

2 The First Law: the concepts

Solutions to exercises

Discussion questions

E2.1(b) Work is a transfer of energy that results in orderly motion of the atoms and molecules in a system; heat is a transfer of energy that results in disorderly motion. See Molecular Interpretation 2.1 for a more detailed discussion.

E2.2(b) Rewrite the two expressions as follows:

(1) adiabatic $p \propto 1/V^\gamma$ (2) isothermal $p \propto 1/V$

The physical reason for the difference is that, in the isothermal expansion, energy flows into the system as heat and maintains the temperature despite the fact that energy is lost as work, whereas in the adiabatic case, where no heat flows into the system, the temperature must fall as the system does work. Therefore, the pressure must fall faster in the adiabatic process than in the isothermal case. Mathematically this corresponds to $\gamma > 1$.

E2.3(b) Standard reaction enthalpies can be calculated from a knowledge of the standard enthalpies of formation of all the substances (reactants and products) participating in the reaction. This is an exact method which involves no approximations. The only disadvantage is that standard enthalpies of formation are not known for all substances.

Approximate values can be obtained from mean bond enthalpies. See almost any general chemistry text, for example, *Chemical Principles*, by Atkins and Jones, Section 6.21, for an illustration of the method of calculation. This method is often quite inaccurate, though, because the average values of the bond enthalpies used may not be close to the actual values in the compounds of interest.

Another somewhat more reliable approximate method is based on thermochemical groups which mimic more closely the bonding situations in the compounds of interest. See Example 2.6 for an illustration of this kind of calculation. Though better, this method suffers from the same kind of defects as the average bond enthalpy approach, since the group values used are also averages.

Computer aided molecular modeling is now the method of choice for estimating standard reaction enthalpies, especially for large molecules with complex three-dimensional structures, but accurate numerical values are still difficult to obtain.

Numerical exercises

E2.4(b) Work done against a uniform gravitational field is

$$w = mgh$$

(a) $w = (5.0 \text{ kg}) \times (100 \text{ m}) \times (9.81 \text{ m s}^{-2}) = \boxed{4.9 \times 10^3 \text{ J}}$

(b) $w = (5.0 \text{ kg}) \times (100 \text{ m}) \times (3.73 \text{ m s}^{-2}) = \boxed{1.9 \times 10^3 \text{ J}}$

E2.5(b) Work done against a uniform gravitational field is

$$w = mgh = (120 \times 10^{-3} \text{ kg}) \times (50 \text{ m}) \times (9.81 \text{ m s}^{-2}) = \boxed{59 \text{ J}}$$

E2.6(b) Work done by a system expanding against a constant external pressure is

$$w = -p_{\text{ex}} \Delta V = -(121 \times 10^3 \text{ Pa}) \times \left(\frac{(15 \text{ cm}) \times (50 \text{ cm}^2)}{(100 \text{ cm m}^{-1})^3} \right) = \boxed{-91 \text{ J}}$$

E2.7(b) For a perfect gas at constant temperature

$$\Delta U = \boxed{0} \quad \text{so} \quad q = -w$$

For a perfect gas at constant temperature, ΔH is also $\boxed{\text{zero}}$

$$dH = d(U + pV)$$

we have already noted that U does not change at constant temperature; nor does pV if the gas obeys Boyle's law. These apply to all three cases below.

(a) Isothermal reversible expansion

$$\begin{aligned} w &= -nRT \ln \frac{V_f}{V_i} \\ &= -(2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (22 + 273) \text{ K} \times \ln \frac{31.7 \text{ L}}{22.8 \text{ L}} = \boxed{-1.62 \times 10^3 \text{ J}} \\ q &= -w = \boxed{1.62 \times 10^3 \text{ J}} \end{aligned}$$

(b) Expansion against a constant external pressure

$$w = -p_{\text{ex}} \Delta V$$

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

$$pV = nRT$$

$$\text{so } p = \frac{(2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (22 + 273) \text{ K}}{31.7 \text{ L}} \times (1000 \text{ L m}^{-3}) = 1.55 \times 10^5 \text{ Pa}$$

$$\text{and } w = \frac{-(1.55 \times 10^5 \text{ Pa}) \times (31.7 - 22.8) \text{ L}}{1000 \text{ L m}^{-3}} = \boxed{-1.38 \times 10^3 \text{ J}}$$

$$q = -w = \boxed{1.38 \times 10^3 \text{ J}}$$

(c) Free expansion is expansion against no force, so $w = \boxed{0}$, and $q = -w = \boxed{0}$ as well.

E2.8(b) The perfect gas law leads to

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

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

$$\begin{aligned} q &= \int C_V dT \approx C_V \Delta T = (2.5) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (2.00 \text{ mol}) \times (356 - 277) \text{ K} \\ &= \boxed{3.28 \times 10^3 \text{ J}} \\ \Delta U &= q + w = \boxed{3.28 \times 10^3 \text{ J}} \end{aligned}$$

$$\mathbf{E2.9(b)} \quad (\mathbf{a}) \quad w = -p_{\text{ex}}\Delta V = \frac{-(7.7 \times 10^3 \text{ Pa}) \times (2.5 \text{ L})}{1000 \text{ L m}^{-3}} = \boxed{-19 \text{ J}}$$

$$\begin{aligned} (\mathbf{b}) \quad w &= -nRT \ln \frac{V_f}{V_i} \\ &= -\left(\frac{6.56 \text{ g}}{39.95 \text{ g mol}^{-1}}\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (305 \text{ K}) \times \ln \frac{(2.5 + 18.5) \text{ L}}{18.5 \text{ L}} \\ &= \boxed{-52.8 \text{ J}} \end{aligned}$$

E2.10(b) Isothermal reversible work is

$$\begin{aligned} w &= -nRT \ln \frac{V_f}{V_i} = -(1.77 \times 10^{-3} \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) \times \ln 0.224 \\ &= \boxed{+6.01 \text{ J}} \end{aligned}$$

$$\mathbf{E2.11(b)} \quad q = \Delta H = n(-\Delta_{\text{vap}}H^\ominus) = (2.00 \text{ mol}) \times (-35.3 \text{ kJ mol}^{-1}) = \boxed{-70.6 \text{ kJ}}$$

Because the condensation also occurs at constant pressure, the work is

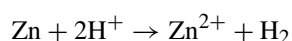
$$w = -\int p_{\text{ex}} dV = -p\Delta V$$

The change in volume from a gas to a condensed phase is approximately equal in magnitude to the volume of the gas

$$\begin{aligned} w &\approx -p(-V_{\text{vapor}}) = nRT = (2.00 \text{ mol}) \times (8.3145 \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (64 + 273) \text{ K} \\ &= \boxed{5.60 \times 10^3 \text{ J}} \end{aligned}$$

$$\Delta U = q + w = (-70.6 + 5.60) \text{ kJ} = \boxed{-65.0 \text{ kJ}}$$

E2.12(b) The reaction is



so it liberates 1 mol $\text{H}_2(\text{g})$ for every 1 mol Zn used. Work at constant pressure is

$$\begin{aligned} w &= -p\Delta V = -pV_{\text{gas}} = -nRT = -\left(\frac{5.0 \text{ g}}{65.4 \text{ g mol}^{-1}}\right) \\ &\quad \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (23 + 273) \text{ K} \\ &= \boxed{-188 \text{ J}} \end{aligned}$$

$$\mathbf{E2.13(b)} \quad q = n\Delta_{\text{fus}}H^\ominus = \left(\frac{500 \text{ kg}}{39.1 \times 10^{-3} \text{ kg mol}^{-1}}\right) \times (2.35 \text{ kJ mol}^{-1}) = \boxed{3.01 \times 10^4 \text{ kJ}}$$

E2.14(b) (a) At constant pressure

$$\begin{aligned} q &= \int C_p dT = \int_{0+273 \text{ K}}^{100+273 \text{ K}} [20.17 + (0.4001)T/\text{K}] dT \text{ J K}^{-1} \\ &= [(20.17)T + \frac{1}{2}(0.4001) \times (T^2/\text{K})] \text{ J K}^{-1} \Big|_{273 \text{ K}}^{373 \text{ K}} \\ &= [(20.17) \times (373 - 273) + \frac{1}{2}(0.4001) \times (373^2 - 273^2)] \text{ J} = \boxed{14.9 \times 10^3 \text{ J}} = \Delta H \end{aligned}$$

$$w = -p\Delta V = -nR\Delta T = -(1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}) = \boxed{-831 \text{ J}}$$

$$\Delta U = q + w = (14.9 - 0.831) \text{ kJ} = \boxed{14.1 \text{ kJ}}$$

(b) ΔU and ΔH depend only on temperature in perfect gases. Thus, $\Delta H = \boxed{14.9 \text{ kJ}}$ and $\Delta U = \boxed{14.1 \text{ kJ}}$ as above. At constant volume, $w = \boxed{0}$ and $\Delta U = q$, so $q = \boxed{+14.1 \text{ kJ}}$

E2.15(b) For reversible adiabatic expansion

$$V_f T_f^c = V_i T_i^c \quad \text{so} \quad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

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

So the final temperature is

$$T_f = (298.15 \text{ K}) \times \left(\frac{500 \times 10^{-3} \text{ L}}{2.00 \text{ L}} \right)^{1/3.463} = \boxed{200 \text{ K}}$$

E2.16(b) Reversible adiabatic work is

$$w = C_V \Delta T = n(C_{p,m} - R) \times (T_f - T_i)$$

where the temperatures are related by [solution to Exercise 2.15b]

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

$$\text{where } c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = \frac{(29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} = 2.503$$

$$\text{So } T_f = [(23.0 + 273.15) \text{ K}] \times \left(\frac{400 \times 10^{-3} \text{ L}}{2.00 \text{ L}} \right)^{1/2.503} = 156 \text{ K}$$

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

E2.17(b) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{so}$$

$$p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma = (87.3 \text{ Torr}) \times \left(\frac{500 \times 10^{-3} \text{ L}}{3.0 \text{ L}} \right)^{1.3} \\ = \boxed{8.5 \text{ Torr}}$$

E2.18(b) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{so} \quad p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma$$

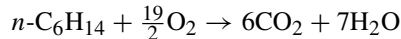
We need p_i , which we can obtain from the perfect gas law

$$pV = nRT \quad \text{so} \quad p = \frac{nRT}{V}$$

$$p_i = \frac{\left(\frac{1.4 \text{ g}}{18 \text{ g mol}^{-1}}\right) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{1.0 \text{ L}} = \boxed{1.9 \text{ atm}}$$

$$p_f = (1.9 \text{ atm}) \times \left(\frac{1.0 \text{ L}}{3.0 \text{ L}}\right)^{1.3} = \boxed{0.46 \text{ atm}}$$

E2.19(b) The reaction is



$$\Delta H^\ominus = \Delta_c H^\ominus$$

$$= 6\Delta_f H^\ominus(\text{CO}_2) + 7\Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_f H^\ominus(n\text{-C}_6\text{H}_{14}) - \frac{19}{2}\Delta_f H^\ominus(\text{O}_2)$$

$$\text{so } \Delta_f H^\ominus(n\text{-C}_6\text{H}_{14}) = 6\Delta_f H^\ominus(\text{CO}_2) + 7\Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_c H^\ominus - \frac{19}{2}\Delta_f H^\ominus(\text{O}_2)$$

$$\Delta_f H^\ominus(n\text{-C}_6\text{H}_{14}) = [6 \times (-393.51) + 7 \times (-285.83) + 4163 - (0)] \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus(n\text{-C}_6\text{H}_{14}) = \boxed{-199 \text{ kJ mol}^{-1}}$$

E2.20(b) $q_p = nC_{p,m}\Delta T$

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

$$C_{V,m} = C_{p,m} - R = (53 - 8.3) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{45 \text{ J K}^{-1} \text{ mol}^{-1}}$$

E2.21(b) $\Delta H = q_p = \boxed{-2.3 \text{ kJ}}$, the energy extracted from the sample.

$$q_p = C\Delta T \quad \text{so} \quad C = \frac{q_p}{\Delta T} = \frac{-2.3 \text{ kJ}}{(275 - 288) \text{ K}} = \boxed{0.18 \text{ kJ K}^{-1}}$$

E2.22(b) $\Delta H = q_p = C_p\Delta T = nC_{p,m}\Delta T = (2.0 \text{ mol}) \times (37.11 \text{ J K}^{-1} \text{ mol}^{-1}) \times (277 - 250) \text{ K}$

$$= \boxed{2.0 \times 10^3 \text{ J mol}^{-1}}$$

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

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

$$= \boxed{1.6 \times 10^3 \text{ J mol}^{-1}}$$

E2.23(b) In an adiabatic process, $q = \boxed{0}$. Work against a constant external pressure is

$$w = -p_{\text{ex}}\Delta V = \frac{-(78.5 \times 10^3 \text{ Pa}) \times (4 \times 15 - 15) \text{ L}}{1000 \text{ L m}^{-3}} = \boxed{-3.5 \times 10^3 \text{ J}}$$

$$\Delta U = q + w = \boxed{-3.5 \times 10^3 \text{ J}}$$

$$w = C_V\Delta T = n(C_{p,m} - R)\Delta T \quad \text{so} \quad \Delta T = \frac{w}{n(C_{p,m} - R)}$$

$$\Delta T = \frac{-3.5 \times 10^3 \text{ J}}{(5.0 \text{ mol}) \times (37.11 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}} = \boxed{-24 \text{ K}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T,$$

$$= -3.5 \times 10^3 \text{ J} + (5.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-24 \text{ K}) = \boxed{-4.5 \times 10^3 \text{ J}}$$

E2.24(b) For adiabatic compression, $q = 0$ and

$$w = C_V \Delta T = (2.5 \text{ mol}) \times (27.6 \text{ J K}^{-1} \text{ mol}^{-1}) \times (255 - 220) \text{ K} = 2.4 \times 10^3 \text{ J}$$

$$\Delta U = q + w = 2.4 \times 10^3 \text{ J}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

$$= 2.4 \times 10^3 \text{ J} + (2.5 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (255 - 220) \text{ K} = 3.1 \times 10^3 \text{ J}$$

The initial and final states are related by

$$V_f T_f^c = V_i T_i^c \quad \text{so} \quad V_f = V_i \left(\frac{T_i}{T_f} \right)^c$$

$$\text{where } c = \frac{C_{V,m}}{R} = \frac{27.6 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} = 3.32$$

$$V_i = \frac{nRT_i}{p_i} = \frac{2.5 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 220 \text{ K}}{200 \times 10^3 \text{ Pa}} = 0.0229 \text{ m}^3$$

$$V_f = (0.0229 \text{ m}^3) \times \left(\frac{220 \text{ K}}{255 \text{ K}} \right)^{3.32} = 0.014 \text{ m}^3 = 14 \text{ L}$$

$$p_f = \frac{nRT_f}{V_f} = \frac{2.5 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 255 \text{ K}}{0.014 \text{ m}^3} = 3.8 \times 10^5 \text{ Pa}$$

E2.25(b) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{so} \quad V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma}$$

$$\text{where } \gamma = \frac{C_{p,m}}{C_{p,m} - R} = \frac{20.8 \text{ J K}^{-1} \text{ mol}^{-1}}{(20.8 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}} = 1.67$$

$$\text{and } V_i = \frac{nRT_i}{p_i} = \frac{(1.5 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (315 \text{ K})}{230 \times 10^3 \text{ Pa}} = 0.0171 \text{ m}^3$$

$$\text{so } V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma} = (0.0171 \text{ m}^3) \times \left(\frac{230 \text{ kPa}}{170 \text{ kPa}} \right)^{1/1.67} = 0.0201 \text{ m}^3$$

$$T_f = \frac{p_f V_f}{nR} = \frac{(170 \times 10^3 \text{ Pa}) \times (0.0201 \text{ m}^3)}{(1.5 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} = 275 \text{ K}$$

$$w = C_V \Delta T = (1.5 \text{ mol}) \times (20.8 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1} \times (275 - 315) \text{ K} = -7.5 \times 10^2 \text{ J}$$

E2.26(b) The expansion coefficient is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial \ln V}{\partial T} \right)_p$$

so for a small change in temperature (see Exercise 2.26a),

$$\Delta V = V_i \alpha \Delta T = (5.0 \text{ cm}^3) \times (0.354 \times 10^{-4} \text{ K}^{-1}) \times (10.0 \text{ K}) = 1.8 \times 10^{-3} \text{ cm}^3$$

E2.27(b) In an adiabatic process, $q = 0$. Work against a constant external pressure is

$$w = -p_{\text{ex}}\Delta V = -(110 \times 10^3 \text{ Pa}) \times \frac{(15 \text{ cm}) \times (22 \text{ cm}^2)}{(100 \text{ cm m}^{-1})^3} = \boxed{-36 \text{ J}}$$

$$\Delta U = q + w = \boxed{-36 \text{ J}}$$

$$w = C_V \Delta T = n(C_{p,m} - R)\Delta T \quad \text{so}$$

$$\Delta T = \frac{w}{n(C_{p,m} - R)}$$

$$= \frac{-36 \text{ J}}{(3.0 \text{ mol}) \times (29.355 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}} = \boxed{-0.57 \text{ K}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

$$= -36 \text{ J} + (3.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-0.57 \text{ K}) = \boxed{-50 \text{ J}}$$

E2.28(b) The amount of N_2 in the sample is

$$n = \frac{15.0 \text{ g}}{28.013 \text{ g mol}^{-1}} = 0.535 \text{ mol}$$

(a) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{so} \quad V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma}$$

$$\text{where } \gamma = \frac{C_{p,m}}{C_{V,m}} \text{ where } C_{V,m} = (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1} = 20.811 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{so } \gamma = \frac{29.125 \text{ J K}^{-1} \text{ mol}^{-1}}{20.811 \text{ J K}^{-1} \text{ mol}^{-1}} = 1.3995$$

$$\text{and } V_i = \frac{nRT_i}{p_i} = \frac{(0.535 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K})}{220 \times 10^3 \text{ Pa}} = 4.04 \times 10^{-3} \text{ m}^3$$

$$\text{so } V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma} = (4.04 \times 10^{-3} \text{ m}^3) \times \left(\frac{220 \times 10^3 \text{ Pa}}{110 \times 10^3 \text{ Pa}} \right)^{1/1.3995} = 6.63 \times 10^{-3} \text{ m}^3.$$

$$T_f = \frac{p_f V_f}{nR} = \frac{(110 \times 10^3 \text{ Pa}) \times (6.63 \times 10^{-3} \text{ m}^3)}{(0.535 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{164 \text{ K}}$$

(b) For adiabatic expansion against a constant external pressure

$$w = -p_{\text{ex}}\Delta V = C_V \Delta T \quad \text{so} \quad -p_{\text{ex}}(V_f - V_i) = C_V(T_f - T_i)$$

In addition, the perfect gas law holds

$$p_f V_f = nRT_f$$

Solve the latter for T_f in terms of V_f , and insert into the previous relationship to solve for V_f

$$T_f = \frac{p_f V_f}{nR} \quad \text{so} \quad -p_{\text{ex}}(V_f - V_i) = C_V \left(\frac{p_f V_f}{nR} - T_i \right)$$

Collecting terms gives

$$C_V T_i + p_{\text{ex}} V_i = V_f \left(p_{\text{ex}} + \frac{C_V p_f}{nR} \right) \quad \text{so} \quad V_f = \frac{C_V T_i + p_{\text{ex}} V_i}{p_{\text{ex}} + \left(\frac{C_{V,m} p_f}{R} \right)}$$

$$V_f = \frac{(20.811 \text{ J K}^{-1} \text{ mol}^{-1}) \times (0.535 \text{ mol}) \times (200 \text{ K}) + (110 \times 10^3 \text{ Pa}) \times (4.04 \times 10^{-3} \text{ m}^3)}{110 \times 10^3 \text{ Pa} + \left[\frac{(20.811 \text{ J K}^{-1} \text{ mol}^{-1}) \times (110 \times 10^3 \text{ Pa})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right]}$$

$$V_f = 6.93 \times 10^{-3} \text{ m}^3$$

Finally, the temperature is

$$T_f = \frac{p_f V_f}{nR} = \frac{(110 \times 10^3 \text{ Pa}) \times (6.93 \times 10^{-3} \text{ m}^3)}{(0.535 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{171 \text{ K}}$$

E2.29(b) At constant pressure

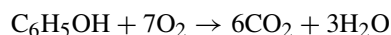
$$q = \Delta H = n \Delta_{\text{vap}} H^\ominus = (0.75 \text{ mol}) \times (32.0 \text{ kJ mol}^{-1}) = \boxed{24.0 \text{ kJ}}$$

$$\begin{aligned} \text{and } w &= -p \Delta V \approx -p V_{\text{vapor}} = -nRT = -(0.75 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (260 \text{ K}) \\ &= -1.6 \times 10^3 \text{ J} = \boxed{-1.6 \text{ kJ}} \end{aligned}$$

$$\Delta U = w + q = 24.0 - 1.6 \text{ kJ} = \boxed{22.4 \text{ kJ}}$$

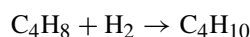
Comment. Because the vapor is here treated as a perfect gas, the specific value of the external pressure provided in the statement of the exercise does not affect the numerical value of the answer.

E2.30(b) The reaction is



$$\begin{aligned} \Delta_c H^\ominus &= 6\Delta_f H^\ominus(\text{CO}_2) + 3\Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_f H^\ominus(\text{C}_6\text{H}_5\text{OH}) - 7\Delta_f H^\ominus(\text{O}_2) \\ &= [6(-393.51) + 3(-285.83) - (-165.0) - 7(0)] \text{ kJ mol}^{-1} \\ &= \boxed{-3053.6 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.31(b) The hydrogenation reaction is

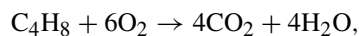


$$\Delta_{\text{hyd}} H^\ominus = \Delta_f H^\ominus(\text{C}_4\text{H}_{10}) - \Delta_f H^\ominus(\text{C}_4\text{H}_8) - \Delta_f H^\ominus(\text{H}_2)$$

The enthalpies of formation of all of these compounds are available in Table 2.5. Therefore

$$\Delta_{\text{hyd}} H^\ominus = [-126.15 - (-0.13)] \text{ kJ mol}^{-1} = -126.02 \text{ kJ mol}^{-1}$$

If we had to, we could find $\Delta_f H^\ominus(\text{C}_4\text{H}_8)$ from information about another of its reactions



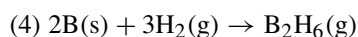
$$\Delta_c H^\ominus = 4\Delta_f H^\ominus(\text{CO}_2) + 4\Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_f H^\ominus(\text{C}_4\text{H}_8) - 6\Delta_f H^\ominus(\text{O}_2)$$

$$\begin{aligned} \text{so } \Delta_f H^\ominus(\text{C}_4\text{H}_8) &= 4\Delta_f H^\ominus(\text{CO}_2) + 4\Delta_f H^\ominus(\text{H}_2\text{O}) - 6\Delta_f H^\ominus(\text{O}_2) - \Delta_c H^\ominus \\ &= [4(-393.51) + 4(-285.83) - 6(0) - (-2717)] \text{ kJ mol}^{-1} \\ &= 0. \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_{\text{hyd}} H^\ominus = -126.15 - (0.) - (0) \text{ kJ mol}^{-1} = \boxed{-126 \text{ kJ mol}^{-1}}$$

This value compares favourably to that calculated above.

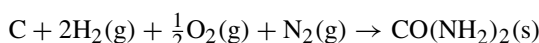
E2.32(b) We need $\Delta_f H^\ominus$ for the reaction



$$\text{reaction (4)} = \text{reaction (2)} + 3 \times \text{reaction (3)} - \text{reaction (1)}$$

$$\begin{aligned} \text{Thus, } \Delta_f H^\ominus &= \Delta_r H^\ominus \{\text{reaction (2)}\} + 3 \times \Delta_r H^\ominus \{\text{reaction (3)}\} - \Delta_r H^\ominus \{\text{reaction (1)}\} \\ &= \{-2368 + 3 \times (-241.8) - (-1941)\} \text{ kJ mol}^{-1} = \boxed{-1152 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.33(b) The formation reaction is



$$\Delta H = \Delta U + \Delta(pV) \approx \Delta U + RT \Delta n_{\text{gas}} \quad \text{so} \quad \Delta_f U^\ominus = \Delta_f H^\ominus - RT \Delta n_{\text{gas}}$$

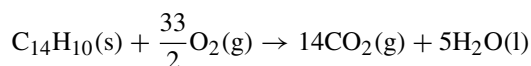
$$\begin{aligned} \Delta_f U^\ominus &= -333.51 \text{ kJ mol}^{-1} - (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times (-7/2) \\ &= \boxed{-324.83 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.34(b) The energy supplied to the calorimeter equals $C\Delta T$, where C is the calorimeter constant. That energy is

$$E = (2.86 \text{ A}) \times (22.5 \text{ s}) \times (12.0 \text{ V}) = 772 \text{ J}$$

$$\text{So } C = \frac{E}{\Delta T} = \frac{772 \text{ J}}{1.712 \text{ K}} = \boxed{451 \text{ J K}^{-1}}$$

E2.35(b) For anthracene the reaction is



$$\Delta_c U^\ominus = \Delta_c H^\ominus - \Delta n_{\text{g}} RT [26] \quad \Delta n_{\text{g}} = -\frac{5}{2} \text{ mol}$$

$$\Delta_c H^\ominus = -7163 \text{ kJ mol}^{-1} \text{ (Handbook of Chemistry and Physics)}$$

$$\begin{aligned} \Delta_c U^\ominus &= -7163 \text{ kJ mol}^{-1} - \left(-\frac{5}{2} \times 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}\right) \text{ (assume } T = 298 \text{ K)} \\ &= -7157 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} |q| = |q_V| = |n \Delta_c U^\ominus| &= \left(\frac{2.25 \times 10^{-3} \text{ g}}{172.23 \text{ g mol}^{-1}} \right) \times (7157 \text{ kJ mol}^{-1}) \\ &= 0.0935 \text{ kJ} \end{aligned}$$

$$C = \frac{|q|}{\Delta T} = \frac{0.0935 \text{ kJ}}{1.35 \text{ K}} = 0.0693 \text{ kJ K}^{-1} = \boxed{69.3 \text{ J K}^{-1}}$$

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

$$\Delta_c H^\ominus = -3054 \text{ kJ mol}^{-1} \text{ (Table 2.5)}$$

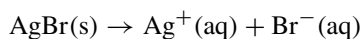
$$\begin{aligned} \Delta_c U^\ominus &= \Delta_c H^\ominus - \Delta n_{\text{g}} RT, \quad \Delta n_{\text{g}} = -\frac{3}{2} \text{ mol} \\ &= (-3054 \text{ kJ mol}^{-1}) + \left(\frac{3}{2}\right) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= -3050 \text{ kJ mol}^{-1} \end{aligned}$$

$$|q| = \left(\frac{135 \times 10^{-3} \text{ g}}{94.12 \text{ g mol}^{-1}} \right) \times (3050 \text{ kJ mol}^{-1}) = 4.375 \text{ kJ}$$

$$\Delta T = \frac{|q|}{C} = \frac{4.375 \text{ kJ}}{0.0693 \text{ kJ K}^{-1}} = \boxed{+63.1 \text{ K}}$$

Comment. In this case $\Delta_c U^\ominus$ and $\Delta_c H^\ominus$ differed by ≈ 0.1 per cent. Thus, to within 3 significant figures, it would not have mattered if we had used $\Delta_c H^\ominus$ instead of $\Delta_c U^\ominus$, but for very precise work it would.

E2.36(b) The reaction is



$$\Delta_{\text{sol}} H^\ominus = \Delta_f H^\ominus(\text{Ag}^+) + \Delta_f H^\ominus(\text{Br}^-) - \Delta_f H^\ominus(\text{AgBr})$$

$$= [105.58 + (-121.55) - (-100.37)] \text{ kJ mol}^{-1} = \boxed{+84.40 \text{ kJ mol}^{-1}}$$

E2.37(b) The difference of the equations is $\text{C}(\text{gr}) \rightarrow \text{C}(\text{d})$

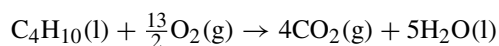
$$\Delta_{\text{trans}} H^\ominus = [-393.51 - (-395.41)] \text{ kJ mol}^{-1} = \boxed{+1.90 \text{ kJ mol}^{-1}}$$

E2.38(b) Combustion of liquid butane can be considered as a two-step process: vaporization of the liquid followed by combustion of the butane gas. Hess's law states that the enthalpy of the overall process is the sum of the enthalpies of the steps

$$\text{(a)} \quad \Delta_c H^\ominus = [21.0 + (-2878)] \text{ kJ mol}^{-1} = \boxed{-2857 \text{ kJ mol}^{-1}}$$

$$\text{(b)} \quad \Delta_c H^\ominus = \Delta_c U^\ominus + \Delta(pV) = \Delta_c U^\ominus + RT \Delta n_g \quad \text{so} \quad \Delta_c U^\ominus = \Delta_c H^\ominus - RT \Delta n_g$$

The reaction is

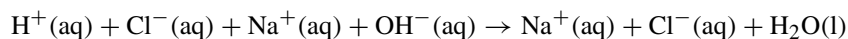


so $\Delta n_g = -2.5$ and

$$\begin{aligned} \Delta_c U^\ominus &= -2857 \text{ kJ mol}^{-1} - (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (-2.5) \\ &= \boxed{-2851 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\text{E2.39(b)} \quad \text{(a)} \quad \Delta_r H^\ominus = \Delta_f H^\ominus(\text{propene, g}) - \Delta_f H^\ominus(\text{cyclopropane, g}) = [(20.42) - (53.30)] \text{ kJ mol}^{-1} = \boxed{-32.88 \text{ kJ mol}^{-1}}$$

(b) The net ionic reaction is obtained from



and is $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{H}_2\text{O, l}) - \Delta_f H^\ominus(\text{H}^+, \text{aq}) - \Delta_f H^\ominus(\text{OH}^-, \text{aq}) \\ &= [(-285.83) - (0) - (-229.99)] \text{ kJ mol}^{-1} \\ &= \boxed{-55.84 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.40(b) reaction (3) = reaction (2) – 2(reaction (1))

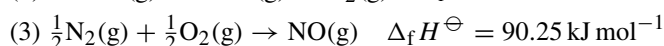
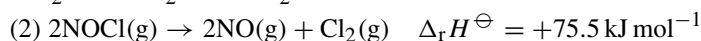
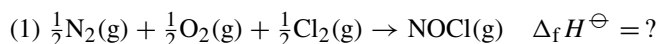
$$\begin{aligned} \text{(a)} \quad \Delta_r H^\ominus(3) &= \Delta_r H^\ominus(2) - 2(\Delta_r H^\ominus(1)) \\ &= -483.64 \text{ kJ mol}^{-1} - 2(52.96 \text{ kJ mol}^{-1}) \\ &= \boxed{-589.56 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT \\ &= -589.56 \text{ kJ mol}^{-1} - (-3) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= -589.56 \text{ kJ mol}^{-1} + 7.43 \text{ kJ mol}^{-1} = \boxed{-582.13 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta_f H^\ominus(\text{HI}) &= \frac{1}{2}(52.96 \text{ kJ mol}^{-1}) = \boxed{26.48 \text{ kJ mol}^{-1}} \\ \Delta_f H^\ominus(\text{H}_2\text{O}) &= -\frac{1}{2}(483.64 \text{ kJ mol}^{-1}) = \boxed{-241.82 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{E2.41(b)} \quad \Delta_r H^\ominus &= \Delta_r U^\ominus + \Delta(pV) = \Delta_r U^\ominus + RT \Delta n_g \\ &= -772.7 \text{ kJ mol}^{-1} + (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (5) \\ &= \boxed{-760.3 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.42(b)



$$(1) = (3) - \frac{1}{2}(2)$$

$$\begin{aligned} \Delta_f H^\ominus(\text{NOCl}, \text{g}) &= (90.25 \text{ kJ mol}^{-1}) - \frac{1}{2}(75.5 \text{ kJ mol}^{-1}) \\ &= \boxed{52.5 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\text{E2.43(b)} \quad \Delta_r H^\ominus(100^\circ\text{C}) - \Delta_r H^\ominus(25^\circ\text{C}) = \int_{25^\circ\text{C}}^{100^\circ\text{C}} \left(\frac{\partial \Delta_r H^\ominus}{\partial T} \right) dT = \int_{25^\circ\text{C}}^{100^\circ\text{C}} \Delta_r C_{p,m} dT$$

Because $C_{p,m}$ can frequently be parametrized as

$$C_{p,m} = a + bT + c/T^2$$

the indefinite integral of $C_{p,m}$ has the form

$$\int C_{p,m} dT = aT + \frac{1}{2}bT^2 - c/T$$

Combining this expression with our original integral, we have

$$\Delta_r H^\ominus(100^\circ\text{C}) = \Delta_r H^\ominus(25^\circ\text{C}) + (T \Delta_r a + \frac{1}{2}T^2 \Delta_r b - \Delta_r c/T) \Big|_{298 \text{ K}}^{373 \text{ K}}$$

Now for the pieces

$$\Delta_r H^\ominus(25^\circ\text{C}) = 2(-285.83 \text{ kJ mol}^{-1}) - 2(0) - 0 = -571.66 \text{ kJ mol}^{-1}$$

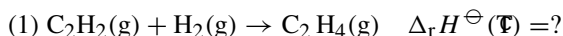
$$\Delta_r a = [2(75.29) - 2(27.28) - (29.96)] \text{ J K}^{-1} \text{ mol}^{-1} = 0.06606 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r b = [2(0) - 2(3.29) - (4.18)] \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1} = -10.76 \times 10^{-6} \text{ kJ K}^{-2} \text{ mol}^{-1}$$

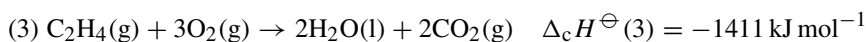
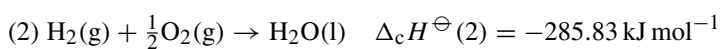
$$\Delta_r c = [2(0) - 2(0.50) \times (-1.67)] \times 10^5 \text{ J K mol}^{-1} = 67 \text{ kJ K mol}^{-1}$$

$$\begin{aligned}\Delta_r H^\ominus(100^\circ\text{C}) &= \left[-571.66 + (373 - 298) \times (0.06606) + \frac{1}{2}(373^2 - 298^2) \right. \\ &\quad \left. \times (-10.76 \times 10^{-6}) - (67) \times \left(\frac{1}{373} - \frac{1}{298} \right) \right] \text{kJ mol}^{-1} \\ &= \boxed{-566.93 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.44(b) The hydrogenation reaction is



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



reaction (1) = reaction (2) – reaction (3) + reaction (4)

Hence,

$$\begin{aligned}\text{(a)} \quad \Delta_r H^\ominus(\mathfrak{T}) &= \Delta_c H^\ominus(2) - \Delta_c H^\ominus(3) + \Delta_c H^\ominus(4) \\ &= \{(-285.83) - (-1411) + (-1300)\} \text{kJ mol}^{-1} \\ &= \boxed{-175 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r U^\ominus(\mathfrak{T}) &= \Delta_r H^\ominus(\mathfrak{T}) - \Delta n_g RT \quad [26] \quad \Delta n_g = -1 \\ &= (-175 \text{ kJ mol}^{-1} + 2.48 \text{ kJ mol}^{-1}) = \boxed{-173 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad \Delta_r H^\ominus(348 \text{ K}) &= \Delta_r H^\ominus(298 \text{ K}) + \Delta_r C_p(348 \text{ K} - 298 \text{ K}) \quad [\text{Example 2.7}] \\ \Delta_r C_p &= \sum_J \nu_J C_{p,m}(J) \quad [47] = C_{p,m}(\text{C}_2\text{H}_4, \text{g}) - C_{p,m}(\text{C}_2\text{H}_2, \text{g}) - C_{p,m}(\text{H}_2, \text{g}) \\ &= (43.56 - 43.93 - 28.82) \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} = -29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \\ \Delta_r H^\ominus(348 \text{ K}) &= (-175 \text{ kJ mol}^{-1}) - (29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K}) \\ &= \boxed{-176 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.45(b) The cycle is shown in Fig. 2.1.

$$\begin{aligned}-\Delta_{\text{hyd}} H^\ominus(\text{Ca}^{2+}) &= -\Delta_{\text{soln}} H^\ominus(\text{CaBr}_2) - \Delta_f H^\ominus(\text{CaBr}_2, \text{s}) + \Delta_{\text{sub}} H^\ominus(\text{Ca}) \\ &\quad + \Delta_{\text{vap}} H^\ominus(\text{Br}_2) + \Delta_{\text{diss}} H^\ominus(\text{Br}_2) + \Delta_{\text{ion}} H^\ominus(\text{Ca}) \\ &\quad + \Delta_{\text{ion}} H^\ominus(\text{Ca}^+) + 2\Delta_{\text{eg}} H^\ominus(\text{Br}) + 2\Delta_{\text{hyd}} H^\ominus(\text{Br}^-) \\ &= [-(-103.1) - (-682.8) + 178.2 + 30.91 + 192.9 \\ &\quad + 589.7 + 1145 + 2(-331.0) + 2(-337)] \text{kJ mol}^{-1} \\ &= \boxed{1587 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\text{and } \Delta_{\text{hyd}} H^\ominus(\text{Ca}^{2+}) = \boxed{-1587 \text{ kJ mol}^{-1}}$$

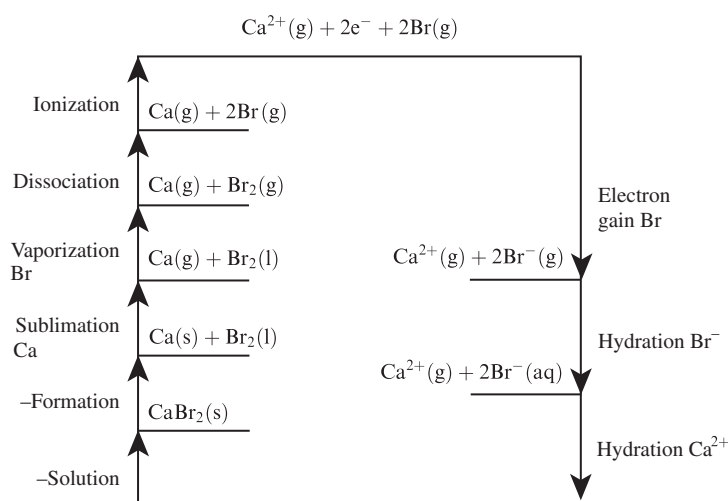


Figure 2.1

- E2.46** (a) 2,2,4-trimethylpentane has five $\text{C}(\text{H})_3(\text{C})$ groups, one $\text{C}(\text{H})_2(\text{C})_2$ group, one $\text{C}(\text{H})(\text{C})_3$ group, and one $\text{C}(\text{C})_4$ group.
- (b) 2,2-dimethylpropane has four $\text{C}(\text{H}_3)(\text{C})$ groups and one $\text{C}(\text{C})_4$ group.
- Using data from Table 2.7

(a) $[5 \times (-42.17) + 1 \times (-20.7) + 1 \times (-6.91) + 1 \times 8.16] \text{ kJ mol}^{-1} = \boxed{-230.3 \text{ kJ mol}^{-1}}$

(b) $[4 \times (-42.17) + 1 \times 8.16] \text{ kJ mol}^{-1} = \boxed{-160.5 \text{ kJ mol}^{-1}}$

Solutions to problems

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298 K.

Solutions to numerical problems

- P2.4** We assume that the solid carbon dioxide has already evaporated and is contained within a closed vessel of 100 cm^3 which is its initial volume. It then expands to a final volume which is determined by the perfect gas equation.

(a) $w = -p_{\text{ex}} \Delta V$

$$V_i = 100 \text{ cm}^3 = 1.00 \times 10^{-4} \text{ m}^3, \quad p = 1.0 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

$$V_f = \frac{nRT}{p} = \left(\frac{5.0 \text{ g}}{44.01 \text{ g mol}^{-1}} \right) \times \left(\frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{1.0 \text{ atm}} \right) = 2.78 \text{ L}$$

$$= 2.78 \times 10^{-3} \text{ m}^3$$

$$\text{Therefore, } w = (-1.013 \times 10^5 \text{ Pa}) \times [(2.78 \times 10^{-3}) - (1.00 \times 10^{-4})] \text{ m}^3$$

$$= -272 \text{ Pa m}^3 = \boxed{-0.27 \text{ kJ}}$$

$$\begin{aligned}
 \text{(b)} \quad w &= -nRT \ln \frac{V_f}{V_i} \quad [2.13] \\
 &= \left(\frac{-5.0 \text{ g}}{44.01 \text{ g mol}^{-1}} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{2.78 \times 10^{-3} \text{ m}^3}{1.00 \times 10^{-4} \text{ m}^3} \right) \\
 &= (-282) \times (\ln 27.8) = \boxed{-0.94 \text{ kJ}}
 \end{aligned}$$

P2.5 $w = -p_{\text{ex}} \Delta V$ [2.10] $V_f = \frac{nRT}{p_{\text{ex}}} \gg V_i$; so $\Delta V \approx V_f$

Hence $w \approx (-p_{\text{ex}}) \times \left(\frac{nRT}{p_{\text{ex}}} \right) = -nRT \approx (-1.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1073 \text{ K})$

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

Even if there is no physical piston, the gas drives back the atmosphere, so the work is also $\boxed{-8.9 \text{ kJ}}$

P2.7 The virial expression for pressure up to the second coefficient is

$$\begin{aligned}
 p &= \left(\frac{RT}{V_m} \right) \left(1 + \frac{B}{V_m} \right) \quad [1.22] \\
 w &= - \int_i^f p \, dV = -n \int_i^f \left(\frac{RT}{V_m} \right) \times \left(1 + \frac{B}{V_m} \right) \, dV_m = -nRT \ln \left(\frac{V_f}{V_i} \right) + nBRT \left(\frac{1}{V_{mf}} - \frac{1}{V_{mi}} \right)
 \end{aligned}$$

From the data,

$$nRT = (70 \times 10^{-3} \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373 \text{ K}) = 217 \text{ J}$$

$$V_{mi} = \frac{5.25 \text{ cm}^3}{70 \text{ mmol}} = 75.0 \text{ cm}^3 \text{ mol}^{-1}, \quad V_{mf} = \frac{6.29 \text{ cm}^3}{70 \text{ mmol}} = 89.9 \text{ cm}^3 \text{ mol}^{-1}$$

and so $B \left(\frac{1}{V_{mf}} - \frac{1}{V_{mi}} \right) = (-28.7 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1}{89.9 \text{ cm}^3 \text{ mol}^{-1}} - \frac{1}{75.0 \text{ cm}^3 \text{ mol}^{-1}} \right)$

$$= 6.34 \times 10^{-2}$$

Therefore, $w = (-217 \text{ J}) \times \ln \left(\frac{6.29}{5.25} \right) + (217 \text{ J}) \times (6.34 \times 10^{-2}) = (-39.2 \text{ J}) + (13.8 \text{ J}) = \boxed{-25 \text{ J}}$

Since $\Delta U = q + w$ and $\Delta U = +83.5 \text{ J}$, $q = \Delta U - w = (83.5 \text{ J}) + (25 \text{ J}) = \boxed{+109 \text{ J}}$

$$\Delta H = \Delta U + \Delta(pV) \quad \text{with } pV = nRT \left(1 + \frac{B}{V_m} \right)$$

$$\begin{aligned}
 \Delta(pV) &= nRTB \Delta \left(\frac{1}{V_m} \right) = nRTB \left(\frac{1}{V_{mf}} - \frac{1}{V_{mi}} \right), \quad \text{as } \Delta T = 0 \\
 &= (217 \text{ J}) \times (6.34 \times 10^{-2}) = 13.8 \text{ J}
 \end{aligned}$$

Therefore, $\Delta H = (83.5 \text{ J}) + (13.8 \text{ J}) = \boxed{+97 \text{ J}}$

P2.8 $q_p = \Delta H = n \Delta_{\text{vap}} H = \boxed{+22.2 \text{ kJ}}$ $\Delta_{\text{vap}} H = \frac{q_p}{n} = \left(\frac{18.02 \text{ g mol}^{-1}}{10 \text{ g}} \right) \times (22.2 \text{ kJ})$

$$= \boxed{+40 \text{ kJ mol}^{-1}}$$

$$\Delta U = \Delta H - \Delta n_g RT, \quad \Delta n_g = \frac{10 \text{ g}}{18.02 \text{ g mol}^{-1}} = 0.555 \text{ mol}$$

$$\text{Hence } \Delta U = (22.2 \text{ kJ}) - (0.555 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373 \text{ K}) = (22.2 \text{ kJ}) - (1.72 \text{ kJ}) = \boxed{+20.5 \text{ kJ}}$$

$$w = \Delta U - q \text{ [as } \Delta U = q + w] = (20.5 \text{ kJ} - 22.2 \text{ kJ}) = \boxed{-1.7 \text{ kJ}}$$

P2.11 This is constant-pressure process; hence $q_p(\text{object}) + q_p(\text{methane}) = 0$.

$$q_p(\text{object}) = -32.5 \text{ kJ} \quad q_p(\text{methane}) = n \Delta_{\text{vap}} H = 32.5 \text{ kJ}$$

$$n = \frac{q_p(\text{methane})}{\Delta_{\text{vap}} H} \quad \Delta_{\text{vap}} H = 8.18 \text{ kJ mol}^{-1} \text{ (Table 2.3)}$$

The volume occupied by the methane gas at a pressure p is $V = \frac{nRT}{p}$; therefore

$$\begin{aligned} V &= \frac{q_p RT}{p \Delta_{\text{vap}} H} = \frac{(32.5 \text{ kJ}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (112 \text{ K})}{(1.013 \times 10^5 \text{ Pa}) \times (8.18 \text{ kJ mol}^{-1})} \\ &= 3.65 \times 10^{-2} \text{ m}^3 = \boxed{36.5 \text{ L}} \end{aligned}$$

P2.14 $\text{Cr}(\text{C}_6\text{H}_6)_2(\text{s}) \rightarrow \text{Cr}(\text{s}) + 2\text{C}_6\text{H}_6(\text{g}) \quad \Delta n_g = +2 \text{ mol}$

$$\Delta_r H^\ominus = \Delta_r U^\ominus + 2RT, \text{ from [26]}$$

$$= (8.0 \text{ kJ mol}^{-1}) + (2) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (583 \text{ K}) = \boxed{+17.7 \text{ kJ mol}^{-1}}$$

In terms of enthalpies of formation

$$\Delta_r H^\ominus = (2) \times \Delta_f H^\ominus(\text{benzene}, 583 \text{ K}) - \Delta_f H^\ominus(\text{metallocene}, 583 \text{ K})$$

$$\text{or } \Delta_r H^\ominus(\text{metallocene}, 583 \text{ K}) = 2\Delta_f H^\ominus(\text{C}_6\text{H}_6, \text{g}, 583 \text{ K}) - 17.7 \text{ kJ mol}^{-1}$$

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

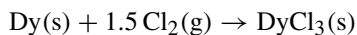
$$\begin{aligned} \Delta_f H^\ominus(\text{benzene}, 583 \text{ K}) &= \Delta_f H^\ominus(\text{benzene}, 298 \text{ K}) + (T_b - 298 \text{ K})C_p(\text{l}) + (583 \text{ K} - T_b)C_p(\text{g}) \\ &\quad + \Delta_{\text{vap}} H^\ominus - 6 \times (583 \text{ K} - 298 \text{ K})C_p(\text{graphite}) \\ &\quad - 3 \times (583 \text{ K} - 298 \text{ K})C_p(\text{H}_2, \text{g}) \end{aligned}$$

where T_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 Table 2.6

$$\begin{aligned} \Delta_f H^\ominus(\text{benzene}, 583 \text{ K}) &= (49.0 \text{ kJ mol}^{-1}) + (353 - 298) \text{ K} \times (136.1 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad + (583 - 353) \text{ K} \times (81.67 \text{ J K}^{-1} \text{ mol}^{-1}) + (30.8 \text{ kJ mol}^{-1}) \\ &\quad - (6) \times (583 - 298) \text{ K} \times (8.53 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - (3) \times (583 - 298) \text{ K} \times (28.82 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= \{(49.0) + (7.49) + (18.78) + (30.8) - (14.59) - (24.64)\} \text{ kJ mol}^{-1} \\ &= +66.8 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Therefore, for the metallocene, } \Delta_f H^\ominus(583 \text{ K}) = (2 \times 66.8 - 17.7) \text{ kJ mol}^{-1} = \boxed{+116.0 \text{ kJ mol}^{-1}}$$

P2.17 We must relate the formation of DyCl_3 to the three reactions for which we have information



This reaction can be seen as a sequence of reaction (2), three times reaction (3), and the reverse of reaction (1), so

$$\Delta_f H^\ominus(\text{DyCl}_3, \text{s}) = \Delta_r H^\ominus(2) + 3\Delta_r H^\ominus(3) - \Delta_r H^\ominus(1),$$

$$\begin{aligned} \Delta_f H^\ominus(\text{DyCl}_3, \text{s}) &= [-699.43 + 3(-158.31) - (-180.06)] \text{kJ mol}^{-1} \\ &= \boxed{-994.30 \text{kJ mol}^{-1}} \end{aligned}$$

P2.19 (a) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{SiH}_3\text{OH}) - \Delta_f H^\ominus(\text{SiH}_4) - \frac{1}{2}\Delta_f H^\ominus(\text{O}_2)$

$$= [-67.5 - 34.3 - \frac{1}{2}(0)] \text{kJ mol}^{-1} = \boxed{-101.8 \text{kJ mol}^{-1}}$$

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{SiH}_2\text{O}) - \Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_f H^\ominus(\text{SiH}_4) - \Delta_f H^\ominus(\text{O}_2)$

$$= [-23.5 + (-285.83) - 34.3 - 0] \text{kJ mol}^{-1} = \boxed{-344.2 \text{kJ mol}^{-1}}$$

(c) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{SiH}_2\text{O}) - \Delta_f H^\ominus(\text{SiH}_3\text{OH}) - \Delta_f H^\ominus(\text{H}_2)$

$$= [-23.5 - (-67.5) - 0] \text{kJ mol}^{-1} = \boxed{44.0 \text{kJ mol}^{-1}}$$

P2.21 When necessary we assume perfect gas behaviour, also, the symbols w , V , q , U , etc. will represent molar quantities in all cases.

$$w = - \int p \, dV = - \int \frac{C}{V^n} \, dV = -C \int \frac{dV}{V^n}$$

For $n \neq 1$, this becomes (we treat the case $n = 1$ later)

$$\begin{aligned} (1) \quad w &= \frac{C}{n-1} V^{-n+1} \Bigg|_{\text{initial state, } V_i}^{\text{final state, } V_f} = \frac{C}{n-1} \left\{ \frac{1}{V_f^{n-1}} - \frac{1}{V_i^{n-1}} \right\} \\ &= \frac{p_i V_i^n}{n-1} \times \left\{ \frac{1}{V_f^{n-1}} - \frac{1}{V_i^{n-1}} \right\} \quad [\text{because } pV^n = C] \\ &= \frac{p_i V_i V_i^{n-1}}{n-1} \times \left\{ \frac{1}{V_f^{n-1}} - \frac{1}{V_i^{n-1}} \right\} \end{aligned}$$

$$(2) \quad w = \frac{p_i V_i}{n-1} \times \left\{ \left(\frac{V_i}{V_f} \right)^{n-1} - 1 \right\} = \frac{RT_i}{n-1} \times \left\{ \left(\frac{V_i}{V_f} \right)^{n-1} - 1 \right\}$$

But $pV^n = C$ or $V = \left(\frac{C}{p} \right)^{1/n}$ for $n \neq 0$ (we treat $n = 0$ as a special case below). So,

$$(3) \quad \left(\frac{V_i}{V_f} \right)^{n-1} = \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} \quad n \neq 0$$

Substitution of eqn 3 into eqn 2 and using '1' and '2' to represent the initial and final states, respectively, yields

$$(4) \quad w = \frac{RT_1}{n-1} \times \left\{ \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right\} \quad \text{for } n \neq 0 \text{ and } n \neq 1$$

In the case for which $n = 0$, eqn 1 gives

$$\begin{aligned} w &= \frac{C}{0-1} \times \left\{ \frac{1}{V_f^{-1}} - \frac{1}{V_i^{-1}} \right\} = -C(V_f - V_i) \\ &= -(pV^0)_{\text{any state}} \times (V_f - V_i) = -(p)_{\text{any state}}(V_f - V_i) \end{aligned}$$

(5) $w = -p\Delta V$ for $n = 0$, isobaric case

In the case for which $n = 1$

$$w = - \int p dV = - \int \frac{C}{V^n} dV = - \int \frac{C}{V} dV = -C \ln \left(\frac{V_f}{V_i} \right)$$

$$\begin{aligned} w &= (pV^n)_{\text{any state}} \ln \left(\frac{V_i}{V_f} \right) = (pV)_{\text{any state}} \ln \left(\frac{V_i}{V_f} \right) \\ &= (RT)_{\text{any state}} \ln \left(\frac{V_i}{V_f} \right) \end{aligned}$$

(6) $w = RT \ln \left(\frac{V_1}{V_2} \right) = RT \ln \left(\frac{p_2}{p_1} \right)$ for $n = 1$, isothermal case

To derive the equation for heat, note that, for a perfect gas, $\Delta U = q + w = C_V(T_f - T_i)$. So

(7) $q + w = C_V T_i \left(\frac{T_f}{T_i} - 1 \right) = C_V T_i \left(\frac{p_f V_f}{p_i V_i} - 1 \right)$

$$= C_V T_i \left(\frac{V_i^{n-1}}{V_f^{n-1}} - 1 \right) \quad [\text{because } pV^n = C]$$

$$= C_V T_i \left(\left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right) \quad [\text{using eqn 3 } (n \neq 0)]$$

$$q = C_V T_i \left(\left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right) - \frac{RT_i}{n-1} \left(\left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right) \quad [\text{using eqn 4 } (n \neq 0, n \neq 1)]$$

$$= \left(C_V T_i - \frac{RT_i}{n-1} \right) \times \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\}$$

$$= \left(\frac{C_V}{R} - \frac{1}{n-1} \right) RT_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\}$$

$$= \left(\frac{C_V}{C_p - C_V} - \frac{1}{n-1} \right) RT_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\} \quad [2.31]$$

$$= \left(\frac{C_V}{C_V \left(\frac{C_p}{C_V} - 1 \right)} - \frac{1}{n-1} \right) RT_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\}$$

$$= \left(\frac{1}{\gamma - 1} - \frac{1}{n-1} \right) RT_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\} \quad [2.37]$$

$$= \frac{(n-1) - (\gamma-1)}{(n-1) \times (\gamma-1)} RT_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\}$$

$$= \left[\frac{n - \gamma}{(n-1) \times (\gamma-1)} \right] RT_i \left\{ \left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right\}$$

Using the symbols '1' and '2' this becomes

$$(8) \quad q = \left[\frac{n - \gamma}{(n - 1) \times (\gamma - 1)} \right] RT_1 \left\{ \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right\} \text{ for } n \neq 0, n \neq 1$$

In the case for which $n = 1$, (the isothermal case) eqns 7 and 6 yield

$$(9) \quad q = -w = RT \ln \frac{V_2}{V_1} = RT \ln \frac{p_1}{p_2} \text{ for } n = 1, \text{ isothermal case}$$

In the case for which $n = 0$ (the isobaric case) eqns 7 and 5 yield

$$\begin{aligned} q &= \Delta U - w = C_V(T_f - T_i) + p(V_f - V_i) \\ &= C_V(T_f - T_i) + R(T_f - T_i) \\ &= (C_V + R) \times (T_f - T_i) = C_p(T_f - T_i) \end{aligned}$$

$$(10) \quad q = C_p \Delta T \text{ for } n = 0, \text{ isobaric case}$$

A summary of the equations for the process $pV^n = C$ is given below

n	w	q	Process type
0	$-p\Delta V$	$C_p \Delta T$	Isobaric [2.29]
1	$RT \ln \left(\frac{p_2}{p_1} \right)$	$RT \ln \left(\frac{p_1}{p_2} \right)$	Isothermal [2.13]
γ	$C_V \Delta T^*$	0	Adiabatic [2.33]
∞	0	$C_V \Delta T^\dagger$	† Isochoric [2.22]
Any n except $n = 0$ and $n = 1$	$\frac{RT_1}{n-1} \left\{ \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right\}$	$\left[\frac{n - \gamma}{(n - 1)(\gamma - 1)} \right] RT_1 \left\{ \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right\}$	

* Equation 8 gives this result when $n = \gamma$

$$q = \left[\frac{\gamma - \gamma}{(\gamma - 1) \times (\gamma - 1)} \right] RT_1 \left\{ \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right\} = 0$$

Therefore, $w = \Delta U - q = \Delta U = C_V \Delta T$.

† Equation 8 gives this result in the limit as $n \rightarrow \infty$

$$\begin{aligned} \lim_{n \rightarrow \infty} q &= \left(\frac{1}{\gamma - 1} \right) RT_1 \left\{ \frac{p_2}{p_1} - 1 \right\} \\ &= \left(\frac{C_V}{C_p - C_V} \right) RT_1 \left\{ \frac{p_2 - p_1}{p_1} \right\} \\ &= \left(\frac{C_V}{C_p - C_V} \right) V_1 (p_2 - p_1) \end{aligned}$$

However, $\lim_{n \rightarrow \infty} V = \lim_{n \rightarrow \infty} \frac{C}{p^{1/n}} = \frac{C}{p^0} = C$. So in this limit an isochoric process is being discussed and $V_2 = V_1 = V$ and

$$\lim_{n \rightarrow \infty} q = \frac{C_V}{C_p - C_V} (p_2 V_2 - p_1 V_1) = \frac{C_V}{R} (RT_2 - RT_1) = C_V \Delta T$$

Solutions to theoretical problems

P2.23

$$dw = -F(x) dx \text{ [2.6], with } z = x$$

Hence to move the mass from x_1 to x_2

$$w = - \int_{x_1}^{x_2} F(x) dx$$

Inserting $F(x) = F \sin\left(\frac{\pi x}{a}\right)$ [$F = \text{constant}$]

$$w = -F \int_{x_1}^{x_2} \sin\left(\frac{\pi x}{a}\right) dx = \frac{Fa}{\pi} \left(\cos \frac{\pi x_2}{a} - \cos \frac{\pi x_1}{a} \right)$$

$$\text{(a) } x_2 = a, \quad x_1 = 0, \quad w = \frac{Fa}{\pi} (\cos \pi - \cos 0) = \boxed{\frac{-2Fa}{\pi}}$$

$$\text{(b) } x_2 = 2a, \quad x_1 = 0, \quad w = \frac{Fa}{\pi} (\cos 2\pi - \cos 0) = \boxed{0}$$

The work done by the machine in the first part of the cycle is regained by the machine in the second part of the cycle, and hence no net work is done by the machine.

P2.25

(a) The amount is a constant; therefore, it can be calculated from the data for any state. In state A, $V_A = 10 \text{ L}$, $p_A = 1 \text{ atm}$, $T_A = 313 \text{ K}$. Hence

$$n = \frac{p_A V_A}{RT_A} = \frac{(1.0 \text{ atm}) \times (10 \text{ L})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (313 \text{ K})} = \boxed{0.389 \text{ mol}}$$

Since T is a constant along the isotherm, Boyle's law applies

$$p_A V_A = p_B V_B; \quad V_B = \frac{p_A}{p_B} V_A = \left(\frac{1.0 \text{ atm}}{20 \text{ atm}} \right) \times (10 \text{ L}) = \boxed{0.50 \text{ L}} \quad V_C = V_B = \boxed{0.50 \text{ L}}$$

(b) Along ACB, there is work only from $A \rightarrow C$; hence

$$w = -p_{\text{ext}} \Delta V [10] = (-1.0 \times 10^5 \text{ Pa}) \times (0.50 - 10) \text{ L} \times (10^{-3} \text{ m}^3 \text{ L}^{-1}) = 9.5 \times 10^2 \text{ J}$$

Along ADB, there is work only from $D \rightarrow B$; hence

$$w = -p_{\text{ext}} \Delta V [10] = (-20 \times 10^5 \text{ Pa}) \times (0.50 - 10) \text{ L} \times (10^{-3} \text{ m}^3 \text{ L}^{-1}) = \boxed{1.9 \times 10^4 \text{ J}}$$

$$\begin{aligned} \text{(c) } w &= -nRT \ln \frac{V_B}{V_A} [13] = (-0.389) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (313 \text{ K}) \times \left(\ln \frac{0.5}{10} \right) \\ &= \boxed{+3.0 \times 10^3 \text{ J}} \end{aligned}$$

The work along each of these three paths is different, illustrating the fact that work is not a state property.

(d) Since the initial and final states of all three paths are the same, ΔU for all three paths is the same. Path AB is isothermal; hence $\Delta U = 0$, since the gas is assumed to be perfect. Therefore, $\Delta U = 0$ for paths ACB and ADB as well and the fact that $C_{V,m} = \frac{3}{2}R$ is not needed for the solution.

In each case, $q = \Delta U - w = -w$, thus for

$$\begin{aligned} \text{path ACB, } q &= \boxed{-9.5 \times 10^2 \text{ J}}; & \text{path ADB, } q &= \boxed{-1.9 \times 10^4 \text{ J}}; \\ \text{path AB, } q &= \boxed{-3.0 \times 10^3 \text{ J}} \end{aligned}$$

The heat is different for all three paths; heat is not a state property.

P2.27

Since ΔU is independent of path $\Delta U(A \rightarrow B) = q(\text{ACB}) + w(\text{ACB}) = 80 \text{ J} - 30 \text{ J} = 50 \text{ J}$

$$\text{(a) } \Delta U = 50 \text{ J} = q(\text{ADB}) + w(\text{ADB})$$

$$q(\text{ADB}) = 50 \text{ J} - (-10 \text{ J}) = \boxed{+60 \text{ J}}$$

$$\text{(b) } q(\text{B} \rightarrow \text{A}) = \Delta U(\text{B} \rightarrow \text{A}) - w(\text{B} \rightarrow \text{A}) = -50 \text{ J} - (+20 \text{ J}) = \boxed{-70 \text{ J}}$$

The system liberates heat.

$$\text{(c) } \Delta U(\text{ADB}) = \Delta U(\text{A} \rightarrow \text{D}) + \Delta U(\text{D} \rightarrow \text{B}); \quad 50 \text{ J} = 40 \text{ J} + \Delta U(\text{D} \rightarrow \text{B})$$

$$\Delta U(\text{D} \rightarrow \text{B}) = 10 \text{ J} = q(\text{D} \rightarrow \text{B}) + w(\text{D} \rightarrow \text{B}); \quad w(\text{D} \rightarrow \text{B}) = 0,$$

$$\text{hence } q(\text{D} \rightarrow \text{B}) = \boxed{+10 \text{ J}}$$

$$q(\text{ADB}) = 60 \text{ J}[\text{part a}] = q(\text{A} \rightarrow \text{D}) + q(\text{D} \rightarrow \text{B})$$

$$60 \text{ J} = q(\text{A} \rightarrow \text{D}) + 10 \text{ J}; \quad q(\text{A} \rightarrow \text{D}) = \boxed{+50 \text{ J}}$$

P2.29

$$\begin{aligned} w &= - \int_{V_1}^{V_2} p \, dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} + n^2a \int_{V_1}^{V_2} \frac{dV}{V^2} \\ &= -nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - n^2a \left(\frac{1}{V_2} - \frac{1}{V_1}\right) \end{aligned}$$

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

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

$$T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}, \quad T_c = \frac{8a}{27Rb}, \quad V_c = 3nb \quad [\text{Table 1.6}]$$

$$w = -\left(\frac{8na}{27b}\right) \times (T_r) \times \ln\left(\frac{V_{r,2} - \frac{1}{3}}{V_{r,1} - \frac{1}{3}}\right) - \left(\frac{na}{3b}\right) \times \left(\frac{1}{V_{r,2}} - \frac{1}{V_{r,1}}\right)$$

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

$$w_r = \boxed{-\frac{8}{9}nT_r \ln\left(\frac{V_{r,2} - 1/3}{V_{r,1} - 1/3}\right) - n\left(\frac{1}{V_{r,2}} - \frac{1}{V_{r,1}}\right)}$$

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

$$\frac{w_r}{n} = \boxed{-\frac{8}{9} \ln\left(\frac{3x-1}{2}\right) - \frac{1}{x} + 1}$$

Solutions to applications

P2.30 (a) $q = n\Delta_c H^\ominus = \frac{1.5 \text{ g}}{342.3 \text{ g mol}^{-1}} \times (-5645 \text{ kJ mol}^{-1}) = \boxed{-25 \text{ kJ}}$

(b) Effective work available is $\approx 25 \text{ kJ} \times 0.25 = 6.2 \text{ kJ}$

Because $w = mgh$, and $m \approx 65 \text{ kg}$

$$h \approx \frac{6.2 \times 10^3 \text{ J}}{65 \text{ kg} \times 9.81 \text{ m s}^{-2}} = \boxed{9.7 \text{ m}}$$

(c) The energy released as heat is

$$q = -\Delta_r H = -n\Delta_c H^\ominus = -\left(\frac{2.5 \text{ g}}{180 \text{ g mol}^{-1}}\right) \times (-2808 \text{ kJ mol}^{-1}) = \boxed{39 \text{ kJ}}$$

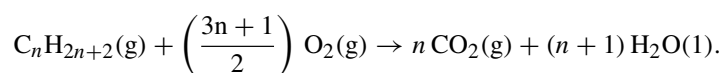
(d) If one-quarter of this energy were available as work a 65 kg person could climb to a height h given by

$$1/4q = w = mgh \quad \text{so} \quad h = \frac{q}{4mg} = \frac{39 \times 10^3 \text{ J}}{4(65 \text{ kg}) \times (9.8 \text{ m s}^{-2})} = \boxed{15 \text{ m}}$$

P2.35 (a) and (b). The table displays computed enthalpies of formation (semi-empirical, PM3 level, PC Spartan Pro™), enthalpies of combustion based on them (and on experimental enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$, -285.83 and $-393.51 \text{ kJ mol}^{-1}$ respectively), experimental enthalpies of combustion from Table 2.5, and the relative error in enthalpy of combustion.

Compound	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	$\Delta_c H^\ominus / \text{kJ mol}^{-1}$ (calc.)	$\Delta_c H^\ominus / \text{kJ mol}^{-1}$ (expt.)	% error
$\text{CH}_4(\text{g})$	-54.45	-910.72	-890	2.33
$\text{C}_2\text{H}_6(\text{g})$	-75.88	-1568.63	-1560	0.55
$\text{C}_3\text{H}_8(\text{g})$	-98.84	-2225.01	-2220	0.23
$\text{C}_4\text{H}_{10}(\text{g})$	-121.60	-2881.59	-2878	0.12
$\text{C}_5\text{H}_{12}(\text{g})$	-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

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

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

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

The agreement is quite good.

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

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

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

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

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

Compound	$M/(\text{g mol}^{-1})$	$\Delta_c H^\ominus/\text{kJ mol}^{-1}$	$\ln M(\text{g mol}^{-1})$	$\ln \Delta_c H^\ominus/\text{kJ mol}^{-1} $
$\text{CH}_4(\text{g})$	16.04	-890	2.775	6.81
$\text{C}_2\text{H}_6(\text{g})$	30.07	-1560	3.404	7.358
$\text{C}_3\text{H}_8(\text{g})$	44.10	-2220	3.786	7.708
$\text{C}_4\text{H}_{10}(\text{g})$	58.12	-2878	4.063	7.966
$\text{C}_5\text{H}_{12}(\text{g})$	72.15	-3537	4.279	8.172

The plot is shown below in Fig 2.2.

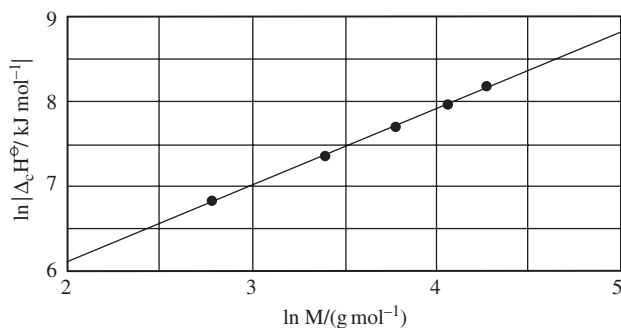


Figure 2.2

The linear least-squares fit equation is:

$$\ln |\Delta_c H^\ominus/\text{kJ mol}^{-1}| = 4.30 + 0.093 \ln M/(\text{g mol}^{-1}) \quad r^2 = 1.00$$

These compounds support the proposed relationships, with

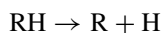
$$n = 0.903$$

$$\text{and } k = -e^{4.30} \text{ kJ mol}^{-1} = [-73.7 \text{ kJ mol}^{-1}]$$

The agreement of these theoretical values of k and n with the experimental values obtained in P2.34 is rather good.

P2.37

In general, the reaction



has a standard enthalpy (the bond dissociation enthalpy) of

$$\Delta H^\ominus(\text{R}-\text{H}) = \Delta_f H^\ominus(\text{R}) + \Delta_f H^\ominus(\text{H}) - \Delta_f H^\ominus(\text{RH})$$

$$\text{so } \Delta_f H^\ominus(\text{R}) = \Delta H^\ominus(\text{R}-\text{H}) - \Delta_f H^\ominus(\text{H}) + \Delta_f H^\ominus(\text{RH})$$

Since we are provided with bond dissociation energies, we need

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + RT \Delta n_g$$

$$\text{So } \Delta_r H^\ominus(\text{R}-\text{H}) = \Delta_r U^\ominus(\text{R}-\text{H}) + RT$$

$$\text{and } \Delta_r H^\ominus(\text{R}) = \Delta_r H^\ominus(\text{R}-\text{H}) + RT - \Delta_f H^\ominus(\text{H}) + \Delta_f H^\ominus(\text{RH})$$

Inserting the bond dissociation energies and enthalpies of formation from Tables 2.5 and 2.6, we obtain

$$\Delta_f H^\ominus(\text{C}_2\text{H}_5) = (420.5 + 2.48 - 217.97 - 84.68) \text{ kJ mol}^{-1} = \boxed{120.3 \text{ kJ mol}^{-1}}$$

$$\begin{aligned} \Delta_f H^\ominus(\text{sec-C}_4\text{H}_9) &= (410.5 + 2.48 - 217.97 - 126.15) \text{ kJ mol}^{-1} \\ &= \boxed{68.9 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\Delta_f H^\ominus(\text{tert-C}_4\text{H}_9) = (398.3 + 2.48 - 217.97 - 134.2) \text{ kJ mol}^{-1} = \boxed{48.1 \text{ kJ mol}^{-1}}$$