

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

## 2 The First Law

### 2A Internal energy

#### Answers to discussion questions

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**2A.2** Work is a precisely defined mechanical concept. It is produced from the application of a force through a distance. The technical definition is based on the realization that both force and displacement are vector quantities and it is the component of the force acting in the direction of the displacement that is used in the calculation of the amount of work, that is, work is the scalar product of the two vectors. In vector notation  $w = -\mathbf{F} \cdot \mathbf{d} = -fd \cos \theta$ , where  $\theta$  is the angle between the force and the displacement. The negative sign is inserted to conform to the standard thermodynamic convention.

Heat is associated with a non-adiabatic process and is defined as the difference between the adiabatic work and the non-adiabatic work associated with the same change in state of the system. This is the formal (and best) definition of heat and is based on the definition of work. A less precise definition of heat is the statement that heat is the form of energy that is transferred between bodies in thermal contact with each other by virtue of a difference in temperature.

The interpretations of heat and work in terms of energy levels and populations is based upon the change in the total energy of a system that arises from a change in the molecular energy levels of a system and from a change in the populations of those levels as explained more fully in Chapter 15 of this text. The statistical thermodynamics of Chapter 15 allows us to express the change in total energy of a system in the following form:

$$Nd\epsilon = \sum_i \epsilon_i dN_i + \sum_i N_i d\epsilon_i$$

The work done by the system in a reversible, isothermal expansion can be identified with the second term on the right of this expression, since there is no change in the populations of the levels which depend only on temperature; hence, the first term on the right is zero. Because the influx of energy as heat does not change the energy levels of a system, but does result in a change in temperature, the second term on the right of the above equation is zero and the heat associated with the process (a constant volume process, with no additional work) can be identified with the first term. The change in populations is due to the change in temperature, which redistributes the molecules over the fixed energy levels.

#### Solutions to exercises

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**2A.1(b)** See the solution to Exercise 2A.1(a) where we introduced the following equation based on the material of Chapter 15.

$$C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

with a mode active if  $T \approx \theta_M$  (where M is T, R, or V).

(i)  $\text{O}_3 : C_{V,m} = \frac{1}{2}(3 + 3 + 0)R = 3R$  [experimental = 3.7R]

$$E = 3RT = 3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = \boxed{7.436 \text{ kJ mol}^{-1}}$$

(ii)  $\text{C}_2\text{H}_6 : C_{V,m} = \frac{1}{2}(3 + 3 + 2 + 1)R = 4R$  [experimental = 6.3R]

$$E = 4RT = 4 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = \boxed{9.915 \text{ kJ mol}^{-1}}$$

$$(iii) \quad SO_2 : C_{V,m} = \frac{1}{2}(3 + 3 + 0)R = 3R \text{ [experimental} = 3.8R]$$

$$E = 3RT = 3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = \boxed{7.436 \text{ kJ mol}^{-1}}$$

Consultation of Herzberg references, G. Herzberg, Molecular spectra and Molecular structure, II, Chapters 13 and 14, Van Nostrand, 1945, turns up only one vibrational mode among these molecules whose frequency is low enough to have a vibrational temperature near room temperature. That mode was in  $C_2H_6$ , corresponding to the “internal rotation” of  $CH_3$  groups. The discrepancies between the estimates and the experimental values suggest that there are vibrational modes in each molecule that contribute to the heat capacity—albeit not to the full equipartition value—that our estimates have classified as inactive.

**2A.2(b)** (i) volume, (iii) internal energy, and (iv) density are state functions.

**2A.3(b)** This is an expansion against a constant external pressure; hence  $w = p_{\text{ex}} \Delta V$  [2A.6]

The change in volume is the cross-sectional area times the linear displacement:

$$\Delta V = (75.0 \text{ cm}^2) (25.0 \text{ cm}) = \frac{1 \text{ m}}{100 \text{ cm}} \times 1.875 \times 10^{-3} \text{ m}^3$$

$$\text{so } w = (150 \times 10^3 \text{ Pa}) (1.875 \times 10^{-3} \text{ m}^3) = \boxed{281 \text{ J}} \text{ as } 1 \text{ Pa m}^3 = 1 \text{ J}$$

**2A.4(b)** For all cases  $\Delta U = 0$  since the internal energy of a perfect gas depends only on temperature. From the definition of enthalpy,  $H = U + pV$ , so  $\Delta H = \Delta U + (pV) = \Delta U + (nRT)$  (perfect gas).  $\Delta H = 0$  as well, at constant temperature for all processes in a perfect gas.

$$(i) \quad \Delta U = \Delta H = 0$$

$$w = nRT \ln \frac{V_f}{V_i} \quad [2A.9]$$

$$(2.00 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K}) \ln \frac{20.0 \text{ dm}^3}{5.0 \text{ dm}^3} = \boxed{6.29 \times 10^3 \text{ J}}$$

$$q = -w = \boxed{6.29 \times 10^3 \text{ J}}$$

$$(ii) \quad \Delta U = \Delta H = 0$$

$$w = p_{\text{ex}} \Delta V \quad [2A.6]$$

where  $p_{\text{ex}}$  in this case can be computed from the perfect gas law

$$pV = nRT$$

$$\text{so } p = \frac{(2.00 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}{20.0 \text{ dm}^3} = (10 \text{ dm m}^{-1})^3 \times 2.22 \times 10^5 \text{ Pa}$$

$$\text{and } w = \frac{(2.22 \times 10^5 \text{ Pa}) (20.0 - 5.0) \text{ dm}^3}{(10 \text{ dm m}^{-1})^3} = \boxed{3.34 \times 10^3 \text{ J}}$$

$$q = -w = \boxed{3.34 \times 10^3 \text{ J}}$$

$$(iii) \quad \Delta U = \Delta H = 0$$

$$w = 0 \text{ [free expansion]} \quad q = \Delta U - w = 0 - 0 = \boxed{0}$$

**Comment.** An isothermal free expansion of a perfect gas is also adiabatic.

**2A.5(b)** The perfect gas law leads to

$$\frac{p_1 V}{p_2 V} = \frac{nRT_1}{nRT_2} \quad \text{or} \quad p_2 = \frac{p_1 T_2}{T_1} = \frac{(111 \text{ kPa})(356 \text{ K})}{277 \text{ K}} = \boxed{143 \text{ kPa}}$$

There is no change in volume, so  $w = 0$ . The heat flow is

$$q = C_V \Delta T = C_V T_2 - T_1 = (2.5)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(356 - 277) \text{ K}$$

$$= \boxed{3.28 \times 10^3 \text{ J}}$$

$$U = q + w = \boxed{3.28 \times 10^3 \text{ J}}$$

**2A.6(b) (i)**  $w = p_{\text{ex}} \Delta V = \frac{(7.7 \times 10^3 \text{ Pa})(2.5 \text{ dm}^3)}{(10 \text{ dm}^3)^3} = \boxed{4.9 \text{ J}}$

**(ii)**  $w = nRT \ln \frac{V_f}{V_i} = [2A.9]$

$$w = \frac{6.56 \text{ g}}{39.95 \text{ g mol}^{-1}} \cdot 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 305 \text{ K} \cdot \ln \frac{2.5 - 18.5 \text{ dm}^3}{18.5 \text{ dm}^3} = \boxed{52.8 \text{ J}}$$

## Solutions to problems

**2A.2**  $w = p_{\text{ex}} \Delta V$  [2A.6]  $V_f = \frac{nRT}{p_{\text{ex}}} = V_i$  ! so  $\Delta V = 0$

Hence  $w = (p_{\text{ex}}) \Delta V = \frac{nRT}{p_{\text{ex}}} \cdot p_{\text{ex}} \Delta V = nRT \ln \left( \frac{V_f}{V_i} \right) = (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(1073 \text{ K})$

$$w \approx \boxed{-8.9 \text{ kJ}}$$

Even if there is no physical piston, the gas drives back the atmosphere, so the work is also

$$w \approx \boxed{-8.9 \text{ kJ}}$$

**2A.4**

$$w = \int_{V_1}^{V_2} p dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = n^2 a \int_{V_1}^{V_2} \frac{dV}{V^2} = nRT \ln \frac{V_2}{V_1} - \frac{n^2 a}{V_1} + \frac{n^2 a}{V_2}$$

By multiplying and dividing the value of each variable by its critical value we obtain

$$w = nR \left( \frac{T}{T_c} \right) \ln \left( \frac{V_2}{V_1} \right) - \frac{n^2 a}{V_c} \left( \frac{1}{V_1} - \frac{1}{V_2} \right) = \frac{n^2 a}{V_c} \left( \frac{V_c}{V_1} - \frac{V_c}{V_2} \right) - \frac{n^2 a}{V_c} \left( \frac{1}{V_1} - \frac{1}{V_2} \right)$$

$$T_r = \frac{T}{T_c} = \frac{V_r}{V_c} = \frac{T_c}{27} \frac{8a}{Rb} = \frac{V_c}{3nb} \quad [\text{Table 1C.4}]$$

$$w_r = \frac{8na}{27b} \left( \frac{1}{V_{r,2}} - \frac{1}{V_{r,1}} \right) \ln \left( \frac{V_{r,2}}{V_{r,1}} \right) - \frac{na}{b} \left( \frac{1}{V_{r,2}} - \frac{1}{V_{r,1}} \right)$$

The van der Waals constants can be eliminated by defining  $w_r = \frac{3bw_r}{a}$ , then  $w_r = \frac{aw_r}{3b}$  and

$$w_r = \frac{8}{9} n T_r \ln \left( \frac{V_{r,2}}{V_{r,1}} \right) - n \left( \frac{1}{V_{r,2}} - \frac{1}{V_{r,1}} \right)$$

Along the critical isotherm,  $T_r = 1$ ,  $V_{r,1} = 1$ , and  $V_{r,2} = x$ . Hence

$$\frac{w_r}{n} = \frac{8}{9} \ln \left( \frac{x}{1} \right) - \left( \frac{1}{x} - 1 \right)$$

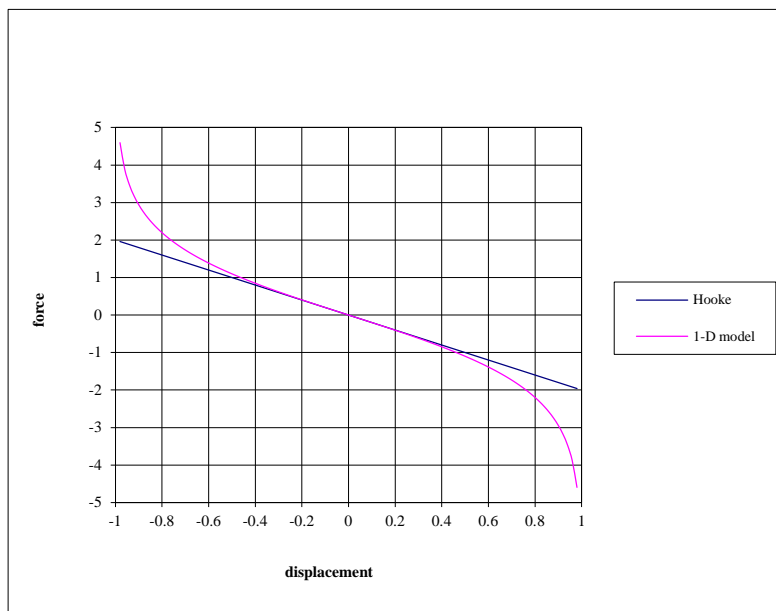
**2A.6** One obvious limitation is that the model treats only displacements along the chain, not displacements that take an end away from the chain. (See Fig. 2A.2 in the Student's Solutions Manual)

(a) The displacement is twice the persistence length, so

$$x = 2l, n = 2, \quad Qn/N = 2/200 = 1/100$$

$$\text{and} \quad |F| = \frac{kT}{2l} \ln \left( \frac{Q}{Q_0} \right) = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{2 \times 45 \times 10^{-9} \text{ m}} \ln \left( \frac{1.01}{0.99} \right) = 9.1 \times 10^{-16} \text{ N}$$

**Figure 2A.1**



(b) Fig. 2A.1 displays a plot of force vs. displacement for Hooke's law and for the one-dimensional freely jointed chain. For small displacements the plots very nearly coincide. However, for large displacements, the magnitude of the force in the one-dimensional model grows much faster. In fact, in the one-dimensional model, the magnitude of the force approaches infinity for a finite displacement,

namely a displacement the size of the chain itself ( $l = Q$ ). (For Hooke's law, the force approaches infinity only for infinitely large displacements.)

(c) Work is  $dw = F dx = \frac{kT}{2l} \ln \frac{l}{l_0} \frac{Q}{l} dx = \frac{kNT}{2} \ln \frac{l}{l_0} \frac{Q}{l} dl$

This integrates to

$$w = \int_0^Q \frac{kNT}{2} \ln \frac{l}{l_0} \frac{Q}{l} dl = \frac{kNT}{2} \int_0^Q \ln(1 - \frac{Q}{l}) dl$$

$$= \frac{kNT}{2} [(1 - \frac{Q}{l}) \ln(1 - \frac{Q}{l}) + Q(1 - \frac{Q}{l})]_0^Q$$

$$= \frac{kNT}{2} [(1 - \frac{Q}{Q}) \ln(1 - \frac{Q}{Q}) + Q(1 - \frac{Q}{Q}) - (1 - \frac{Q}{l_0}) \ln(1 - \frac{Q}{l_0}) + Q(1 - \frac{Q}{l_0})]$$

(d) The expression for work is well behaved for displacements less than the length of the chain; however, for  $Q \rightarrow l$ , we must be a bit more careful, for the expression above is indeterminate at these points. In particular, for expansion to the full length of the chain

$$w = \lim_{Q \rightarrow l} \frac{kNT}{2} [(1 - \frac{Q}{l}) \ln(1 - \frac{Q}{l}) + Q(1 - \frac{Q}{l}) - (1 - \frac{Q}{l_0}) \ln(1 - \frac{Q}{l_0}) + Q(1 - \frac{Q}{l_0})]$$

$$= \frac{kNT}{2} (1 - \frac{Q}{l_0}) \ln(1 - \frac{Q}{l_0}) - \lim_{Q \rightarrow l} \frac{kNT}{2} (1 - \frac{Q}{l}) \ln(1 - \frac{Q}{l})$$

where we have written the indeterminate term in the form of a ratio in order to apply l'Hospital's rule. Focusing on the problematic limit and taking the required derivatives of numerator and denominator yields:

$$\lim_{Q \rightarrow l} \frac{\ln(1 - \frac{Q}{l})}{(1 - \frac{Q}{l})} = \lim_{Q \rightarrow l} \frac{-\frac{1}{1 - \frac{Q}{l}}}{(1 - \frac{Q}{l})^2} = \lim_{Q \rightarrow l} [-(1 - \frac{Q}{l})^{-3}] = 0$$

Therefore;  $w = \frac{kNT}{2} (2 \ln 2) = kNT \ln 2$

## 2B Enthalpy

### Answers to discussion questions

**2B.2** See figure 2B.3 of the text. There are two related reasons that can be given as to why  $C_p$  is greater than  $C_v$ . For ideal gases  $C_p - C_v = nR$ . For other gases that can be considered roughly ideal the difference is still approximately  $nR$ . Upon examination of figure 2B.3, we see that the slope of the curve of enthalpy against temperature is in most cases greater than the slope of the curve of energy against temperature; hence  $C_p$  is in most cases greater than  $C_v$ .

### Solutions to exercises

**2B.1(b)**  $q_p = nC_{p,m} T$  [2B.7]

$$C_{p,m} = \frac{q_p}{n T} = \frac{178 \text{ J}}{1.9 \text{ mol} \cdot 1.78 \text{ K}} = 53 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{v,m} = C_{p,m} - R = (53 - 8) \text{ J K}^{-1} \text{ mol}^{-1} = 45 \text{ J K}^{-1} \text{ mol}^{-1}$$

**2B.2(b) (i)** At constant pressure,  $q = \Delta H$ .

$$q = C_p \Delta T = \int_{273\text{ K}}^{373\text{ K}} [20.17 + (0.004001)T/\text{K}] dT \text{ J K}^{-1}$$

$$= 20.17 T + \frac{1}{2}(0.004001) \frac{T^2}{\text{K}} \Big|_{273\text{ K}}^{373\text{ K}} \text{ J K}^{-1}$$

$$= (20.17)(373 - 273) + \frac{1}{2}(0.004001)(373^2 - 273^2) \text{ J} = \boxed{11.6 \times 10^3 \text{ J}} = H$$

$$w = p \Delta V = nR \Delta T = 1.00 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times (373 - 273) \text{ K} = \boxed{623 \text{ J}}$$

$$U = q - w = 11.6 - 0.623 \text{ kJ} = \boxed{11.0 \text{ kJ}}$$

**(ii)** The energy and enthalpy of a perfect gas depend on temperature alone. Thus,  $H = \boxed{11.6 \text{ kJ}}$  and  $U = \boxed{11.0 \text{ kJ}}$ , as above. At constant volume,  $w = 0$  and  $U = q$ , so  $q = \boxed{11.0 \text{ kJ}}$ .

**2B.3(b)**  $H = q_p = C_p \Delta T$  [2B.2, 2B.7]  $= nC_{p,m} \Delta T$

$$H = q_p = (2.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (277 - 250) \text{ K} = \boxed{2.0 \times 10^3 \text{ J mol}^{-1}}$$

$$H = U + (pV) = U + nR \Delta T \text{ so } U = H - nR \Delta T$$

$$U = 2.0 \times 10^3 \text{ J mol}^{-1} - (2.0 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (277 - 250) \text{ K}$$

$$= \boxed{1.0 \times 10^3 \text{ J mol}^{-1}}$$

## Solutions to problems

**2B.2** In order to explore which of the two proposed equations best fit the data we have used PSI-PLOT<sup>®</sup>. The parameters obtained with the fitting process to eqn. 2B.8 along with their standard deviations are given in the following table.

parameters	$a$	$b/10^{-3} \text{ K}^{-1}$	$c/10^5 \text{ K}^2$
values	28.796	27.89	-1.490
std dev of parameter	0.820	0.91	0.6480

The correlation coefficient is 0.99947. The parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows:

parameters	$\alpha$	$\beta/10^{-3} \text{ K}^{-1}$	$\gamma/10^{-6} \text{ K}^{-2}$
values	24.636	38.18	-6.495
std dev of parameter	0.437	1.45	1.106

The correlation coefficient is 0.99986. It appears that the alternate form for the heat capacity equation fits the data slightly better, but there is very little difference.

2B.4

$$C_V = \frac{\partial G_V}{\partial w_T}$$

$$\left[ \frac{\partial G_V}{\partial w_T} = \frac{\partial}{\partial w_T} \left( \frac{\partial G_V}{\partial w_T} \right) = \frac{\partial}{\partial w_T} \left( \frac{\partial G_V}{\partial w_T} \right) \right] \text{ [Derivatives may be taken in any order.]}$$

$$\frac{\partial G_V}{\partial w_T} = 0 \text{ for a perfect gas [Section 2D.2(a)]}$$

Hence,  $\frac{\partial G_V}{\partial w_T} = 0$

Likewise  $C_p = \frac{\partial H_p}{\partial w_T}$  so

$$\left[ \frac{\partial H_p}{\partial w_T} = \frac{\partial}{\partial w_T} \left( \frac{\partial H_p}{\partial w_T} \right) = \frac{\partial}{\partial w_T} \left( \frac{\partial H_p}{\partial w_T} \right) \right]$$

$$\frac{\partial H_p}{\partial w_T} = 0 \text{ for a perfect gas.}$$

Hence,  $\frac{\partial G_p}{\partial w_T} = 0$ .

## 2C Thermochemistry

### Answers to discussion questions

- 2C.2 The standard state of a substance is the pure substance at a pressure of 1 bar and a specified temperature. The term reference state generally refers to elements and is the thermodynamically most stable state of the element at the temperature of interest. The distinction between standard state and reference state for elements may seem slight but becomes clear for those elements that can exist in more than one form at a specified temperature. So an element can have more than one standard state, one for each form that exists at the specified temperature.

### Solutions to exercises

- 2C.1(b) At constant pressure

$$q = H - n_{\text{vap}} H^\ominus = (1.75 \text{ mol}) (43.5 \text{ kJ mol}^{-1}) = \boxed{76.1 \text{ kJ}}$$

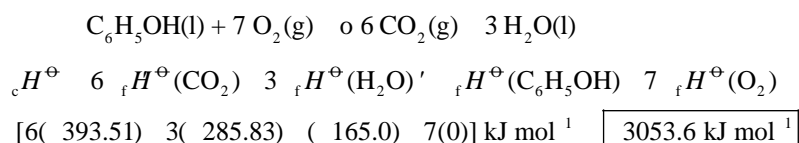
$$\text{and } w = p \Delta V = p V_{\text{vapor}} - nRT = (1.75 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (260 \text{ K})$$

$$w = 3.78 \times 10^3 \text{ J} = \boxed{3.78 \text{ kJ}}$$

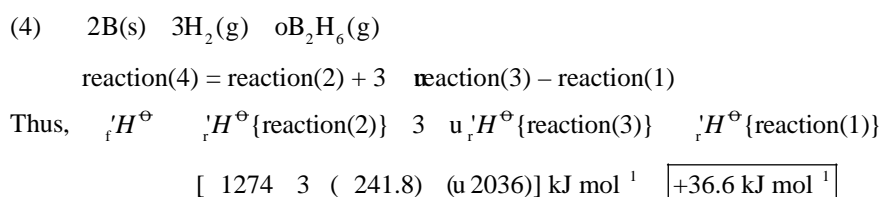
$$U = w + q = 3.78 + 76.1 = \boxed{72.3 \text{ kJ}}$$

**Comment.** Because the vapor is treated as a perfect gas, the specific value of the external pressure provided in the statement of the exercise does not affect the numerical value of the answer.

**2C.2(b)** The reaction is



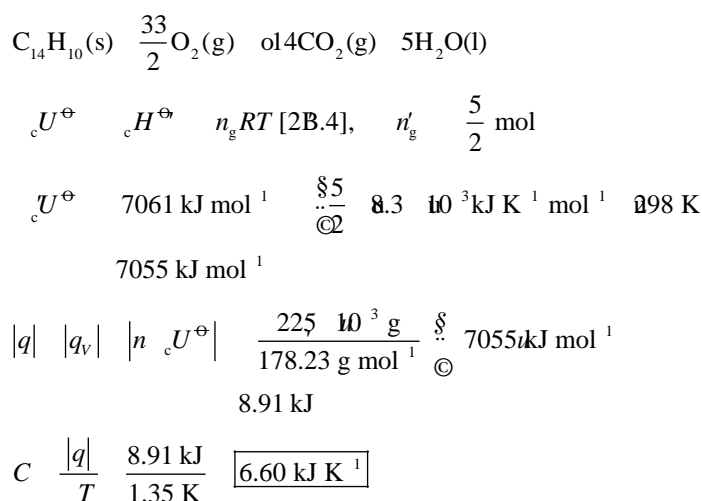
**2C.3(b)** We need  ${}_f H^\ominus$  for the reaction



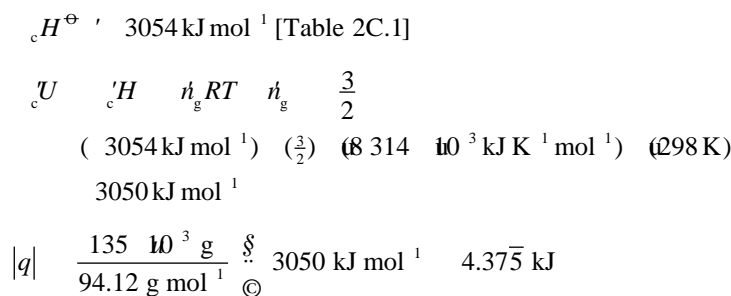
**2C.4(b)** Because  ${}_f H^\ominus(\text{H}^+, \text{aq}) = 0$  the whole of  ${}_f H^\ominus(\text{HI, aq})$  is ascribed to  ${}_f H^\ominus(\text{I}^-, \text{aq})$ . Therefore,

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

**2C.5(b)** For anthracene the reaction is



When phenol is used the reaction is  $\text{C}_6\text{H}_5\text{OH(s)} + \frac{15}{2} \text{O}_2\text{(g)} \rightarrow 6 \text{CO}_2\text{(g)} + 3 \text{H}_2\text{O(l)}$





$$T = \frac{|q|}{C} = \frac{4.375 \text{ kJ}}{6.60 \text{ kJ K}^{-1}} = \boxed{0.663 \text{ K}}$$

**2C.6(b)** (a)  $\Delta_{\text{r}}H^{\ominus}(3) = (-2) \Delta_{\text{r}}H^{\ominus}(1) + \Delta_{\text{r}}H^{\ominus}(2)$  and  $n_{\text{g}} = 1$

The enthalpies of reactions are combined in the same manner as the equations (Hess's law).

$$\Delta_{\text{r}}H^{\ominus}(3) = (-2) \Delta_{\text{r}}H^{\ominus}(1) + \Delta_{\text{r}}H^{\ominus}(2)$$

$$[( -2) (-52.96) + (-483.64)] \text{ kJ mol}^{-1}$$

$$\boxed{589.56 \text{ kJ mol}^{-1}}$$

$$\Delta_{\text{r}}U^{\ominus} = \Delta_{\text{r}}H^{\ominus} - n_{\text{g}}RT$$

$$589.56 \text{ kJ mol}^{-1} - (1) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

$$589.56 \text{ kJ mol}^{-1} - 2.48 \text{ kJ mol}^{-1} = \boxed{587.08 \text{ kJ mol}^{-1}}$$

(b)  $\Delta_{\text{f}}H^{\ominus}$  refers to the formation of one mole of the compound, so

$$\Delta_{\text{f}}H^{\ominus}(\text{HI}) = \frac{1}{2} (-52.96 \text{ kJ mol}^{-1}) = \boxed{-26.48 \text{ kJ mol}^{-1}}$$

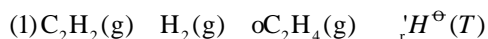
$$\Delta_{\text{f}}H^{\ominus}(\text{H}_2\text{O}) = \frac{1}{2} (-483.64 \text{ kJ mol}^{-1}) = \boxed{-241.82 \text{ kJ mol}^{-1}}$$

**2C.7(b)**  $\Delta_{\text{r}}H^{\ominus} = \Delta_{\text{r}}U^{\ominus} + RT \Delta n_{\text{g}}$  [2B.4]

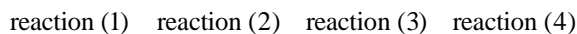
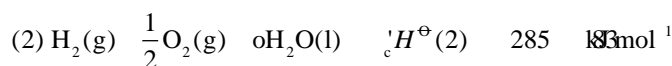
$$772.7 \text{ kJ mol}^{-1} - (5) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})$$

$$\boxed{760.3 \text{ kJ mol}^{-1}}$$

**2C.8(b)** The hydrogenation reaction is



The reactions and accompanying data which are to be combined in order to yield reaction (1) and  $\Delta_{\text{r}}H^{\ominus}(T)$  are



Hence, at 298 K:

$$\Delta_{\text{r}}H^{\ominus} = \Delta_{\text{c}}H^{\ominus}(2) - \Delta_{\text{c}}H^{\ominus}(3) + \Delta_{\text{c}}H^{\ominus}(4)$$

$$[(-285.83) - (-1411) + (-1300)] \text{ kJ mol}^{-1} = \boxed{175 \text{ kJ mol}^{-1}}$$

$$\Delta_{\text{r}}U^{\ominus} = \Delta_{\text{r}}H^{\ominus} - n_{\text{g}}RT \quad [2B.4]; \quad n_{\text{g}} = 1$$

$$175 \text{ kJ mol}^{-1} - (1) (2.48 \text{ kJ mol}^{-1}) = \boxed{172.5 \text{ kJ mol}^{-1}}$$

(ii) At 427 K:

$$\Delta_{\text{r}}H^{\ominus}(427 \text{ K}) = \Delta_{\text{r}}H^{\ominus}(298 \text{ K}) + \Delta_{\text{r}}C_p^{\ominus}(427 \text{ K} - 298 \text{ K}) \quad [\text{Example 2C.2}]$$

$$\begin{aligned}
{}_r C_p' &= \int_J Q_{p,m}^{\oplus}(J) [2C.7c] \quad C_{p,m}^{\oplus}(C_2H_4, g) \quad C_{p,m}^{\oplus}(C_2H_2, g) \quad C_{p,m}^{\oplus}(H_2, g) \\
&= (43.56 \quad 43.93 \quad 28.82) \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \quad 29.19 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \\
{}_r H^{\oplus}(427 \text{ K}) &= (-175 \text{ kJ mol}^{-1}) - (29.19 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \cdot (129 \text{ K}) \\
&\quad \boxed{171 \text{ kJ mol}^{-1}}
\end{aligned}$$

**2C.9(b)** For the reaction  $C_{10}H_8(l) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(g)$

$${}_r H^{\oplus} = 10 \cdot {}_f H^{\oplus}(CO_2, g) + 4 \cdot {}_f H^{\oplus}(H_2O, g) - {}_f H^{\oplus}(C_{10}H_8, l)$$

In order to calculate the enthalpy of reaction at 478 K we first calculate its value at 298 K using data in Tables 2C.1 and 2C.2. Note at 298 K naphthalene is a solid. It melts at  $80.2^\circ\text{C} = 353.4 \text{ K}$ .

$${}_r H^{\oplus}(298 \text{ K}) = 10 \cdot (-393.51 \text{ kJ mol}^{-1}) + 4 \cdot (-241.82 \text{ kJ mol}^{-1}) - (78.53 \text{ kJ mol}^{-1}) = -4980.91 \text{ kJ mol}^{-1}$$

Then, using data on the heat capacities and transition enthalpies of all the reacting substances, we can calculate the change in enthalpy,  $\Delta H$ , of each substance as the temperature increases from 298 K to 478 K. The enthalpy of reaction at 478 K can be obtained by adding all these enthalpy changes to the enthalpy of reaction at 298 K. This process is shown below:

$${}_r H^{\oplus}(478 \text{ K}) = {}_r H^{\oplus}(298 \text{ K}) + 10 \cdot \Delta H(CO_2, g) + 4 \cdot \Delta H(H_2O, g) - \Delta H(C_{10}H_8) - 12 \cdot \Delta H(O_2, g)$$

For  $H_2O(g)$ ,  $CO_2(g)$ , and  $O_2(g)$  we have

$${}_f H^{\oplus}(478 \text{ K}) - {}_f H^{\oplus}(298 \text{ K}) = \int_{298 \text{ K}}^{478 \text{ K}} C_{p,m}^{\oplus} dT$$

For naphthalene we have to take into account the change in state from solid to liquid at  $80.2^\circ\text{C} = 353.4 \text{ K}$ . Then

$${}_f H^{\oplus}(478 \text{ K}) = {}_f H^{\oplus}(298 \text{ K}) + \int_{298 \text{ K}}^{353.4 \text{ K}} C_{p,m}^{\oplus} dT + H_{\text{fus}} + \int_{353.4 \text{ K}}^{478 \text{ K}} C_{p,m}^{\oplus} dT$$

We will express the temperature dependence of the heat capacities in the form of the equation given in Problem 2C.7 because data for the heat capacities of the substances involved in this reaction are only available in that form. They are not available for all the substances in the form of the equation of Table 2B.1. We use

$$C_{p,m}^{\oplus} = AT + BT^2$$

For  $H_2O(g)$ ,  $CO_2(g)$ , and  $O_2(g)$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  values are given in Problem 2C.7. For naphthalene, solid and liquid,  $\gamma$  is zero and the two forms of the heat capacity equation are then identical and we take  $\alpha = a$  and  $\beta = b$  from Table 2B.1.

$$H_{\text{fus}}(C_{10}H_8) = 19.01 \text{ kJ mol}^{-1}$$

Using the data given in Problem 2C.7 we calculate

$$H(CO_2, g) = 5.299 \text{ kJ mol}^{-1}, \quad H(H_2O, g) = 6.168 \text{ kJ mol}^{-1}, \quad \text{and} \quad H(O_2, g) = 5.430 \text{ kJ mol}^{-1}$$

Using the data from Table 2C.1 we calculate for naphthalene

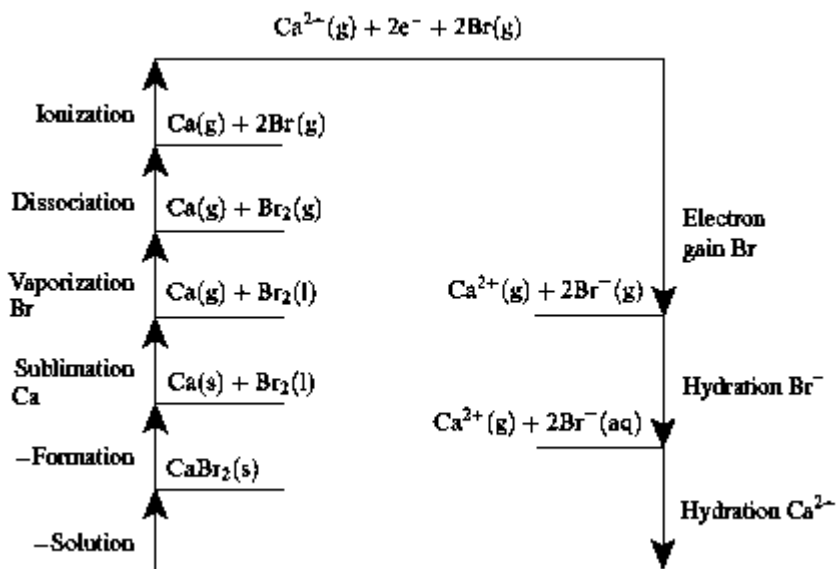
$$H(C_{10}H_8) = 55.36 \text{ kJ mol}^{-1}$$

Collecting all these enthalpy changes we have

$${}_r H^{\oplus}(478 \text{ K}) = {}_r H^{\oplus}(298 \text{ K}) + (10 \cdot 5.299 + 4 \cdot 6.168 - 55.36 - 12 \cdot 5.430) \text{ kJ mol}^{-1} = \boxed{5023.77 \text{ kJ mol}^{-1}}$$

**2C.10(b)** The cycle is shown in Fig. 2C.1.

**Figure 2C.1**



$$\begin{aligned}
 {}_{\text{hyd}}H^{\ominus}(\text{Ca}^{2+}) &= {}_{\text{soln}}H^{\ominus}(\text{CaBr}_2) - {}_{\text{f}}H^{\ominus}(\text{CaBr}_2\text{ s}) - {}_{\text{sub}}H^{\ominus}(\text{Ca}) \\
 &\quad - {}_{\text{vap}}H^{\ominus}(\text{Br}_2) - {}_{\text{diss}}H^{\ominus}(\text{Br}_2) - {}_{\text{ion}}H^{\ominus}(\text{Ca}) - 2' \\
 &\quad - {}_{\text{ion}}H^{\ominus}(\text{Ca}) - 2' {}_{\text{eg}}H^{\ominus}(\text{Br}) - 2' {}_{\text{hyd}}H^{\ominus}(\text{Br}^-) \\
 &= [(-103.1) - (-682.8) - 178.2 - 30.91 - 192.9 \\
 &\quad - 589.7 - 1145 - 2(-331.0) - 2(-289)] \text{ kJ mol}^{-1} \\
 &= \boxed{1684 \text{ kJ mol}^{-1}}
 \end{aligned}$$

so  ${}_{\text{hyd}}H^{\ominus}(\text{Ca}^{2+}) = \boxed{1684 \text{ kJ mol}^{-1}}$

## Solutions to problems

**2C.2**  $\text{Cr}(\text{C}_6\text{H}_6)_2(\text{s}) \rightarrow \text{oCr}(\text{s}) + 2\text{C}_6\text{H}_6(\text{g})$   $\dot{n}_{\text{g}} = 2 \text{ mol}$

$$\begin{aligned}
 {}_{\text{r}}H^{\ominus} &= {}_{\text{r}}U^{\ominus} - 2RT \text{ from [2B.4]} \\
 &= (8.0 \text{ kJ mol}^{-1}) - (2) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (583 \text{ K}) = \boxed{17.7 \text{ kJ mol}^{-1}}
 \end{aligned}$$

In terms of enthalpies of formation

$${}_{\text{r}}H^{\ominus} = (2) {}_{\text{u}}H^{\ominus}(\text{benzene } 583 \text{ K}) - {}_{\text{f}}H^{\ominus}(\text{metallocene } 583 \text{ K})$$

or  ${}_{\text{r}}H^{\ominus}(\text{metallocene } 583 \text{ K}) = 2 {}_{\text{f}}H^{\ominus}(\text{benzene } 583 \text{ K}) - 17.7 \text{ kJ mol}^{-1}$

The enthalpy of formation of benzene gas at 583 K is related to its value at 298 K by

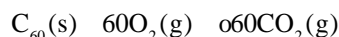
$$\begin{aligned}
 {}_{\text{f}}H^{\ominus}(\text{benzene } 583 \text{ K}) &= {}_{\text{f}}H^{\ominus}(\text{benzene } 298 \text{ K}) \\
 &\quad + (T_{\text{b}} - 298 \text{ K})C_{p,\text{m}}(\text{l}) + {}_{\text{vap}}H^{\ominus}(583 \text{ K} - T_{\text{b}})C_{p,\text{m}}(\text{g}) \\
 &\quad + 6 (583 \text{ K} - 298 \text{ K})C_{p,\text{m}}(\text{gr}) - 3 (583 \text{ K} - 298 \text{ K})C_{p,\text{m}}(\text{H}_2 \text{ g})
 \end{aligned}$$

where  $T_{\text{b}}$  is the boiling temperature of benzene (353 K). We shall assume that the heat capacities of graphite and hydrogen are approximately constant in the range of interest and use their values from Tables 2B.1 and 2B.2.

$$\begin{aligned}
{}_fH^\ominus(\text{benzene } 583\text{ K}) &= (49.0\text{ kJ mol}^{-1}) - (353 - 298)\text{ K} (-136.1\text{ J K}^{-1}\text{ mol}^{-1}) \\
&= (30.8\text{ kJ mol}^{-1}) - (583 - 353)\text{ K} (-81.67\text{ J K}^{-1}\text{ mol}^{-1}) \\
&= (6) - (583 - 298)\text{ K} (-85.3\text{ J K}^{-1}\text{ mol}^{-1}) \\
&= (3) - (583 - 298)\text{ K} (-28.82\text{ J K}^{-1}\text{ mol}^{-1}) \\
&= \{(49.0) - (7.49) - (18.78) - (30.8) - (14.59) - (24.64)\}\text{ kJ mol}^{-1} \\
&= 66.8\text{ kJ mol}^{-1}
\end{aligned}$$

Therefore,  ${}_fH^\ominus(\text{metallocene}, 583\text{ K}) = (2 - 66.8 - 17.7)\text{ kJ mol}^{-1} = \boxed{116.0\text{ kJ mol}^{-1}}$

**2C.4** The reaction is



Because the reaction does not change the number of moles of gas,  ${}_rH = {}_rU$  [2B.4]. Therefore

$${}_cH^\ominus = (-36.0334\text{ kJ g}^{-1}) (60 \times 12.011\text{ g mol}^{-1}) = \boxed{25968\text{ kJ mol}^{-1}}$$

Now relate the enthalpy of combustion to enthalpies of formation and solve for that of  $\text{C}_{60}$ .

$$\begin{aligned}
{}_cH^\ominus &= 60 {}_fH^\ominus(\text{CO}_2) - 60 {}_fH^\ominus(\text{O}_2) - {}_fH^\ominus(\text{C}_{60}) \\
{}_fH^\ominus(\text{C}_{60}) &= 60 {}_fH^\ominus(\text{CO}_2) - 60 {}_fH^\ominus(\text{O}_2) - {}_cH^\ominus \\
&= [60(-393.51) - 60(0) - (-25968)]\text{ kJ mol}^{-1} = \boxed{2357\text{ kJ mol}^{-1}}
\end{aligned}$$

**2C.6 (a)**

$$\begin{aligned}
{}_rH^\ominus &= {}_fH^\ominus(\text{SiH}_2) - {}_fH^\ominus(\text{H}_2) - {}_fH^\ominus(\text{SiH}_4) \\
&= (274 - 0 - 34.3)\text{ kJ mol}^{-1} = \boxed{240\text{ kJ mol}^{-1}}
\end{aligned}$$

**(b)**

$$\begin{aligned}
{}_rH^\ominus &= {}_fH^\ominus(\text{SiH}_2) - {}_fH^\ominus(\text{SiH}_4) - {}_fH^\ominus(\text{Si}_2\text{H}_6) \\
&= (274 - 34.3 - 80.3)\text{ kJ mol}^{-1} = \boxed{228\text{ kJ mol}^{-1}}
\end{aligned}$$

**2C.8** In order to calculate the enthalpy of the protein's unfolding we need to determine the area under the plot of  $C_{p,\text{ex}}$  against  $T$ , from the baseline value of  $C_{p,\text{ex}}$  at  $T_1$ , the start of the process, to the baseline value of  $C_{p,\text{ex}}$  at  $T_2$ , the end of the process. We are provided with an illustration that shows the plot, but no numerical values are provided. Approximate numerical values can be extracted from the plot and

then the value of the integral  $\int_{T_1}^{T_2} C_{p,\text{ex}} dT$  can be obtained by numerical evaluation of the area

under the curve. The first two columns in the table below show the data estimated from the curve, the last column gives the approximate area under the curve from the beginning of the process to the end. The final value,  $\boxed{1889\text{ kJ mol}^{-1}}$ , is the enthalpy of unfolding of the protein. The four significant figures shown are not really justified because of the imprecise estimation process involved.

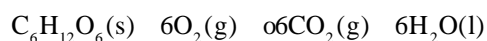
$T/K$	$C_{p,ex}/\text{kJ K}^{-1} \text{mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$
30	20	0
40	23	215
50	26	460
54	28	567
56	33	626
57	40	663
58	46	706
59	52	755
60	58	810
61	63	870
62	70	937
63	80	1011
64	89	1096
64.5	90	1141
65	85	1185
66	80	1267
67	68	1342
68	60	1405
69	52	1461
70	47	1511
72	41	1598
74	37	1676
80	36	1889

**2C.10 (a)**  $q_v = n C_v U^\ominus$ ; hence

**(ii)**  $C_v U^\ominus = \frac{q_v}{n} = \frac{C}{n} \frac{T}{m} = \frac{MC}{m} \frac{T}{m}$  where  $m$  is sample mass and  $M$  molar mass

so  $C_v U^\ominus = \frac{(180.16 \text{ g mol}^{-1}) (641 \text{ J K}^{-1}) (7.793 \text{ K})}{0.3212 \text{ g}} = \boxed{2802 \text{ kJ mol}^{-1}}$

**(i)** The complete aerobic oxidation is



Since there is no change in the number of moles of gas,  $\Delta_r H^\ominus = \Delta_r U^\ominus$  [2.21] and

$$\Delta_r H^\ominus = \Delta_r U^\ominus = \boxed{2802 \text{ kJ mol}^{-1}}$$

**(iii)**  $\Delta_r H^\ominus = 6 \Delta_f H^\ominus(\text{CO}_2, \text{g}) - 6 \Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\ominus(\text{C}_6\text{H}_{12}\text{O}_6, \text{s}) - 6 \Delta_f H^\ominus(\text{O}_2, \text{g})$

so  $\Delta_f H^\ominus(\text{C}_6\text{H}_{12}\text{O}_6, \text{s}) = 6 \Delta_f H^\ominus(\text{CO}_2, \text{g}) - 6 \Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - 6 \Delta_f H^\ominus(\text{O}_2, \text{g}) - \Delta_r H^\ominus$

$$\Delta_f H^\ominus(\text{C}_6\text{H}_{12}\text{O}_6, \text{s}) = [6(-393.51) - 6(-285.83) - 6(0) - (-2802)] \text{ kJ mol}^{-1}$$

$$\boxed{1274 \text{ kJ mol}^{-1}}$$

**(b)** The anaerobic glycolysis to lactic acid is



$$\Delta_r H^\ominus = 2 \Delta_f H^\ominus(\text{lactic acid}) - \Delta_f H^\ominus(\text{glucose})$$

$$= \{2(-694.0) - (-1274)\} \text{ kJ mol}^{-1} = -114 \text{ kJ mol}^{-1}$$

Therefore, aerobic oxidation is more exothermic by  $\boxed{2688 \text{ kJ mol}^{-1}}$  than glycolysis.

## 2D State functions and exact differentials

### Answers to discussion questions

**2D.2** An inversion temperature is the temperature at which the Joule-Thomson coefficient,  $\mu_{JT}$ , changes sign from negative to positive or *vice-versa*. For a perfect gas  $\mu_{JT}$  is always zero, thus it cannot have an inversion temperature. As explained in detail in Section 2D.3, 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

**2D.1(b)** Also see exercises E2D.1(a) and E2D.2(a) and their solutions. The internal pressure of a van der Waals gas is  $\pi = a/V_m^2$ . The molar volume can be estimated from the perfect gas equation:

$$V_m = \frac{RT}{p} = \frac{0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1.00 \text{ bar} \times \frac{1.000 \text{ atm}}{1.013 \text{ bar}}} = 24.76 \text{ dm}^3 \text{ mol}^{-1}$$

$$\pi = \frac{a}{V_m^2} = \frac{6.775 \text{ atm dm}^6 \text{ mol}^{-2}}{(24.76 \text{ dm}^3 \text{ mol}^{-1})^2} = 1.11 \times 10^{-2} \text{ atm} = \boxed{11.2 \text{ mbar}}$$

**2D.2(b)** The internal energy is a function of temperature and volume,  $U_m = U_m(T, V_m)$ , so

$$dU_m = \left( \frac{\partial U_m}{\partial T} \right)_{V_m} dT + \left( \frac{\partial U_m}{\partial V_m} \right)_T dV_m = [C_{V,m} + (\pi - p)] dV_m$$

For an isothermal expansion  $dT = 0$ ; hence

$$dU_m = \left( \frac{\partial U_m}{\partial V_m} \right)_T dV_m = \pi dV_m = \frac{a}{V_m^2} dV_m$$

$$U_m = \int_{V_{m,1}}^{V_{m,2}} dU_m = \int_{V_{m,1}}^{V_{m,2}} \frac{a}{V_m^2} dV_m = a \left[ -\frac{1}{V_m} \right]_{V_{m,1}}^{V_{m,2}} = \frac{a}{V_{m,1}} - \frac{a}{V_{m,2}}$$

$$= \frac{a}{30.00 \text{ dm}^3 \text{ mol}^{-1}} - \frac{a}{1.00 \text{ dm}^3 \text{ mol}^{-1}} = \frac{29.00a}{30.00 \text{ dm}^3 \text{ mol}^{-1}} = 0.9667a \text{ dm}^3 \text{ mol}^{-1}$$

From Table 1C.3,  $a = 1.337 \text{ dm}^6 \text{ atm mol}^{-1}$

$$U_m = 0.9667 \text{ mol dm}^3 \times (1.337 \text{ atm dm}^6 \text{ mol}^{-1}) = 1.2924 \text{ atm dm}^3 \text{ mol}^{-1}$$

$$(1.2924 \text{ atm dm}^3 \text{ mol}^{-1}) \times (1.01325 \times 10^5 \text{ Pa atm}^{-1}) \times \frac{1 \text{ m}^3}{10^3 \text{ dm}^3} =$$

$$131.0 \text{ Pa m}^3 \text{ mol}^{-1} = \boxed{131.0 \text{ J mol}^{-1}}$$

$$w = p \Delta V_m \quad \text{where} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{for a van der Waals gas. Hence,}$$

$$w = \int_{V_{m,1}}^{V_{m,2}} p dV_m = \int_{V_{m,1}}^{V_{m,2}} \left( \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) dV_m = q - \Delta U_m$$

Thus

$$q = \frac{30.00 \text{ dm}^3 \text{ mol}^{-1}}{1.00 \text{ dm}^3 \text{ mol}^{-1}} \frac{RT}{V_m} \ln \left( \frac{30.00 \text{ dm}^3 \text{ mol}^{-1}}{1.00 \text{ dm}^3 \text{ mol}^{-1}} \right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \ln \frac{30.00}{1.00} = 8505 \text{ J mol}^{-1}$$

$$\text{and } w = q - \Delta U_m = (8505 \text{ J mol}^{-1}) - (131 \text{ J mol}^{-1}) = 8374 \text{ J mol}^{-1} = 8.37 \text{ kJ mol}^{-1}$$

**2D.3(b)** The expansion coefficient is

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\partial}{\partial T} \left[ \frac{V}{1 - \frac{b}{V}} \right] \right)_p = \frac{1}{V} \left( \frac{V}{1 - \frac{b}{V}} \right) \left( \frac{1}{V} \right) = \frac{1}{V - b}$$

$$= \frac{1}{0.77 \times 10^{-4} \text{ m}^3 - 1.52 \times 10^{-6} \text{ m}^3} = 1.27 \times 10^3 \text{ K}^{-1}$$

**2D.4(b)** Isothermal compressibility is

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad \text{so} \quad \beta = \frac{V}{\kappa}$$

A density increase of 0.10 per cent means  $V' = V - 0.0010V$ . So the additional pressure that must be applied is

$$p' = \frac{0.0010}{2.21 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} = 4.5 \times 10^2 \text{ atm}$$

**2D.5(b)** The isothermal Joule-Thomson coefficient is

$$\frac{H_m}{p} = \left( \frac{\partial H_m}{\partial p} \right)_T = \left( 1 - \frac{1}{p} \right) \left( \frac{\partial H_m}{\partial T} \right)_p = 41.2 \text{ J atm}^{-1} \text{ mol}^{-1}$$

If this coefficient is constant in an isothermal Joule-Thomson experiment, then the heat which must be supplied to maintain constant temperature is  $H'$  in the following relationship

$$\frac{H'}{p} = 41.2 \text{ J atm}^{-1} \text{ mol}^{-1} \quad \text{so} \quad H' = (41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) n p$$

$$H' = (41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) (10.0 \text{ mol}) (75 \text{ atm}) = 30.9 \times 10^3 \text{ J}$$

## Solutions to problems

**2D.2**

$$c_s = \frac{\sqrt{RT}}{M} \left( \frac{C_{p,m}}{C_{v,m}} \right) = \frac{C_{p,m}}{C_{v,m}} \sqrt{RT} = \sqrt{RT} \left( \frac{C_{p,m}}{C_{v,m}} \right)$$

(a)  $C_{v,m} = \frac{1}{2} R (3 - 2) = \frac{5}{2} R$

$$C_{p,m} = \frac{5}{2} R + R = \frac{7}{2} R$$

$$\sqrt{\frac{7}{5}} = 1.40 \quad \text{hence} \quad c_s = \frac{\sqrt{40RT}}{M}$$

(b)  $C_{v,m} = \frac{1}{2} R (3 - 2) = \frac{5}{2} R$   $\sqrt{\frac{7}{5}} = 1.40$   $c_s = \frac{\sqrt{40RT}}{M}$

(c)  $C_{V_m} = \frac{1}{2} R(3 + 3) = 3R$

$$C_{p,m} = 3R + R + 4R = J \frac{4}{3} R$$

For air,  $M = 29 \text{ g mol}^{-1}$ ,  $T = 298 \text{ K}$ ,  $J = 1.40$

$$c_s = \frac{(1.40) (2.48 \text{ kJ mol}^{-1})^{1/2}}{29 \times 10^3 \text{ kg mol}^{-1}} \approx 350 \text{ m s}^{-1}$$

$$\mathbf{2D.4} \quad (\mathbf{a}) \quad V = V(p, T); \text{ hence, } dV = \left( \frac{\partial V}{\partial p} \right)_T dp + \left( \frac{\partial V}{\partial T} \right)_p dT$$

Likewise  $p = p(V, T)$ , so  $dp$

$$\frac{\partial p}{\partial V} dV + \frac{\partial p}{\partial T} dT$$

(b) We use  $D \cdot \frac{\mathfrak{f}}{\mathbb{C}} \cdot \frac{SW}{CW} \cdot [2D.6]$  and  $N \cdot \frac{\mathfrak{f}}{\mathbb{C}} \cdot \frac{SW}{CW} \cdot [2D.7]$  and obtain

$$d \ln V = \frac{1}{V} dV = \frac{\frac{\delta}{V} \cdot \frac{\delta W}{Q_W}}{\frac{\delta}{V} \cdot \frac{\delta W}{Q_W}} \cdot dp = \frac{\frac{\delta}{V} \cdot \frac{\delta W}{Q_W}}{\frac{\delta}{V} \cdot \frac{\delta W}{Q_W}} \cdot dT = \frac{dp}{dT}.$$

Likewise  $d \ln p = \frac{dp}{p} = \frac{1}{p} \frac{\$_{pw}}{\$_w} \cdot dV = \frac{1}{p} \frac{\$_{pw}}{\$_w} \cdot dT$

We express  $\frac{\dot{S}_{PW}}{\dot{Q}_T}$  in terms of  $T_N$

$$T^N \sim \frac{1}{V} \frac{\mathcal{S}W}{\mathcal{Q}W} \cdot \frac{a}{V_K} \frac{\mathcal{S}pW}{\mathcal{Q}W} \cdot \frac{b}{T} \gg \text{so } \frac{\mathcal{S}pW}{\mathcal{Q}W} \cdot \frac{1}{T^N}$$

We express  $\frac{\delta p_w}{\delta w}$  in terms of  $N$  and  $D$

[illegible]

so  $d \ln p = \frac{dV}{p_T V} - \frac{dT}{p_T} \left[ \frac{1}{p_T} + \frac{dV}{N V} \right]$

**2D.6**  $D \frac{1}{V} \frac{W}{T_W} = \frac{1}{V} \frac{W}{T_W}$  [reciprocal identity, *Mathematical Background 2*]

$$D \frac{1}{V} = \frac{\mu}{\frac{T}{V}} \cdot \frac{1}{nb} \cdot \frac{2na}{RV^3} \cdot \frac{\$}{(V)} \cdot \frac{(V)}{nb} \cdot \frac{(V)}{u} \cdot \frac{(V)}{I}$$

$$\frac{(RV^2)}{(RTV^3)} \frac{(V unb)}{(2na) (V nb)^2 u}$$



$$\alpha = \frac{1}{V} \left( \frac{\partial W}{\partial p} \right)_T = \frac{1}{V} \left( \frac{\partial p}{\partial W} \right)_T^{-1} \quad [\text{reciprocal identity}]$$

$$\alpha = \frac{1}{V} \left( \frac{\partial}{\partial p} \left( \frac{nRT}{(V-nb)^2} + \frac{2n^2a}{V^3} \right) \right)_T \quad [\text{Problem 2D.5}]$$

$$\frac{V^2(V-nb)^2}{nRTV^3 - 2n^2a(V-nb)^2}$$

Then  $\alpha = \frac{1}{D} \frac{V-nb}{nR}$ , implying that  $\alpha = (V_m - b)$

Alternatively, from the definitions of  $\alpha$  and  $\beta$  above

$$\frac{\alpha}{D} = \frac{\left( \frac{\partial W}{\partial p} \right)_T}{\left( \frac{\partial W}{\partial T} \right)_p} = \frac{\left( \frac{\partial p}{\partial W} \right)_T^{-1}}{\left( \frac{\partial p}{\partial T} \right)_p} \quad [\text{reciprocal identity}]$$

$$= \frac{\left( \frac{\partial T}{\partial p} \right)_W}{\left( \frac{\partial T}{\partial p} \right)_W} \quad [\text{Euler chain relation}]$$

$$= \frac{V-nb}{nR} \quad [\text{Problem 2D.5}],$$

$$\alpha = \frac{(V_m - b)}{n}$$

Hence,  $\alpha = (V_m - b)$

## 2D.8

$$p = \left( \frac{\partial W}{\partial V} \right)_T = \frac{1}{C_p} \left( \frac{\partial W}{\partial T} \right)_p \quad [\text{Justification 2D.2}]$$

$$p = \frac{1}{C_p} \left( \frac{\partial W}{\partial T} \right)_p = V \quad [\text{See the section below for a derivation of this result}]$$

$$\text{But } V = \frac{nRT}{p} - nb \quad \text{or} \quad \left( \frac{\partial W}{\partial T} \right)_p = \frac{nR}{p}$$

Therefore,

$$p = \frac{1}{C_p} \left( \frac{\partial W}{\partial T} \right)_p = V = \frac{1/2}{3/4} \frac{1}{C_p} \left( \frac{\partial W}{\partial T} \right)_p = \frac{nRT}{p} - nb = \frac{1/2}{3/4} \frac{nb}{C_p}$$

Since  $b > 0$  and  $C_p > 0$ , we conclude that for this gas  $\alpha < 0$  or  $\left( \frac{\partial W}{\partial p} \right)_T < 0$ . This says that when the pressure drops during a Joule–Thomson expansion the temperature must increase.

**Derivation of expression for  $\left( \frac{\partial W}{\partial p} \right)_T$  follows:**



With vibrations  $C_{V,m}/R = 3 \frac{1}{2} + 2 \frac{1}{2} + (3 + 4 + 5) \times 6.5$  and  $u \approx \frac{7.5}{6.5}$  1.15

Without vibrations  $C_{V,m}/R = 3 \frac{1}{2} + 2 \frac{1}{2} + 2.5$  and  $u \approx \frac{3.5}{2.5}$  1.40

Experimental  $J \frac{37.11 \text{ J mol}^{-1} \text{ K}^{-1}}{(37.11 - 8.3145) \text{ J mol}^{-1} \text{ K}^{-1}}$  1.29

The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely.

$$T = \frac{hc\tilde{B}}{k} = \frac{(6.626 \times 10^{-34} \text{ J s})u(2.998 \times 10^{10} \text{ cm s}^{-1})(0.39 \text{ cm}^{-1})}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 0.56 \text{ K} \quad 298 \text{ K}$$

and therefore rotational contributions cannot be neglected.

**2E.2(b)** For reversible adiabatic expansion

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\frac{1}{c}} \quad [2E.2a]$$

where  $c = \frac{C_{V,m}}{R} = \frac{C_{p,m}}{R} - 1 = \frac{37.11 - 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} = 3.463$ ;

therefore, the final temperature is

$$T_f = (298.15 \text{ K}) \left( \frac{0.0200 \text{ dm}^3}{2.00 \text{ dm}^3} \right)^{\frac{1}{3.463}} = 200 \text{ K}$$

**2E.3(b)** In an adiabatic process, the initial and final pressures are related by (eqn. 2E.3)

$$p_f V_f^{\frac{1}{c}} = p_i V_i^{\frac{1}{c}} \quad \text{where} \quad \frac{1}{c} = \frac{C_{p,m}}{C_{V,m}} - 1 = \frac{20.8 \text{ J K}^{-1} \text{ mol}^{-1}}{(20.8 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1}} = 1.67$$

Find  $V_i$  from the perfect gas law:

$$V_i = \frac{nRT_i}{p_i} = \frac{(2.5 \text{ mol})(8.31 \text{ J K}^{-1} \text{ mol}^{-1})(325 \text{ K})}{240 \times 10^3 \text{ Pa}} = 0.0281 \text{ m}^3$$

so  $V_f = V_i \left( \frac{p_i}{p_f} \right)^{\frac{1}{c}} = (0.0281 \text{ m}^3) \left( \frac{240 \text{ kPa}}{150 \text{ kPa}} \right)^{\frac{1}{1.67}} = 0.0372 \text{ m}^3$

Find the final temperature from the perfect gas law:

$$T_f = \frac{p_f V_f}{nR} = \frac{(150 \times 10^3 \text{ Pa})(0.0372 \text{ m}^3)}{(2.5 \text{ mol})(8.31 \text{ J K}^{-1} \text{ mol}^{-1})} = 269 \text{ K}$$

Adiabatic work is (eqn. 2E.1)

$$w = C_V \Delta T = (20.8 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1} \times 2.5 \text{ mol} \times (269 - 325) \text{ K} = 1.7 \times 10^3 \text{ J}$$

**2E.4(b)** Reversible adiabatic work is

$$w = C_V \Delta T \quad [2E.1] \quad n(C_{p,m} - R)(T_f - T_i)$$

where the temperatures are related by

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\frac{1}{c}} \quad [2E.2a] \quad \text{where} \quad c = \frac{C_{V,m}}{R} = \frac{C_{p,m}}{R} - 1 = 2.503$$

$$\text{So } T_f = 23.0 + 273.15 \text{ K} = \frac{400 \text{ dm}^3}{2.00 \text{ dm}^3}^{1/2.503} = 156 \text{ K}$$

$$\text{and } w = \frac{3.12 \text{ g}}{28.0 \text{ g mol}^{-1}} \cdot 29.125 \cdot 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 156 \cdot 296 \text{ K} = \boxed{325 \text{ J}}$$

**2E.5(b)** For reversible adiabatic expansion

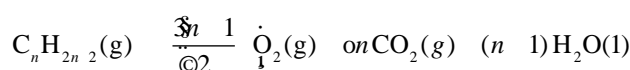
$$p_f V_f^\gamma = p_i V_i^\gamma \quad [2E.3] \quad \text{so } p_f = p_i \left( \frac{V_i}{V_f} \right)^\gamma = 97.3 \text{ Torr} \cdot \left( \frac{400 \text{ dm}^3}{5.0 \text{ dm}^3} \right)^{1.3} = \boxed{3.6 \text{ Torr}}$$

## Integrated activities

**2.2** (a) and (b). The table below displays computed enthalpies of formation (semi-empirical, PM3 level, PC Spartan Pro<sup>TM</sup>), enthalpies of combustion based on them (and on experimental enthalpies of formation of H<sub>2</sub>O(l) and CO<sub>2</sub>(g), −285.83 and −393.51 kJ mol<sup>−1</sup> respectively), experimental enthalpies of combustion (Table 2.6), and the relative error in enthalpy of combustion.

Compound	${}_f H^\ominus / \text{kJ mol}^{-1}$	${}_c H^\ominus / \text{kJ mol}^{-1} (\text{calc.})$	${}_c H^\ominus / \text{kJ mol}^{-1} (\text{expt.})$	% error
CH <sub>4</sub> (g)	−54.45	−910.72	−890	2.33
C <sub>2</sub> H <sub>6</sub> (g)	−75.88	−1568.63	−1560	0.55
C <sub>3</sub> H <sub>8</sub> (g)	−98.84	−2225.01	−2220	0.23
C <sub>4</sub> H <sub>10</sub> (g)	−121.60	−2881.59	−2878	0.12
C <sub>5</sub> H <sub>12</sub> (g)	−142.11	−3540.42	−3537	0.10

The combustion reactions can be expressed as:



The enthalpy of combustion, in terms of enthalpies of reaction, is

$${}_c H^\ominus = n {}_f H^\ominus(\text{CO}_2) + (n+1) {}_f H^\ominus(\text{H}_2\text{O}) - {}_f H^\ominus(\text{C}_n\text{H}_{2n+2}),$$

Where we have left out  ${}_f H^\ominus(\text{O}_2) = 0$ . The % error is defined as:

$$\% \text{ error} = \frac{{}_c H^\ominus(\text{calc}) - {}_c H^\ominus(\text{expt.})}{{}_c H^\ominus(\text{expt.})} \cdot 100\%$$

The agreement is quite good.

(c) If the enthalpy of combustion is related to the molar mass by

$${}_c H^\ominus = k[M / (\text{g mol}^{-1})]^n$$

then one can take the natural log of both sides to obtain:

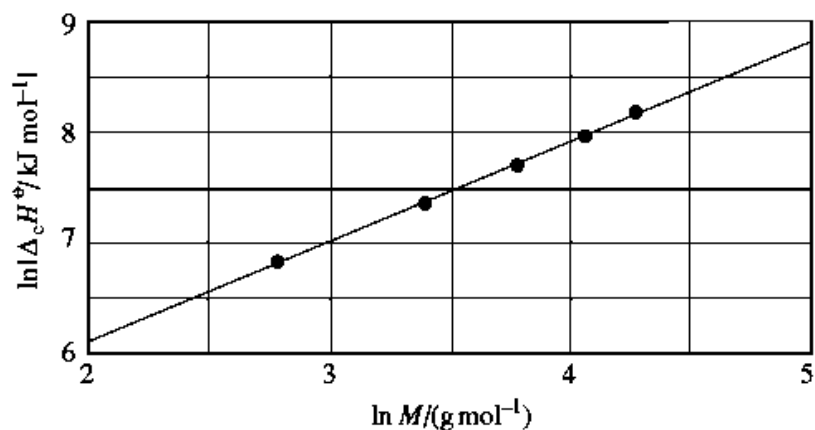
$$\ln |{}_c H^\ominus| = \ln |k| + n \ln M / (\text{g mol}^{-1}).$$

Thus, if one plots  $\ln |{}_c H^\ominus|$  vs.  $\ln [M / (\text{g mol}^{-1})]$ , one ought to obtain a straight line with slope  $n$  and y-intercept  $\ln |k|$ . Draw up the following table:

Compound	$M/(\text{g mol}^{-1})$	${}_{\text{c}}H^{\ominus}/\text{kJ mol}^{-1}$	$\ln M/(\text{g mol}^{-1})$	$\ln  {}_{\text{c}}H^{\ominus}/\text{kJ mol}^{-1} $
$\text{CH}_4(\text{g})$	16.04	-910.72	2.775	6.814
$\text{C}_2\text{H}_6(\text{g})$	30.07	-1568.63	3.404	7.358
$\text{C}_3\text{H}_8(\text{g})$	44.10	-2225.01	3.786	7.708
$\text{C}_4\text{H}_{10}(\text{g})$	58.12	-2881.59	4.063	7.966
$\text{C}_5\text{H}_{12}(\text{g})$	72.15	-3540.42	4.279	8.172

The plot is shown below in Fig I2.1.

**Figure I2.1**



The linear least-squares fit equation is:

$$\ln |{}_{\text{c}}H^{\ominus}/\text{kJ mol}^{-1}| = 4.30 + 0.903 \ln M/(\text{g mol}^{-1}) \quad R^2 = 1.00$$

These compounds support the proposed relationships, with

$$n = \boxed{0.903} \quad \text{and} \quad k = -e^{4.30} \text{ kJ mol}^{-1} = \boxed{-73.7 \text{ kJ mol}^{-1}}.$$

The agreement of these theoretical values of  $k$  and  $n$  with the experimental values obtained in Problem 2C.3 is rather good.