_f} = \frac{(2.00\ \mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(273.15\ \mathrm{K})}{(20.0\times10^{-3}\ \mathrm{m^3})} \\ &= 2.27...\times10^5\ \mathrm{Pa} \end{aligned}$$

This pressure equals the constant external pressure against which the gas is expanding, therefore the work of expansion is

$$\begin{aligned} w &= -p_{\text{ex}} \times \Delta V = (2.27... \times 10^5\ \text{Pa}) \times (20.0 \times 10^{-3}\ \text{m}^3 - 5.0 \times 10^{-3}\ \text{m}^3) \\ &= -3.41 \times 10^3\ \text{J} = \boxed{-3.41\ \text{kJ}} \end{aligned}$$

and hence $q = \boxed{+3.41\ \text{kJ}}$

(iii) Free expansion is expansion against zero force, so $\boxed{w = 0}$ and therefore $\boxed{q = 0}$ as well.

E2A.5(b) For a perfect gas at constant volume $p_{\text{i}}/T_{\text{i}} = p_{\text{f}}/T_{\text{f}}$ therefore,

$$p_{\text{f}} = p_{\text{i}} \times \frac{T_{\text{f}}}{T_{\text{i}}} = (111\ \text{kPa}) \times \left(\frac{356\ \text{K}}{277\ \text{K}}\right) = \boxed{143\ \text{kPa}}$$

The change in internal energy at constant volume is given by [2A.15b–*45*]

$$\begin{aligned} \Delta U &= nC_{V,\text{m}}\Delta T = (2.00\ \text{mol}) \times \left(\frac{5}{2} \times 8.3145\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\right) \times (356\ \text{K} - 277\ \text{K}) \\ &= +3.28 \times 10^3\ \text{J} = \boxed{+3.28\ \text{kJ}} \end{aligned}$$

The volume of the gas is constant, so the work of expansion is zero, $\boxed{w = 0}$. The First Law of thermodynamics gives $q = \Delta U - w = +3.28\ \text{kJ} - 0 = \boxed{+3.28\ \text{kJ}}$.

E2A.6(b) (i) The work of expansion against constant external pressure is given by [2A.6–*40*], $w = -p_{\text{ex}}\Delta V = -(7.7\ \text{kPa}) \times (2.5\ \text{dm}^3) = \boxed{-19\ \text{J}}$.

(ii) The work done in a reversible, isothermal expansion is given by [2A.9–*41*] $w = -nRT\ln(V_{\text{f}}/V_{\text{i}})$. The amount in moles of argon is

$$\begin{aligned} n &= \frac{m}{M} = \frac{(6.56\ \text{g})}{(39.95\ \text{g}\,\text{mol}^{-1})} = 0.164...\ \text{mol} \\ w &= -(0.164...\ \text{mol}) \times (8.3145\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (305\ \text{K}) \\ &\quad \times \ln\left(\frac{[18.5 + 2.5]\ \text{dm}^3}{18.5\ \text{dm}^3}\right) = \boxed{-53\ \text{J}} \end{aligned}$$

Note that the modulus of the work done in a reversible expansion is greater than the work for expansion against constant external pressure because the latter is an irreversible process.

Solutions to problems

P2A.2 The First Law of thermodynamics states that $\Delta U = q + w$. Work is done on the electric heater, so $w = +1$ kJ. Heat is transferred to the surroundings, so $q = -1$ kJ. Therefore overall

$$\Delta U = q + w = (-1\ \text{kJ}) + (1\ \text{kJ}) = \boxed{0}$$

P2A.4 (a) $n = x/l = (90\ \text{nm})/(45\ \text{nm}) = 2.0$ therefore $\nu = n/N = 2.0/200 = 0.01$

$$F = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)$$

$$= \frac{(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298.15\ \text{K})}{(2\times45\times10^{-9}\ \text{m})}\times\ln\left(\frac{1+0.01}{1-0.01}\right) = \boxed{9.1\times10^{-16}\ \text{N}}$$

(b) The equation to be plotted is $F/\text{N} = 4.57\times10^{-14}\ln\left[(1+\nu)/(1-\nu)\right]$; this is shown in Fig. 2.1.

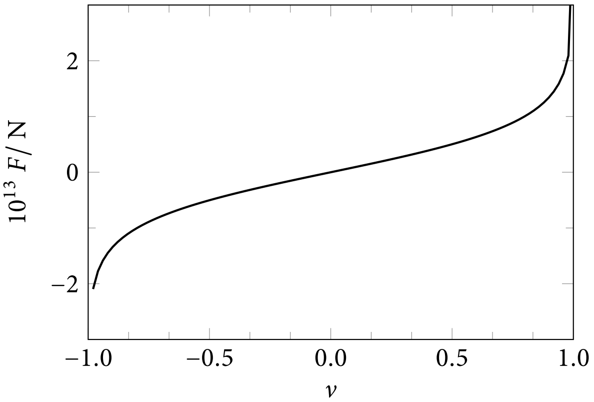

Figure 2.1

The natural logarithm can be expanded using the Taylor series as $\ln(1+\nu) \approx \nu + \nu^2/2! + \nu^3/3! + \ldots$, which, for $\nu \ll 1$, can be approximated as $\ln(1+\nu) \approx \nu$, and similarly, $\ln(1-\nu) \approx -\nu$. Therefore,

$$F = \frac{kT}{2l}[\ln(1+\nu) - \ln(1-\nu)] \approx \frac{kT}{2l}[\nu - (-\nu)] = \frac{\nu kT}{l}$$

Because $\nu = n/N$, it follows that

$$F = \frac{\nu kT}{l} = \frac{nkT}{Nl}$$

Hooke's law predicts $F = \text{const}\times x$, that is the restoring force is directly proportional to the displacement. Using $n = x/l$, the expression for the force obtained in part (a) is rewritten as

$$\frac{nkT}{Nl} = \frac{kTx}{Nl^2} \equiv \text{const}\times x$$

Therefore Hooke's law applies and kT/Nl^2 is the force constant.

(c)

$$\mathrm{d}w = F\,\mathrm{d}x = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)\mathrm{d}x = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)(Nl\,\mathrm{d}\nu)$$

$$= \frac{NkT}{2}\ln\left(\frac{1+\nu}{1-\nu}\right)\mathrm{d}\nu$$

Integrating both sides and using $\int \ln(1 \pm x)\,\mathrm{d}x = (x \pm 1)\ln(1 \pm x) - x$ gives

$$\begin{aligned}
\int \mathrm{d}w &= \frac{NkT}{2}\int_0^{V_\mathrm{f}} \ln\left(\frac{1+\nu}{1-\nu}\right)\mathrm{d}\nu \\
w &= \frac{NkT}{2}\left[(\nu+1)\ln(1+\nu) + \nu - (\nu-1)\ln(1-\nu) - \nu\right]_0^{\nu_\mathrm{f}} \\
&= \frac{NkT}{2}\left[\ln(1+\nu)(1-\nu) + \nu\ln\left(\frac{1+\nu}{1-\nu}\right)\right]_0^{\nu_\mathrm{f}} \\
&= \frac{NkT}{2}\left[\ln(1+\nu_\mathrm{f})(1-\nu_\mathrm{f}) + \nu_\mathrm{f}\ln\left(\frac{1+\nu_\mathrm{f}}{1-\nu_\mathrm{f}}\right)\right]
\end{aligned}$$

P2A.6 The expansion work is given by [2A.6–*40*], $\mathrm{d}w = -p_\mathrm{ex}\mathrm{d}V$. For a reversible expansion p_ex is always equal to the pressure of the gas so

$$\mathrm{d}w = -p_\mathrm{gas}\mathrm{d}V = -\left(\frac{nRT}{V} - \frac{n^2a}{V^2}\right)\mathrm{d}V$$

Integrating both sides gives

$$\begin{aligned}
w &= \int_{V_\mathrm{i}}^{V_\mathrm{f}} -\left(\frac{nRT}{V} - \frac{n^2a}{V^2}\right)\mathrm{d}V \\
&= \left[-nRT\ln V - \frac{n^2a}{V}\right]_{V_\mathrm{i}}^{V_\mathrm{f}} = -nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) - n^2a\left(\frac{1}{V_\mathrm{f}} - \frac{1}{V_\mathrm{i}}\right)
\end{aligned}$$

The work done on the surroundings is the opposite of the work done on the gas.

$$w_\mathrm{surr} = nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) + n^2a\left(\frac{1}{V_\mathrm{f}} - \frac{1}{V_\mathrm{i}}\right)$$

The first term is identical to the work done on the surroundings by a perfect gas expanding under reversible isothermal conditions. $V_\mathrm{f} > V_\mathrm{i}$, therefore $n^2a(1/V_\mathrm{f} - 1/V_\mathrm{i})$ is negative, so the overall work done on the surroundings by the gas is smaller than it would be for a perfect gas. The attraction between the gas molecules has to be overcome when expanding, meaning that less energy is available as work.

P2A.8 Decomposition of 1.0 mol of calcium carbonate liberates 1.0 mol of carbon dioxide. In either case the expansion is against constant external atmospheric pressure, $p_\mathrm{ex} = 1.0\,\mathrm{atm} = 1.01325 \times 10^5\,\mathrm{Pa}$. The final volume of the expanding gas is found using the perfect gas equation, $V = nRT/p_\mathrm{ex}$. The change in volume of the solid is negligible compared to the change in volume due to the formation of the gas, therefore the overall change in volume of the system is $\Delta V = V$. The work against constant external pressure is

$$\begin{aligned}
w &= -p_\mathrm{ex}\Delta V = -p_\mathrm{ex} \times \frac{nRT}{p_\mathrm{ex}} = -nRT = -(1.0\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \\
&\quad \times ([800 + 273.15]\,\mathrm{K}) = -8.9 \times 10^3\,\mathrm{J} = \boxed{-8.9\,\mathrm{kJ}}
\end{aligned}$$

P2A.10 The reduced pressure of a van der Waals gas is given by [1C.9–*26*]

$$p_\mathrm{r}=\frac{8T_\mathrm{r}n}{3V_\mathrm{r}-1}-\frac{3n}{V_\mathrm{r}^2}$$

The reduced volume, pressure and temperature are given in terms of the van der Waals parameters in [1C.7–*26*] and [1C.8–*26*], $V_\mathrm{m,r}=V_\mathrm{m}/V_\mathrm{c}=V_\mathrm{m}/(3b)$, $p_\mathrm{r}=p/p_\mathrm{c}=27b^2p/a$ and $T_\mathrm{r}=T/T_\mathrm{c}=27RbT/8a$. In *Problem* P2A.7 the work done during the isothermal reversible expansion of a van der Waals gas is found as

$$w=-nRT\ln\left(\frac{V_\mathrm{f}-nb}{V_\mathrm{i}-nb}\right)-n^2a\left(\frac{1}{V_\mathrm{f}}-\frac{1}{V_\mathrm{i}}\right)$$

This expression is first rewritten in term of the molar volume and then in terms of the reduced volume, temperature and pressure.

$$\begin{aligned}w&=-nRT\ln\left(\frac{nV_\mathrm{m,f}-nb}{nV_\mathrm{m,i}-nb}\right)-n^2a\left(\frac{1}{nV_\mathrm{m,f}}-\frac{1}{nV_\mathrm{m,i}}\right)\\&=-nRT\ln\left(\frac{V_\mathrm{m,f}-b}{V_\mathrm{m,i}-b}\right)-na\left(\frac{1}{V_\mathrm{m,f}}-\frac{1}{V_\mathrm{m,i}}\right)\\&=-nR\left(\frac{8a}{27Rb}\right)T_\mathrm{r}\ln\left(\frac{3bV_\mathrm{r,f}-b}{3bV_\mathrm{r,i}-b}\right)-na\left(\frac{1}{3bV_\mathrm{r,f}}-\frac{1}{3bV_\mathrm{r,i}}\right)\\&=-n\left(\frac{8a}{27b}\right)T_\mathrm{r}\ln\left(\frac{3V_\mathrm{r,f}-1}{3V_\mathrm{r,i}-1}\right)-\frac{na}{3b}\left(\frac{1}{V_\mathrm{r,f}}-\frac{1}{V_\mathrm{r,i}}\right)\end{aligned}$$

The reduced work is defined as $w_\mathrm{r}=(3b/a)w$, with this it follows that

$$w_\mathrm{r}=-n\left(\frac{8}{9}\right)T_\mathrm{r}\ln\left(\frac{3V_\mathrm{r,f}-1}{3V_\mathrm{r,i}-1}\right)-n\left(\frac{1}{V_\mathrm{r,f}}-\frac{1}{V_\mathrm{r,i}}\right)$$

For expansion along the critical isotherm from $V_\mathrm{m,i}=V_\mathrm{c}$ to $V_\mathrm{m,f}=xV_\mathrm{c}$. It follows that $V_\mathrm{r,i}=V_\mathrm{m,i}/V_\mathrm{c}=V_\mathrm{c}/V_\mathrm{c}=1$ and $V_\mathrm{r,f}=V_\mathrm{m,f}/V_\mathrm{c}=xV_\mathrm{c}/V_\mathrm{c}=x$. Along the critical isotherm $T_\mathrm{c}=1$, therefore w_r is

$$w_\mathrm{r}=-n\left(\frac{8}{9}\right)\ln\left(\frac{3x-1}{2}\right)-n\left(\frac{1}{x}-1\right)$$

2B Enthalpy

Answers to discussion questions

D2B.2 If a substance is heated at constant volume all of the energy as heat is transformed into internal energy of the substance. If the same process is carried out under conditions of constant pressure some of the energy as heat will be used to expand the substance against the external pressure and so less of the energy as heat is transformed into internal energy. This effect is largest for gases whose volumes change much more rapidly with temperature than do solids or liquids.

The temperature of a substance is related to its internal energy, and therefore as energy as heat is supplied the temperature increases. For a given amount of energy as heat this increase in internal energy is smaller for the constant-pressure case than for the constant-volume case. Therefore the rise in temperate is smaller for the constant-pressure process, and this implies that the heat capacity is greater.

Solutions to exercises

E2B.1(b) The heat transferred under constant pressure equals the change in enthalpy of the system, [2B.2b–*47*], $q_\mathrm{p} = \Delta H$. The relationship between the change in enthalpy, change in temperature and the heat capacity is given by [2B.6b–*49*]

$$C_{p,\mathrm{m}} = \frac{\Delta H}{n\Delta T} = \frac{(178\,\mathrm{J})}{(1.9\,\mathrm{mol}) \times (1.78\,\mathrm{K})} = 52.6...\,\mathrm{J\,K\,mol^{-1}} = \boxed{53\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

For a perfect gas $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$, [2B.9–*49*], therefore

$$C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R = (52.6...\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{44\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E2B.2(b) There is no change in the number of gaseous species on going from reactants to products, therefore $\Delta n_\mathrm{g} = 0$ and $\Delta H_\mathrm{m} = \Delta U_\mathrm{m}$.

E2B.3(b) (i) The heat capacity can be expressed as $C_p = a + bT$ where $a = 20.17\,\mathrm{J\,K^{-1}}$ and $b = 0.3665\,\mathrm{J\,K^{-2}}$. Integrating the relationship $\mathrm{d}H = C_p\mathrm{d}T$ on both sides gives

$$\int_{T_1}^{T_2} \mathrm{d}H = \int_{T_1}^{T_2} C_p \mathrm{d}T = \int_{T_1}^{T_2} (a + bT)\mathrm{d}T = \left[aT + \tfrac{1}{2}bT^2\right]_{T_1}^{T_2}$$

$$\begin{aligned} H(T_2) - H(T_1) &= na(T_2 - T_1) + \frac{1}{2}nb(T_2^2 - T_1^2) \\ &= (20.17\,\mathrm{J\,K^{-1}}) \times (373.15\,\mathrm{K} - 298.15\,\mathrm{K}) \\ &\quad + \tfrac{1}{2} \times (0.4001\,\mathrm{J\,K^{-2}}) \times [(373.15\,\mathrm{K})^2 - (298.15\,\mathrm{K})^2] \\ &= +11.5...\,\mathrm{kJ} = \boxed{+11.6\,\mathrm{kJ}} \end{aligned}$$

Under constant pressure conditions $\Delta H = \boxed{q_\mathrm{p} = +11.6\,\mathrm{kJ}}$.
The work of expansion against constant pressure p_ex is given by [2A.6–*40*], $w = -p_\mathrm{ex}\Delta V = -p_\mathrm{ex}(V_\mathrm{f} - V_\mathrm{i})$. Assume that the gas is in mechanical equilibrium with its surroundings, therefore p_ex is the same as the pressure of the gas, p. The initial and final volumes are calculated from T_f and T_i by $V_\mathrm{f} = nRT_\mathrm{f}/p$ and $V_\mathrm{i} = nRT_\mathrm{i}/p$, therefore $V_\mathrm{f} - V_\mathrm{i} = (T_\mathrm{f} - T_\mathrm{i})nR/p$. Hence

$$\begin{aligned} w &= -p \times \frac{nR}{p}(T_\mathrm{f} - T_\mathrm{i}) = -nR\Delta T \\ &= -(1.00\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (373.15\,\mathrm{K} - 298.15\,\mathrm{K}) \\ &= -6.23... \times 10^2\,\mathrm{J} = \boxed{-624\,\mathrm{J}} \end{aligned}$$

$$\Delta U = q + w = (+11.6...\,\mathrm{kJ}) + (-0.623...\,\mathrm{kJ}) = \boxed{+11.0\,\mathrm{kJ}}$$

(ii) The energy and enthalpy of a perfect gas depends on the temperature alone, hence ΔH and ΔU is the same as above, $\boxed{\Delta H = \Delta U = +11.6\ \text{kJ}}$. Under constant volume conditions there is no expansion work, $\boxed{w = 0}$, therefore the heat is equal to the change in internal energy, $q_V = \Delta U = \boxed{+11.0\ \text{kJ}}$.

E2B.4(b) Under constant pressure $q_p = \Delta H$, therefore

$$\begin{aligned} q_p = \Delta H = nC_{p,\text{m}}\Delta T &= (2.0\ \text{mol}) \times (37.11\ \text{J K mol}^{-1}) \times (277\ \text{K} - 250\ \text{K}) \\ &= 2.00...\ \text{kJ} = \boxed{+2.0\ \text{kJ}} \end{aligned}$$

The definition of enthalpy is given by [2B.1–*46*], $H = U + pV$. For a change at constant pressure, it follows that $\Delta H = \Delta U + p\Delta V$, where $\Delta V = V_\text{f} - V_\text{i}$. If the gas is assumed to be perfect, then $V_\text{f} = nRT_\text{f}/p$ and $V_\text{i} = nRT_\text{i}/p$, so $\Delta V = (T_\text{f} - T_\text{i})nR/p$. Hence $p\Delta V = nR(T_\text{f} - T_\text{i}) = nR\Delta T$.

$$\begin{aligned} \Delta U &= \Delta H - nR\Delta T \\ &= (2.0...\ \text{kJ}) - (2.0\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (277\ \text{K} - 250\ \text{K}) \\ &= \boxed{+1.6\ \text{kJ}} \end{aligned}$$

Solutions to problems

P2B.2 The volume of the room is $V = (5.5\ \text{m}) \times (6.5\ \text{m}) \times (3.0\ \text{m}) = 107.25\ \text{m}^3$. Using 1 atm = 1.01325×10^5 Pa, the amount in moles of gas in the room initially is

$$n = \frac{pV}{RT} = \frac{(1.01325 \times 10^5\ \text{Pa}) \times (107.25\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})} = 4.38... \times 10^3\ \text{mol}$$

Assuming that the heat is transferred under constant pressure

$$q_p = nC_{p,\text{m}}\Delta T = (4.38... \times 10^3\ \text{mol}) \times (21\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (10\ \text{K}) = 9.21 \times 10^5\ \text{J}$$

The time needed to transfer this heat is $\Delta t = (9.21... \times 10^5\ \text{J})/(1500\ \text{J s}^{-1}) = \boxed{6.1 \times 10^2\ \text{s}}$.

P2B.4 Fitting the data set using a computer program to an expression in the form of $C^\ominus_{p,\text{m}}(T) = a + bT + cT^{-2}$ yields $a = 28.8\ \text{J K}^{-1}\ \text{mol}^{-1}$, $b = 2.79 \times 10^{-2}\ \text{J K}^{-2}\ \text{mol}^{-1}$ and $c = -1.51 \times 10^5\ \text{J K mol}^{-1}$. Fitting the data set to an expression in the form of $C^\ominus_{p,\text{m}}(T) = \alpha + \beta T + \gamma T^2$ yields $\alpha = 24.6\ \text{J K}^{-1}\ \text{mol}^{-1}$, $\beta = 3.83 \times 10^{-2}\ \text{J K}^{-2}\ \text{mol}^{-1}$ and $\gamma = -6.58 \times 10^{-6}\ \text{J K}^{-3}\ \text{mol}^{-1}$. This second expression gives a slightly better fit to the data set than the first expression.

2C Thermochemistry

Answers to discussion questions

D2C.2 When a system is subjected to constant pressure conditions, and only expansion work can occur, the energy supplied as heat is the change in enthalpy of the system. Thus enthalpy changes in the system can be determined by measuring the amount of heat supplied under constant-pressure conditions.

A very simple example often encountered in elementary laboratory classes is a thermally insulated vessel (for example, a foam plastic coffee cup) left open to the atmosphere: the heat released in the reaction is determined by measuring the change in temperature of the contents.

For a combustion reaction a constant-pressure flame calorimeter (Section 2B.1(b) on page 47) may be used. In this apparatus a certain amount of substance burns in a supply of oxygen and the rise in temperature is monitored. More sophisticated methods include isothermal titration calorimetry and differential scanning calorimetry, both described in Section 2C.4 on page 56.

D2C.4 The main objection to the use of the term 'heat' to describe the energy change associated with a physical or chemical process is that heat is not a state function. The value of the heat therefore depends on the path chosen.

If, in fact, the processes being described takes place at constant pressure, the heat is equal to the enthalpy change. Because enthalpy is a state function, the heat measured under these circumstance is a property of the physical or chemical change itself, and not affected by the path taken, and so is a meaningful and useful quantity to discuss.

It is more appropriate to talk about the enthalpy change, the change in a state function, rather to talk about the heat which, because of an unstated restriction, just so happens to have the same value.

Solutions to exercises

E2C.1(b) Ethanol is vaporized at constant pressure, therefore $q = \Delta H$.

$$q = \Delta H = n\Delta_{\text{vap}}H^{\ominus} = (1.75\ \text{mol}) \times (43.5\ \text{kJ mol}^{-1}) = +76.1...\ \text{kJ} = \boxed{+76.1\ \text{kJ}}$$

The work of expansion under constant pressure is given by [2A.6–*40*], $w = -p_{\text{ex}}\Delta V$. Note that $\Delta V = V_{\text{f}}$ because the final state (gas) has a much larger volume than the initial state (liquid). The perfect gas law is used to calculate V_{f}.

$$\begin{aligned} w &= -p_{\text{ex}}\Delta V = -p_{\text{ex}}(V_{\text{f}} - V_{\text{i}}) \approx -p_{\text{ex}}V_{\text{f}} = -p_{\text{ex}} \times \frac{nRT}{p_{\text{ex}}} = -nRT \\ &= -(1.75\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (260\ \text{K}) = -3.78...\ \text{kJ} = \boxed{-3.78\ \text{kJ}} \end{aligned}$$

The First Law of thermodynamics [2A.2–*38*] gives

$$\Delta U = q + w = (+76.1\ \text{kJ}) + (-3.78...\ \text{kJ}) = \boxed{+72.3\ \text{kJ}}$$

E2C.2(b) The chemical equation for combustion of phenol is $C_6H_6O(s) + 7\,O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$. The standard enthalpy of combustion is calculated using [2C.5a–*55*] and using values for the standard enthalpies of formation from Table 2C.7.

$$\begin{aligned}\Delta_c H^\ominus &= \sum_{\text{products}} \nu\Delta_f H^\ominus - \sum_{\text{reactants}} \nu\Delta_f H^\ominus\\ &= 6\Delta_f H^\ominus(CO_2,g) + 3\Delta_f H^\ominus(H_2O,l) - 7\Delta_f H^\ominus(O_2,g) - \Delta_f H^\ominus(C_6H_6O,s)\\ &= 6\times(-393.51\ \text{kJ mol}^{-1}) + 3\times(-285.83\ \text{kJ mol}^{-1})\\ &\quad -0-(-165.0\ \text{kJ mol}^{-1}) = \boxed{-3054\ \text{kJ mol}^{-1}}\end{aligned}$$

E2C.3(b) The standard enthalpy of formation of HI(aq) is $\Delta_r H^\ominus$ for the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \longrightarrow HI(aq)$$

Because HI is a strong acid, the reaction is effectively

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \longrightarrow H^+(aq) + I^-(aq)$$

By definition, $\Delta_f H^\ominus(H^+,aq) = 0$, so $\Delta_r H^\ominus$ for this reaction is $\Delta_f H^\ominus(I^-,aq)$.

$$\Delta_r H^\ominus = \Delta_f H^\ominus(I^-,aq) = \boxed{-55\ \text{kJ mol}^{-1}}$$

E2C.4(b) The equation for combustion of anthracene is $C_{14}H_{10}(s) + \frac{33}{2}\,O_2(g) \longrightarrow 14\,CO_2(g) + 5\,H_2O(l)$. In a bomb calorimeter the heat is at constant volume and is given by $q_V = n\Delta_c U^\ominus$. $\Delta_c U^\ominus$ is related to $\Delta_c H^\ominus$ by [2B.3–*48*], $\Delta_r H^\ominus = \Delta_r U^\ominus + \Delta n_g RT$, where Δn_g is the change in the amount of gas molecules in the reaction. In this case $\Delta n_g = 16.5\ \text{mol} - 14\ \text{mol} = -2.5\ \text{mol}$, hence

$$\begin{aligned}\Delta_c U^\ominus &= \Delta_c H^\ominus - \Delta n_g RT\\ &= (-7.06...\times 10^6\ \text{J}) - (-2.5\ \text{mol})\times(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1})\times(298\ \text{K})\\ &= -7.05...\times 10^3\ \text{kJ mol}^{-1}\end{aligned}$$

The heat released in the bomb calorimeter on combustion of 2.25 mg of anthracene ($M = 178.219\ \text{g mol}^{-1}$) is

$$q_V = n\Delta_c U^\ominus = \left(\frac{2.25\times 10^{-3}\ \text{g}}{178.219\ \text{g mol}^{-1}}\right)\times(-7.05...\times 10^3\ \text{kJ mol}^{-1}) = -8.90...\times 10^{-2}\ \text{kJ}$$

Therefore the calorimeter constant is

$$C = \frac{|q_V|}{\Delta T} = \frac{(8.90\ ...\times 10^{-2}\ \text{kJ})}{(1.75\ \text{K})} = 5.08...\times 10^{-2}\ \text{kJ K}^{-1} = \boxed{5.09\times 10^{-2}\ \text{kJ K}^{-1}}$$

The chemical equation for combustion of phenol is $C_6H_6O(s) + 7\,O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$. Following the same logic as above, $\Delta_c H^\ominus = -3054\ \text{kJ mol}^{-1}$,

$\Delta n_g = -1$ mol and $\Delta_c U^\ominus = -3.05... \times 10^3$ kJ mol^{-1}. The heat released on combustion of 125 mg of phenol ($M = 94.10$ g mol^{-1}) is

$$q_V = n\Delta_c U^\ominus = \left(\frac{0.125\ \text{g}}{94.1074\ \text{g mol}^{-1}}\right) \times (-3.05... \times 10^3\ \text{kJ mol}^{-1}) = -4.05...\ \text{kJ}$$

Therefore $\Delta T = |q_V|/C = (4.05...\ \text{kJ})/(5.08... \times 10^{-2}\text{kJ K}^{-1}) = \boxed{+79.6\ \text{K}}$

E2C.5(b) (i) Reaction(3) is reaction(2) − 2 × reaction(1), therefore

$$\begin{aligned}\Delta_r H^\ominus(3) &= \Delta_r H^\ominus(2) - 2\Delta_r H^\ominus(1)\\ &= (-483.64\ \text{kJ mol}^{-1}) - 2 \times (+52.96\ \text{kJ mol}^{-1})\\ &= \boxed{-589.56\ \text{kJ mol}^{-1}}\end{aligned}$$

The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction Δn_g = 2 mol + 2 mol − 4 mol − 1 mol = −1 mol

$$\begin{aligned}\Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT\\ &= (-589.56 \times 10^3\ \text{J mol}^{-1})\\ &\quad - (-3.0\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) = \boxed{-582\ \text{kJ mol}^{-1}}\end{aligned}$$

(ii) Reaction(1) represents the formation of 2 moles of HI(g) from its elements in their reference states, therefore the standard enthalpy of formation of HI(g) is

$$\Delta_f H^\ominus(\text{HI, g}) = \tfrac{1}{2}\Delta_r H^\ominus(1) = \tfrac{1}{2} \times (+52.96\ \text{kJ mol}^{-1}) = \boxed{+26.48\ \text{kJ mol}^{-1}}$$

Reaction(2) represents the formation of 2 moles of H_2O(g) from its elements in their reference states, therefore

$$\Delta_f H^\ominus(\text{H}_2\text{O, g}) = \tfrac{1}{2}\Delta_r H^\ominus(2) = \tfrac{1}{2}\times(-483.64\ \text{kJ mol}^{-1}) = \boxed{-241.82\ \text{kJ mol}^{-1}}$$

E2C.6(b) The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction Δn_g = 14 mol + 6 mol − 15 mol = +5 mol

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r U^\ominus + \Delta n_g RT\\ &= (-772.7 \times 10^3\ \text{J mol}^{-1}) + (+5.0\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})\\ &= \boxed{-760.3\ \text{kJ mol}^{-1}}\end{aligned}$$

E2C.7(b) The following reactions are used to construct a thermodynamic cycle which gives the standard enthalpy of hydrogenation of ethyne to ethene.

	reaction	$\Delta_r H^{\ominus}/\mathrm{kJ\,mol^{-1}}$
(1)	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1300
(2)	$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$	−1411
(3)	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.83
(4)	$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$	$\Delta_r H^{\ominus}(4)$

$$\begin{aligned}\Delta_r H^{\ominus}(4) &= \Delta_r H^{\ominus}(1) + \Delta_r H^{\ominus}(3) - \Delta_r H^{\ominus}(2)\\ &= (-1300\ \mathrm{kJ\,mol^{-1}}) + (-285.83\ \mathrm{kJ\,mol^{-1}}) - (-1411\ \mathrm{kJ\,mol^{-1}})\\ &= \boxed{-174.83\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction $\Delta n_g = 1\ \mathrm{mol} - 1\ \mathrm{mol} - 1\ \mathrm{mol} = -1\ \mathrm{mol}$

$$\begin{aligned}\Delta_r U^{\ominus}(298\ \mathrm{K}) &= \Delta_r H^{\ominus}(298\ \mathrm{K}) - \Delta n_g RT\\ &= (-174.83\times10^3\ \mathrm{J\,mol^{-1}}) - (-1.0\ \mathrm{mol})\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad\times(298\ \mathrm{K}) = \boxed{-172\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

The difference of the molar heat capacities of products and reactants is calculated using [2C.7b–*55*] and the corresponding heat capacity data from the *Resource section*

$$\begin{aligned}\Delta_r C_p^{\ominus} &= \sum_{\text{products}} \nu C_{p,m}^{\ominus} - \sum_{\text{reactants}} \nu C_{p,m}^{\ominus}\\ &= C_{p,m}^{\ominus}(C_2H_4,g) - C_{p,m}^{\ominus}(C_2H_2,g) - C_{p,m}^{\ominus}(H_2,g)\\ &= (43.56\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (43.93\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (28.824\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -29.1...\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

It is assumed that all heat capacities are constant over the temperature range of interest, therefore the integrated form of Kirchhoff's Law is applicable, [2C.7d–*56*]

$$\begin{aligned}\Delta_r H^{\ominus}(427\ \mathrm{K}) &= \Delta_r H^{\ominus}(298\ \mathrm{K}) + \Delta T \Delta_r C_p^{\ominus}\\ &= (-174.83\times10^3\ \mathrm{J\,mol^{-1}})\\ &\quad + (427\ \mathrm{K} - 298\ \mathrm{K})\times(-29.1...\ \mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{-179\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2C.8(b) The reaction equation $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ represents the formation of $NH_3(g)$ from its elements in their reference states, therefore $\Delta_r H^{\ominus}(298\ \mathrm{K}) = \Delta_f H^{\ominus}(NH_3, g) = -46.11\ \mathrm{kJ\,mol^{-1}}$. The variation of standard reaction enthalpy with temperature is given by Kirchhoff's Law, [2C.7a–*55*]

$$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus}\, dT$$

The difference of the molar heat capacities of products and reactants is given by [2C.7b–55]

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus \\ &= C_{p,m}^\ominus(\mathrm{NH_3,g}) - \tfrac{3}{2}C_{p,m}^\ominus(\mathrm{H_2,g}) - \tfrac{1}{2}C_{p,m}^\ominus(\mathrm{N_2,g})\end{aligned}$$

The heat capacities in Table 2B.1 are expressed in the form of $C_{p,m}^\ominus = a + bT + c/T^2$ therefore $\Delta_r C_p^\ominus = \Delta a + \Delta b T + \Delta c/T^2$ where $\Delta a = a(\mathrm{NH_3,g}) - \frac{3}{2}a(\mathrm{H_2,g}) - \frac{1}{2}a(\mathrm{N_2,g})$ and likewise for Δb and Δc.

$$\begin{aligned}\Delta a &= (29.75\ \mathrm{J\,K^{-1}\,mol^{-1}}) - \tfrac{3}{2}\times(27.28\ \mathrm{J\,K^{-1}\,mol^{-1}}) - \tfrac{1}{2}\times(28.58\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= -25.46\ \mathrm{J\,K^{-1}\,mol^{-1}} \\ \Delta b &= (25.1\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) - \tfrac{3}{2}\times(3.26\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) \\ &\quad - \tfrac{1}{2}\times(3.77\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) = +18.325\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}} \\ \Delta c &= (-1.55\times10^{5}\ \mathrm{J\,K\,mol^{-1}}) - \tfrac{3}{2}\times(0.50\times10^{5}\ \mathrm{J\,K\,mol^{-1}}) \\ &\quad - \tfrac{1}{2}\times(-0.50\times10^{5}\ \mathrm{J\,K\,mol^{-1}}) = -2.05\times10^{5}\ \mathrm{J\,K\,mol^{-1}}\end{aligned}$$

Integrating Kirchhoff's Law gives

$$\begin{aligned}\Delta_r H^\ominus(T_2) &= \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2}\left(\Delta a + \Delta b T + \frac{\Delta c}{T^2}\right)\mathrm{d}T \\ &= \Delta_r H^\ominus(T_1) + \Delta a(T_2 - T_1) + \tfrac{1}{2}\Delta b(T_2^2 - T_1^2) - \Delta c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &= (-46.11\times10^{3}\ \mathrm{J\,mol^{-1}}) + (-25.46\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(750\ \mathrm{K} - 298\ \mathrm{K}) \\ &\quad + \tfrac{1}{2}\times(+18.325\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}})\times[(750\ \mathrm{K})^2 - (298\ \mathrm{K})^2] \\ &\quad - (-2.05\times10^{5}\ \mathrm{J\,K\,mol^{-1}})\times\left(\frac{1}{750\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right) \\ &= \boxed{-53.7\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Solutions to problems

P2C.2 The combustion equation for octane is $\mathrm{C_8H_{18}(l)} + 12.5\,\mathrm{O_2(g)} \longrightarrow 8\,\mathrm{CO_2(g)} + 9\,\mathrm{H_2O(l)}$. The standard enthalpy of combustion of octane is given in Table 2C.6 as $-5471\ \mathrm{kJ\,mol^{-1}}$. The amount in moles in $1.0\ \mathrm{dm^3}$ octane is

$$n = \frac{m}{M} = \frac{\rho V}{M} = \frac{(0.703\ \mathrm{g\,cm^{-3}})\times(1.0\times10^{3}\ \mathrm{cm^3})}{(114.2222\ \mathrm{g\,mol^{-1}})} = 6.15...\ \mathrm{mol}$$

The heat is

$$q_p = n\Delta_c H^\ominus = (6.15...\ \mathrm{mol})\times(-5471\ \mathrm{kJ\,mol^{-1}}) = \boxed{3.4\times10^{4}\ \mathrm{kJ}}$$

P2C.4 $\Delta_f H^\ominus(\mathrm{B_2H_6,g})$ is the standard enthalpy change of $2\,\mathrm{B(s)} + 3\,\mathrm{H_2(g)} \longrightarrow \mathrm{B_2H_6(g)}$. This reaction is 3 × reaction(3) + reaction(2) − reaction(1) = reaction(4), and so

$$\Delta_f H^\ominus(\mathrm{B_2H_6,g}) = 3\Delta_r H^\ominus(3) + \Delta_r H^\ominus(2) - \Delta_r H^\ominus(1)$$
$$\Delta_f H^\ominus(\mathrm{B_2H_6,g}) = 3\times(-241.8\ \mathrm{kJ\,mol^{-1}}) + (-2368\ \mathrm{kJ\,mol^{-1}}) - (-1941\ \mathrm{kJ\,mol^{-1}})$$
$$= \boxed{-1152.4\ \mathrm{kJ\,mol^{-1}}}$$

P2C.6 The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction $\Delta n_g = 2\ \mathrm{mol} - 0\ \mathrm{mol} = +2\ \mathrm{mol}$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r U^\ominus + \Delta n_g RT\\ &= (+8.0\times10^3\ \mathrm{J\,mol^{-1}}) + (2.0\ \mathrm{mol})\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(583\ \mathrm{K})\\ &= 17.6...\ \mathrm{kJ\,mol^{-1}} = \boxed{+18\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Applying [2C.5a–*55*] to this reaction gives

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus(\mathrm{C_6H_6,g}) + \Delta_f H^\ominus(\mathrm{Cr,s}) - \Delta_f H^\ominus(\mathrm{Cr(C_6H_6)_2,s})$$

The standard enthalpies of formation of elements in their reference states are zero at *all* temperatures, therefore $\Delta_f H^\ominus(\mathrm{Cr,s,583\,K}) = \Delta_f H^\ominus(\mathrm{Cr,s,298\,K}) = 0$. $\Delta_f H^\ominus(\mathrm{C_6H_6,g,298\,K})$ is equal to $\Delta_r H^\ominus$ of the reaction $6\,\mathrm{C(s)} + 3\,\mathrm{H_2(g)} \longrightarrow \mathrm{C_6H_6(g)}$ at 298 K. The difference of the molar heat capacities of products and reactants of this reaction is calculated using [2C.7b–*55*] and data from Table 2C.7

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_{\text{products}} \nu C_{p,\mathrm{m}}^\ominus - \sum_{\text{reactants}} \nu C_{p,\mathrm{m}}^\ominus\\ &= C_{p,\mathrm{m}}^\ominus(\mathrm{C_6H_6,g}) - 3C_{p,\mathrm{m}}^\ominus(\mathrm{H_2,g}) - 6C_{p,\mathrm{m}}^\ominus(\mathrm{graphite,s})\\ &= (81.67\ \mathrm{J\,K^{-1}\,mol^{-1}}) - 3\times(28.824\ \mathrm{J\,K^{-1}\,mol^{-1}}) - 6\times(8.527\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -55.9...\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

Assuming that $\Delta_r C_p^\ominus$ is independent of temperature in the given range, using data from Table 2C.6 and applying Kirchhoff's Law [2C.7d–*56*] gives

$$\begin{aligned}\Delta_f H^\ominus(\mathrm{C_6H_6,g,583\,K}) &= \Delta_r H^\ominus(583\ \mathrm{K}) + \Delta_r H^\ominus(298\ \mathrm{K}) + \Delta T\Delta_r C_p^\ominus\\ &= (+82.93\times10^3\ \mathrm{J\,mol^{-1}}) + (583\ \mathrm{K} - 298\ \mathrm{K})\\ &\quad\times(-55.9...\ \mathrm{J\,K^{-1}\,mol^{-1}}) = +66.9...\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Therefore the standard enthalpy of formation of the chromium complex at 583 K is

$$\begin{aligned}\Delta_f H^\ominus(\mathrm{Cr(C_6H_6)_2,s,583\,K}) &= 2\Delta_f H^\ominus(\mathrm{C_6H_6,g,583\,K}) + \Delta_f H^\ominus(\mathrm{Cr,s}) - \Delta_r H^\ominus\\ &= 2\times(+66.9...\ \mathrm{kJ\,mol^{-1}}) + 0 - (+17.6...\ \mathrm{kJ\,mol^{-1}})\\ &= \boxed{+116\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

P2C.8 (a) Using [2C.5a–*55*] and the values for the standard enthalpies of formation given in the problem

$$\begin{aligned}\Delta_r H^\ominus &= \sum_{\text{products}} \nu\Delta_f H^\ominus - \sum_{\text{reactants}} \nu\Delta_f H^\ominus\\ &= \Delta_f H^\ominus(\text{SiH}_2,\text{g}) + \Delta_f H^\ominus(\text{H}_2,\text{g}) - \Delta_f H^\ominus(\text{SiH}_4,\text{g})\\ &= (+274\ \text{kJ mol}^{-1}) + 0 - (+34.3\ \text{kJ mol}^{-1}) = \boxed{+239.7\ \text{kJ mol}^{-1}}\end{aligned}$$

(b) Similarly to part (a)

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(\text{SiH}_2,\text{g}) + \Delta_f H^\ominus(\text{SiH}_4,\text{g}) - \Delta_f H^\ominus(\text{Si}_2\text{H}_6,\text{g})\\ &= (+274\ \text{kJ mol}^{-1}) + (+34.3\ \text{kJ mol}^{-1}) - (+80.3\ \text{kJ mol}^{-1})\\ &= \boxed{+228.0\ \text{kJ mol}^{-1}}\end{aligned}$$

P2C.10 The enthalpy change is found using [2C.9–*57*], $\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}}\,\text{d}T$, where $C_{p,\text{ex}}$ is the excess heat capacity reported by the instrument. The integral is the area under the trace, which is estimated to be 230 mJ: this is the estimate for ΔH.

From the data given the amount in moles in the sample volume of 0.80 cm^3 is $(0.80\ \text{cm}^3) \times (2.17 \times 10^{-3}\ \text{g cm}^{-3})/(14.3 \times 10^3\ \text{g mol}^{-1}) = 1.21... \times 10^{-7}$ mol. The molar enthalpy of unfolding is therefore

$$\Delta H_\text{m} = (230 \times 10^{-3}\ \text{J})/(1.21... \times 10^{-7}\ \text{mol}) = \boxed{1.9 \times 10^3\ \text{kJ mol}^{-1}}$$

2D State functions and exact differentials

Answers to discussion questions

D2D.2 An inversion temperature is the temperature at which the Joule–Thomson coefficient μ changes sign from negative to positive or vice-versa. For a perfect gas μ is always zero, thus it cannot have an inversion temperature. As explained in detail in Section 2D.4 on page 64, the existence of the Joule–Thomson effect depends upon intermolecular attractions and repulsions. A perfect gas has by definition no intermolecular attractions and repulsions, so it cannot exhibit the Joule–Thomson effect.

Solutions to exercises

E2D.1(b) The molar volume of a perfect gas at 298 K is calculated as

$$V_\text{m} = \frac{RT}{p} = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})}{(1.00\ \text{bar}) \times [(10^5\ \text{Pa})/(1.00\ \text{bar})]} = 2.47... \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1}$$

The van der Waals parameter a of sulfur dioxide is found in Table 1C.3, and needs to be converted to SI units

$$a = (6.775\ \mathrm{dm^6\,atm\,mol^{-2}}) \times \left(\frac{10^{-6}\ \mathrm{m^6}}{1\ \mathrm{dm^6}}\right) \times \left(\frac{1.01325 \times 10^5\ \mathrm{Pa}}{1\ \mathrm{atm}}\right)$$

$$= 0.686...\ \mathrm{m^6\,Pa\,mol^{-2}}$$

Therefore the internal pressure is

$$\pi_T = \frac{a}{V_\mathrm{m}^2} = \frac{(0.686...\ \mathrm{m^6\,Pa\,mol^{-2}})}{(2.47... \times 10^{-2}\ \mathrm{m^3\,mol^{-1}})^2} = \boxed{1.12 \times 10^3\ \mathrm{Pa}}$$

E2D.2(b) The internal energy of a closed system of constant composition is a function of temperature and volume. For a change in V and T, $\mathrm{d}U$ is given by [2D.5–*61*], $\mathrm{d}U = \pi_T \mathrm{d}V + C_V \mathrm{d}T$. At constant temperature, this reduces to $\mathrm{d}U = \pi_T \mathrm{d}V$. Substituting in the given expression for π_T for a van der Waals gas and using molar quantities

$$\mathrm{d}U_\mathrm{m} = \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$

This expression is integrated between $V_\mathrm{m,i}$ and $V_\mathrm{m,f}$ to give

$$\int_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} \mathrm{d}U_\mathrm{m} = \int_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$

hence

$$\Delta U_\mathrm{m} = -\left.\frac{a}{V_\mathrm{m}^2}\right|_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} = -a\left(\frac{1}{V_\mathrm{m,f}} - \frac{1}{V_\mathrm{m,i}}\right)$$

The van der Waals parameter a for argon is found in Table 1C.3, and needs to be converted to SI units

$$a = (1.337\ \mathrm{dm^6\,atm\,mol^{-2}}) \times \left(\frac{10^{-6}\ \mathrm{m^6}}{1\ \mathrm{dm^6}}\right) \times \left(\frac{1.01325 \times 10^5\ \mathrm{Pa}}{1\ \mathrm{atm}}\right)$$

$$= 0.135...\ \mathrm{m^6\,Pa\,mol^{-2}}$$

$$\Delta U_\mathrm{m} = -(0.135...\ \mathrm{m^6\,Pa\,mol^{-2}})\left(\frac{1}{30.00 \times 10^{-3}\ \mathrm{m^3\,mol^{-1}}} - \frac{1}{1.00 \times 10^{-3}\ \mathrm{m^3\,mol^{-1}}}\right)$$

$$= +1.30... \times 10^2\ \mathrm{J\,mol^{-1}} = \boxed{+131\ \mathrm{J\,mol^{-1}}}$$

The work done by an expanding gas is given by [2A.5a–*39*], $\mathrm{d}w = -p_\mathrm{ex}\mathrm{d}V$. For a reversible expansion p_ex is the pressure of the gas, hence

$$w = -\int p\mathrm{d}V_\mathrm{m}$$

Substituting in the expression for the pressure of a van der Waals gas, [1C.5b–*24*]

$$w = -\int \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m} = -\int \frac{RT}{V_\mathrm{m} - b}\mathrm{d}V_\mathrm{m} + \int \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$

$$= -\int \frac{RT}{V_\mathrm{m} - b}\mathrm{d}V_\mathrm{m} + \Delta U_\mathrm{m}$$

The second term is identified as ΔU_{m} from the above. According to the First Law, $\Delta U = q + w$, the first term in the expression above must be $-q$, therefore

$$\begin{aligned} q &= \int_{V_{\mathrm{m,i}}}^{V_{\mathrm{m,f}}} \frac{RT}{V_{\mathrm{m}} - b}\,\mathrm{d}V_{\mathrm{m}} = RT\ln(V_{\mathrm{m}} - b)\big|_{V_{\mathrm{m,i}}}^{V_{\mathrm{m,f}}} = RT\ln\left(\frac{V_{\mathrm{m,f}} - b}{V_{\mathrm{m,i}} - b}\right) \\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{30.00\,\mathrm{dm^3} - 3.20 \times 10^{-2}\,\mathrm{dm^3}}{1.00\,\mathrm{dm^3} - 3.20 \times 10^{-2}\,\mathrm{dm^3}}\right) \\ &= +8.50\ldots \times 10^{3}\,\mathrm{J\,mol^{-1}} = \boxed{+8.51\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

where the value for b is taken from the Resource section. From the First Law the work done is $w = -q + \Delta U_{\mathrm{m}}$, hence

$$w = -q + \Delta U_{\mathrm{m}} = -8.50\ldots \times 10^{3}\,\mathrm{J\,mol^{-1}} + 1.30\ldots \times 10^{2}\,\mathrm{J\,mol^{-1}} = \boxed{-8.37\,\mathrm{kJ\,mol^{-1}}}$$

E2D.3(b) The volume of the liquid can be written as

$$V = V'(a + bT + cT^2)$$

where $a = 0.77$, $b = 3.7 \times 10^{-4}\,\mathrm{K^{-1}}$ and $c = 1.52 \times 10^{-6}\,\mathrm{K^{-2}}$. The expansion coefficient is defined in [2D.6–62] as $\alpha = (1/V)(\partial V/\partial T)_p$. The derivative with respect to T is

$$\left(\frac{\partial V}{\partial T}\right)_p = V'(b + 2cT)$$

Therefore

$$\alpha = \frac{1}{V'(a + bT + cT^2)} \times [V'(b + 2cT)] = \frac{b + 2cT}{a + bT + cT^2}$$

Evaluating this expression at 310 K gives

$$\begin{aligned} \alpha_{310} &= \frac{(3.7 \times 10^{-4}\,\mathrm{K^{-1}}) + 2 \times (1.52 \times 10^{-6}\,\mathrm{K^{-2}}) \times (310\,\mathrm{K})}{(0.77) + (3.7 \times 10^{-4}\,\mathrm{K^{-1}}) \times (310\,\mathrm{K}) + (1.52 \times 10^{-6}\,\mathrm{K^{-2}}) \times (310\,\mathrm{K})^2} \\ &= \boxed{+1.3 \times 10^{-3}\,\mathrm{K^{-1}}} \end{aligned}$$

E2D.4(b) The isothermal compressibility is defined in [2D.7–62], $\kappa_T = -(1/V)(\partial V/\partial p)_T$, therefore at constant temperature $\mathrm{d}V/V = -\kappa_T\mathrm{d}p$. This question is concerned with changes in density, so the next step is to rewrite the volume in terms of the density, ρ. If the mass is m, $V = m/\rho$, and therefore $\mathrm{d}V = (-m/\rho^2)\mathrm{d}\rho$. Therefore

$$\frac{\mathrm{d}V}{V} = \frac{1}{V}\left(-\frac{m}{\rho^2}\mathrm{d}\rho\right) = -\left(\frac{\rho}{m}\right)\left(\frac{m}{\rho^2}\right)\mathrm{d}\rho = -\frac{1}{\rho}\mathrm{d}\rho$$

It therefore follows that

$$\frac{\mathrm{d}\rho}{\rho} = \kappa_T\mathrm{d}p \quad \text{and hence} \quad \mathrm{d}p = \frac{1}{\kappa_T\rho}\mathrm{d}\rho$$

This expression gives the relationship between the change in pressure and the change in density. Approximating $\mathrm{d}\rho$ by $\delta\rho$ and $\mathrm{d}p$ by δp for sufficiently small changes gives

$$\delta p = \frac{1}{\kappa_T} \times \frac{\delta\rho}{\rho} = \left(\frac{1}{2.21 \times 10^{-6}\ \mathrm{atm}^{-1}}\right) \times (1.0 \times 10^{-3}) = \boxed{+4.5 \times 10^{2}\ \mathrm{atm}}$$

E2D.5(b) The difference $C_{p,\mathrm{m}} - C_{V,\mathrm{m}}$ is given by [2D.11–*63*], $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \alpha^2 T V_\mathrm{m}/\kappa_T$. In this expression the molar volume is found from the mass density ρ and the molar mass M by $V_\mathrm{m} = M/\rho$. The values of α and κ are available in the *Resource section*, as is the mass density.

$$\begin{aligned} C_{p,\mathrm{m}} - C_{V,\mathrm{m}} &= \frac{\alpha^2 T V_\mathrm{m}}{\kappa_T} = \frac{\alpha^2 T M}{\kappa_T \rho} \\ &= \frac{(11.2 \times 10^{-4}\ \mathrm{K}^{-1})^2 \times (298\ \mathrm{K}) \times (46.0674\ \mathrm{g\,mol}^{-1})}{[(76.8 \times 10^{-6}\ \mathrm{bar}) \times (1\ \mathrm{bar}/10^5\ \mathrm{Pa})] \times (0.789 \times 10^6\ \mathrm{g\,m}^{-3})} \\ &= \boxed{+28.4\ \mathrm{J\,K}^{-1}\ \mathrm{mol}^{-1}} \end{aligned}$$

The units are $\mathrm{K}^{-1}\ \mathrm{Pa\,m}^3\ \mathrm{mol}^{-1} = \mathrm{K}^{-1}\ (\mathrm{N\,m}^{-2})\ \mathrm{m}^3\ \mathrm{mol}^{-1} = \mathrm{K}^{-1}\ \mathrm{N\,m\,mol}^{-1} = \mathrm{J\,K}^{-1}\ \mathrm{mol}^{-1}$

Solutions to problems

P2D.2 The pressure p is a function of T and V, therefore according to the Euler chain relation and the reciprocal identity

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Substituting this into the expression given for $C_p - C_V$ gives

$$\begin{aligned} C_p - C_V &= T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -T\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial V}{\partial T}\right)_p \\ &= -\frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T} \end{aligned}$$

For a perfect gas $pV = nRT$, therefore

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \quad \text{and} \quad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

It follows that

$$C_p - C_V = -\frac{T(nR/p)^2}{(-nRT/p^2)} = nR$$

which is the expected result quoted in [2B.9–*49*].

P2D.4 Rearranging the van der Waals equation of state to give T as a function of p and V gives

$$T = \frac{p(V-nb)}{nR} + \frac{na(V-nb)}{V^2R}$$

The partial differentials are

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{V-nb}{nR} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

As expected, these two partial differentials are the reciprocals of each other.

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{1}{(\partial p/\partial T)_V}$$

P2D.6 From the perfect gas law, [1A.4–*8*], $pV = nRT$. Writing $n = m/M$, where m is the mass, it follows that

$$pV = \frac{m}{M}RT \quad \text{and hence} \quad \frac{RT}{M} = \frac{pV}{m}$$

The mass density, ρ is $\rho = m/V$, therefore $(RT/M) = \rho/p$.

$$c_s = \left(\frac{\gamma RT}{M}\right)^{1/2} = \left(\frac{\gamma p}{\rho}\right)^{1/2}$$

For argon, a monoatomic gas, $C_{V,m} = \frac{3}{2}R$ and $C_{p,m} = \frac{5}{2}R$ therefore $\gamma = C_{p,m}/C_{V,m}$ $= 5/3$.

$$c_s = \left(\frac{\frac{5}{3} \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(39.95 \times 10^{-3}\,\text{kg mol}^{-1})}\right)^{1/2} = \boxed{322\,\text{m s}^{-1}}$$

P2D.8 In *How is that done?* 2D.1 on page 63 is is shown that

$$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

An expression for $(\partial H/\partial p)_T$ is developed as follows

$$\begin{aligned}
\left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial H}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \quad [\text{change of variable}]\\
&= \left(\frac{\partial (U+pV)}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \quad [\text{definition of } H]\\
&= \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T\\
&= \left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\}\left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial p}\right)_T \left[\text{ equation for } \left(\frac{\partial U}{\partial V}\right)_T\right]\\
&= T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T\\
&= T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T + V = \frac{-T}{(\partial T/\partial V)_p} + V \quad [\text{chain relation}]\\
&= -T\left(\frac{\partial V}{\partial T}\right)_p + V \quad [\text{reciprocal identity}]
\end{aligned}$$

With this result

$$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right)$$

In order to compute the partial derivative $(\partial V/\partial T)_p$ it is convenient to take the van der Waals equation and re-express it in the form of a virial expansion

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2} = \frac{RT}{V_\mathrm{m}}\left(\frac{1}{1 - b/V_\mathrm{m}} - \frac{a}{RTV_\mathrm{m}}\right)$$

Assuming $b/V_\mathrm{m} \ll 1$, the first fraction can be approximated using $(1-x)^{-1} \approx 1 + x$

$$\begin{aligned}
p &= \frac{RT}{V_\mathrm{m}}\left(1 + \frac{b}{V_\mathrm{m}} - \frac{a}{RTV_\mathrm{m}}\right)\\
\text{hence } V_\mathrm{m} &= \frac{RT}{p}\left(1 + \frac{b}{V_\mathrm{m}} - \frac{a}{RTV_\mathrm{m}}\right) = RT\left(\frac{1}{p} + \frac{b}{pV_\mathrm{m}} - \frac{a}{RTpV_\mathrm{m}}\right)
\end{aligned}$$

Within the parentheses the perfect gas equation is used to approximate $pV_\mathrm{m} = RT$

$$V_\mathrm{m} = RT\left(\frac{1}{p} + \frac{b}{RT} - \frac{a}{R^2T^2}\right) = \frac{RT}{p} + b - \frac{a}{RT}$$

It is now straightforward to compute the required partial derivative

$$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2}$$