

**Chem 401—Physical Chemistry**  
**Chapter 2 Homework Solution**

**E2.31(b)** The expansion coefficient is

$$\begin{aligned}\alpha &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{V'(3.7 \times 10^{-4} \text{ K}^{-1} + 2 \times 1.52 \times 10^{-6} T \text{ K}^{-2})}{V} \\ &= \frac{V'[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6} (T/\text{K})] \text{ K}^{-1}}{V'[0.77 + 3.7 \times 10^{-4} (T/\text{K}) + 1.52 \times 10^{-6} (T/\text{K})^2]} \\ &= \frac{[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6} (310)] \text{ K}^{-1}}{0.77 + 3.7 \times 10^{-4} (310) + 1.52 \times 10^{-6} (310)^2} = \boxed{1.27 \times 10^{-3} \text{ K}^{-1}}\end{aligned}$$

**E2.32(b)** Isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \approx -\frac{\Delta V}{V \Delta p} \quad \text{so} \quad \Delta p = -\frac{\Delta V}{V \kappa_T}$$

A density increase of 0.08 percent means  $\Delta V/V = -0.0008$ . So the additional pressure that must be applied is

$$\Delta p = \frac{0.0008}{2.21 \times 10^{-6} \text{ atm}^{-1}} = \boxed{3.6 \times 10^2 \text{ atm}}$$

**E2.33(b)** The isothermal Joule–Thomson coefficient is

$$\left( \frac{\partial H}{\partial p} \right)_T = -\mu C_p = -(1.11 \text{ K atm}^{-1}) \times (37.11 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-41.2 \text{ J atm}^{-1} \text{ mol}^{-1}}$$

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

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

$$\Delta H = -(41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) \times (12.0 \text{ mol}) \times (-55 \text{ atm}) = \boxed{27.2 \times 10^3 \text{ J}}$$

### Solutions to problems

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

### Solutions to numerical problems

**P2.1** The temperatures are readily obtained from the perfect gas equation,  $T = \frac{pV}{nR}$ ,

$$T_1 = \frac{(1.00 \text{ atm}) \times (22.4 \text{ dm}^3)}{(1.00 \text{ mol}) \times (0.0821 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})} = \boxed{273 \text{ K}} = T_3 \text{ [isotherm].}$$

Similarly,  $T_2 = \boxed{546 \text{ K}}$ .

In the solutions that follow all steps in the cycle are considered to be reversible.

Step 1 → 2

$$w = -p_{\text{ex}}\Delta V = -p\Delta V = -nR\Delta T \quad [\Delta(pV) = \Delta(nRT)],$$

$$w = -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (546 - 273) \text{ K} = \boxed{-2.27 \times 10^3 \text{ J}}.$$

$$\Delta U = nC_{V,m}\Delta T = (1.00 \text{ mol}) \times \frac{3}{2} \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) = +3.40 \times 10^3 \text{ J}.$$

$$q = \Delta U - w = +3.40 \times 10^3 \text{ J} - (-2.27 \times 10^3 \text{ J}) = \boxed{+5.67 \times 10^3 \text{ J}}.$$

$$\Delta H = q_p = \boxed{+5.67 \times 10^3 \text{ J}}.$$

If this step is not reversible, then  $w$ ,  $q$ , and  $\Delta H$  would be indeterminate.

Step 2 → 3

$$\boxed{w = 0} \text{ [constant volume].}$$

$$q_V = \Delta U = nC_{V,m}\Delta T = (1.00 \text{ mol}) \times \left(\frac{3}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-273 \text{ K})$$

$$= \boxed{-3.40 \times 10^3 \text{ J}}.$$

From  $H \equiv U + pV$

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

$$= (-3.40 \times 10^3 \text{ J}) + (1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-273 \text{ K}) = \boxed{-5.67 \times 10^3 \text{ J}}.$$

Step 3 → 1

$\Delta U$  and  $\Delta H$  are  $\boxed{\text{zero}}$  for an isothermal process in a perfect gas; hence for the reversible compression

$$-q = w = -nRT \ln \frac{V_1}{V_3} = (-1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) \times \ln \left( \frac{22.4 \text{ dm}^3}{44.8 \text{ dm}^3} \right)$$

$$= \boxed{+1.57 \times 10^3 \text{ J}}, \quad q = \boxed{-1.57 \times 10^3 \text{ J}}.$$

If this step is not reversible, then  $q$  and  $w$  would have different values which would be determined by the details of the process.

Total cycle

State	$p/\text{atm}$	$V/\text{dm}^3$	$T/\text{K}$
1	1.00	22.44	273
2	1.00	44.8	546
3	0.50	44.8	273

*Thermodynamic quantities calculated for reversible steps*

Step	Process	$q/\text{kJ}$	$w/\text{kJ}$	$\Delta U/\text{kJ}$	$\Delta H/\text{kJ}$
1 $\rightarrow$ 2	$p$ constant = $p_{ex}$	+5.67	-2.27	+3.40	+5.67
2 $\rightarrow$ 3	$V$ constant	-3.40	0	-3.40	-5.67
3 $\rightarrow$ 1	Isothermal, reversible	-1.57	+1.57	0	0
Cycle		+0.70	-0.70	0	0

**COMMENT.** All values can be determined unambiguously for the reversible cycle. The net result of the overall process is that 700 J of heat has been converted to work.

**P2.3** Since the volume is fixed,  $w = 0$ .

Since  $\Delta U = q$  at constant volume,  $\Delta U = +2.35 \text{ kJ}$ .

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + V\Delta p \quad [\Delta V = 0].$$

From the van der Waals equation [Table 1.6]

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{so} \quad \Delta p = \frac{R\Delta T}{V_m - b} \quad [\Delta V_m = 0 \text{ at constant volume}].$$

$$\text{Therefore, } \Delta H = \Delta U + \frac{RV\Delta T}{V_m - b}.$$

From the data,

$$V_m = \frac{15.0 \text{ dm}^3}{2.0 \text{ mol}} = 7.5 \text{ dm}^3 \text{ mol}^{-1}, \quad \Delta T = (341 - 300) \text{ K} = 41 \text{ K}.$$

$$V_m - b = (7.5 - 4.3 \times 10^{-2}) \text{ dm}^3 \text{ mol}^{-1} = 7.46 \text{ dm}^3 \text{ mol}^{-1}.$$

$$\frac{RV\Delta T}{V_m - b} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (15.0 \text{ dm}^3) \times (41 \text{ K})}{7.46 \text{ dm}^3 \text{ mol}^{-1}} = 0.68 \text{ kJ}.$$

Therefore,  $\Delta H = (2.35 \text{ kJ}) + (0.68 \text{ kJ}) = +3.03 \text{ kJ}$ .

**P2.5** This cycle is represented in Figure 2.2. Assume that the initial temperature is 298 K.

(a) First, note that  $w = 0$  (constant volume). Then calculate  $\Delta U$  since  $\Delta T$  is known ( $\Delta T = 298 \text{ K}$ ) and then calculate  $q$  from the First Law.

$$\Delta U = nC_{V,m}\Delta T \quad [2.16b]; \quad C_{V,m} = C_{p,m} - R = \frac{7}{2}R - R = \frac{5}{2}R,$$

$$\Delta U = (1.00 \text{ mol}) \times \left(\frac{5}{2}\right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) = 6.19 \times 10^3 \text{ J} = +6.19 \text{ kJ}.$$

$$q = q_V = \Delta U - w = 6.19 \text{ kJ} - 0 = +6.19 \text{ kJ}.$$

## Solutions to numerical problems

**P2.2**  $w = -p_{\text{ex}}\Delta V$  [2.8]  $V_f = \frac{nRT}{p_{\text{ex}}} \gg V_i$ ; so  $\Delta V \approx V_f$

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

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

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

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

**P2.4** The virial expression for pressure up to the second coefficient is

$$p = \left(\frac{RT}{V_m}\right) \left(1 + \frac{B}{V_m}\right) \quad [1.19]$$

$$w = -\int_i^f p dV = -n \int_i^f \left(\frac{RT}{V_m}\right) \times \left(1 + \frac{B}{V_m}\right) dV_m = -nRT \ln\left(\frac{V_{m,f}}{V_{m,i}}\right) + nBRT \left(\frac{1}{V_{m,f}} - \frac{1}{V_{m,i}}\right)$$

From the data,

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

$$V_{m,i} = \frac{5.25 \text{ cm}^3}{70 \times 10^{-3} \text{ mol}} = 75.0 \text{ cm}^3 \text{ mol}^{-1}, \quad V_{m,f} = \frac{6.29 \text{ cm}^3}{70 \times 10^{-3} \text{ mol}} = 89.9 \text{ cm}^3 \text{ mol}^{-1}$$

$$\begin{aligned} \text{and so } B \left(\frac{1}{V_{m,f}} - \frac{1}{V_{m,i}}\right) &= (-28.7 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1}{89.9 \text{ cm}^3 \text{ mol}^{-1}} - \frac{1}{75.0 \text{ cm}^3 \text{ mol}^{-1}}\right) \\ &= 6.34 \times 10^{-2} \end{aligned}$$

Therefore,

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

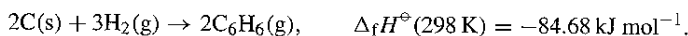
Since  $\Delta U = q + w$  and  $\Delta U = +83.5 \text{ J}$ ,  $q = \Delta U - w = (83.5 \text{ J}) + (25 \text{ J}) = \boxed{+109 \text{ J}}$

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

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

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

**P2.7** The formation reaction is



In order to determine  $\Delta_f H^\ominus(350 \text{ K})$  we employ Kirchoff's law [2.36] with  $T_2 = 350 \text{ K}$ ,  $T_1 = 298 \text{ K}$ ,

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

$$\text{where } \Delta_r C_p = \sum_j \nu_j C_{p,m}(\text{J}) = C_{p,m}(\text{C}_6\text{H}_6) - 2C_{p,m}(\text{C}) - 3C_{p,m}(\text{H}_2).$$

From Table 2.2

$$C_{p,m}(\text{C}_6\text{H}_6)/(\text{J K}^{-1} \text{ mol}^{-1}) = 14.73 + \left(\frac{0.1272}{\text{K}}\right) T,$$

$$C_{p,m}(\text{C, s})/(\text{J K}^{-1} \text{ mol}^{-1}) = 16.86 + \left(\frac{4.77 \times 10^{-3}}{\text{K}}\right) T - \left(\frac{8.54 \times 10^5 \text{ K}^2}{T^2}\right),$$

$$C_{p,m}(\text{H}_2, \text{g})/(\text{J K}^{-1} \text{ mol}^{-1}) = 27.28 + \left(\frac{3.26 \times 10^{-3}}{\text{K}}\right) T - \left(\frac{0.50 \times 10^5 \text{ K}^2}{T^2}\right),$$

$$\Delta_r C_p/(\text{J K}^{-1} \text{ mol}^{-1}) = -100.83 + \left(\frac{0.1079T}{\text{K}}\right) - \left(\frac{1.56 \times 10^6 \text{ K}^2}{T^2}\right).$$

$$\begin{aligned} \int_{T_1}^{T_2} \frac{\Delta_r C_p dT}{\text{J K}^{-1} \text{ mol}^{-1}} &= -100.83 \times (T_2 - T_1) + \left(\frac{1}{2}\right) (0.1079 \text{ K}^{-1}) (T_2^2 - T_1^2) \\ &\quad - (1.56 \times 10^6 \text{ K}^2) \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &= -100.83 \times (52 \text{ K}) + \left(\frac{1}{2}\right) (0.1079)(350^2 - 298^2) \text{ K} \\ &\quad - (1.56 \times 10^6) \left(\frac{1}{350} - \frac{1}{298}\right) \text{ K} \\ &= -2.65 \times 10^3 \text{ K}. \end{aligned}$$

Multiplying by the units  $\text{J K}^{-1} \text{ mol}^{-1}$ , we obtain

$$\begin{aligned} \int_{T_1}^{T_2} \Delta_r C_p dT &= -(2.65 \times 10^3 \text{ K}) \times (\text{J K}^{-1} \text{ mol}^{-1}) = -2.65 \times 10^3 \text{ J mol}^{-1} \\ &= -2.65 \text{ kJ mol}^{-1}. \end{aligned}$$

Hence  $\Delta_f H^\ominus(350 \text{ K}) = \Delta_f H^\ominus(298 \text{ K}) - 2.65 \text{ kJ mol}^{-1}$

$$= -84.68 \text{ kJ mol}^{-1} - 2.65 \text{ kJ mol}^{-1} = \boxed{-87.33 \text{ kJ mol}^{-1}}.$$

**P2.9**  $\text{Cr}(\text{C}_6\text{H}_6)_2(\text{s}) \rightarrow \text{Cr}(\text{s}) + 2\text{C}_6\text{H}_6(\text{g}), \quad \Delta n_g = +2 \text{ mol}.$

$$\Delta_r H^\ominus = \Delta_r U^\ominus + 2RT, \text{ from [2.21]}$$

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

In terms of enthalpies of formation

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

or  $\Delta_f H^\ominus(\text{metallocene, 583 K}) = 2\Delta_f H^\ominus(\text{benzene, 583 K}) - 17.7 \text{ kJ mol}^{-1}$ .

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

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

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 2.7.

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

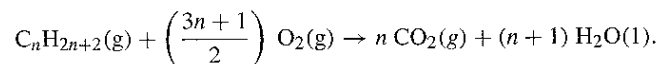
Therefore  $\Delta_f H^\ominus(\text{metallocene, 583 K}) = (2 \times 66.8 - 17.7) \text{ kJ mol}^{-1} = \boxed{+116.0 \text{ kJ mol}^{-1}}$ .

**P2.11**

(a) and (b). The table 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  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$ ,  $-285.83$  and  $-393.51 \text{ kJ mol}^{-1}$  respectively), experimental enthalpies of combustion (Table 2.5), and the relative error in enthalpy of combustion.

Compound	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	$\Delta_c H^\ominus / \text{kJ mol}^{-1}(\text{calc.})$	$\Delta_c H^\ominus / \text{kJ mol}^{-1}(\text{expt.})$	% 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

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

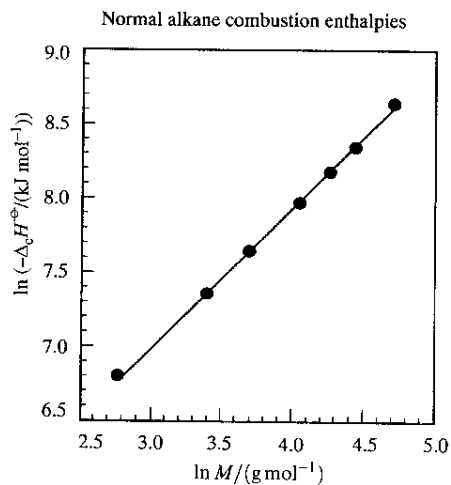
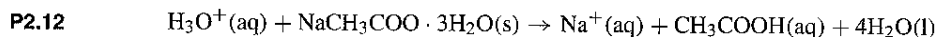


Figure 2.3



$$n_{\text{salt}} = m_{\text{salt}}/M_{\text{salt}} = 1.3584 \text{ g}/(136.08 \text{ g mol}^{-1}) = 0.0099824 \text{ mol}$$

Application of eqns 2.14 and 2.19b gives:

$$\begin{aligned} \Delta_r H_m &= -\Delta_{\text{calorimeter}} H/n_{\text{salt}} = -C_{\text{calorimeter+contents}} \Delta T/n_{\text{salt}} \\ &= -(C_{\text{calorimeter}} + C_{\text{solution}})\Delta T/n_{\text{salt}} \\ &= -(91.0 \text{ J K}^{-1} + 4.144 \text{ J K}^{-1} \text{ cm}^{-3} \times 100 \text{ cm}^3) \times (-0.397 \text{ K})/0.0099824 \text{ mol} \\ &= 20.1 \text{ kJ mol}^{-1} \end{aligned}$$

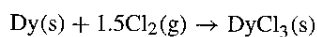
Application of eqn 2.32 gives:

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{Na}^+, \text{aq}) + \Delta_f H^\ominus(\text{CH}_3\text{COOH}, \text{aq}) + 3\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) \\ &\quad - \Delta_f H^\ominus(\text{H}^+, \text{aq}) - \Delta_f H^\ominus(\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}, \text{s}) \end{aligned}$$

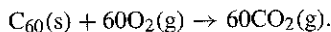
(where the water coefficient is 3 not 4 because one water in the chemical equation is part of the hydrated hydrogen ion). Solving for  $\Delta_f H^\ominus(\text{Na}^+, \text{aq})$  and substituting  $\Delta_f H^\ominus$  values found in Tables 2.5 and 2.7 gives:

$$\begin{aligned} \Delta_f H^\ominus(\text{Na}^+, \text{aq}) &= \Delta_r H^\ominus - \Delta_f H^\ominus(\text{CH}_3\text{COOH}, \text{aq}) - 3\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) + \Delta_f H^\ominus(\text{H}^+, \text{aq}) \\ &\quad + \Delta_f H^\ominus(\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}, \text{s}) \\ \Delta_f H^\ominus(\text{Na}^+, \text{aq}) &= \{20.1 - (-485.76) - 3(-285.83) + (0) + (-1604)\} \text{ kJ mol}^{-1} \\ &= \boxed{241 \text{ kJ mol}^{-1}} \end{aligned}$$

**P2.14** We must relate the formation of  $\text{DyCl}_3$



**P2.13** The reaction is



Because the reaction does not change the number of moles of gas,  $\Delta_c H = \Delta_c U$  [2.21]. Therefore

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

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

$$\Delta_c H^\ominus = 60\Delta_f H^\ominus(\text{CO}_2) - 60\Delta_f H^\ominus(\text{O}_2) - \Delta_f H^\ominus(\text{C}_{60}),$$

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

**P2.15** (a) 
$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{SiH}_2) + \Delta_f H^\ominus(\text{H}_2) - \Delta_f H^\ominus(\text{SiH}_4) \\ &= (274 + 0 - 34.3) \text{ kJ mol}^{-1} = \boxed{240 \text{ kJ mol}^{-1}}. \end{aligned}$$

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

**P2.17** The temperatures and volumes in reversible adiabatic expansion are related by eqn 2.28a:

$$T_f = T_i \left( \frac{V_f}{V_i} \right)^{1/c} \quad \text{where } c = \frac{C_{V,m}}{R}.$$

From eqn 2.29, we can relate the pressures and volumes:

$$p_f = p_i \left( \frac{V_f}{V_i} \right)^\gamma \quad \text{where } \gamma = \frac{C_{p,m}}{C_{V,m}}.$$

We are looking for  $C_{p,m}$ , which can be related to  $c$  and  $\gamma$ .

$$c\gamma = \left( \frac{C_{V,m}}{R} \right) \times \left( \frac{C_{p,m}}{C_{V,m}} \right) = \frac{C_{p,m}}{R}.$$

Solving both relationships for the ratio of volumes, we have

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

Therefore

$$C_{p,m} = R \frac{\ln \left( \frac{p_f}{p_i} \right)}{\ln \left( \frac{T_f}{T_i} \right)} = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left( \frac{\ln \left( \frac{202.94 \text{ kPa}}{81.840 \text{ kPa}} \right)}{\ln \left( \frac{298.15 \text{ K}}{248.44 \text{ K}} \right)} \right) = \boxed{41.40 \text{ J K}^{-1} \text{ mol}^{-1}}.$$



$$\begin{aligned}\Delta H &= (-0.248\bar{3} \text{ dm}^3 \text{ mol}^{-1}) \times (2.43\bar{8} \text{ atm} - 1.225 \text{ atm}) \\ &= (-0.301 \text{ dm}^3 \text{ atm mol}^{-1}) \times \left(\frac{1 \text{ m}}{10 \text{ dm}}\right)^3 \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{\text{atm}}\right) = \boxed{-30.5 \text{ J mol}^{-1}}\end{aligned}$$

## Solutions to theoretical problems

**P2.20** A function has an exact differential if its mixed partial derivatives are equal. That is,  $f(x, y)$  has an exact differential if

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)$$

$$(a) \quad \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right) = \frac{\partial}{\partial y} (2xy) = 2x \quad \text{and} \quad \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial x} (x^2 + 6y) = 2x$$

$$(b) \quad \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right) = \frac{\partial}{\partial y} (\cos xy - xy \sin xy) \\ = -x \sin xy - x \sin xy - x^2 y \cos xy = -2x \sin xy - x^2 y \cos xy$$

$$\text{and} \quad \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial x} (-x^2 \sin xy) = -2x \sin xy - x^2 y \cos xy$$

$$(c) \quad \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right) = \frac{\partial}{\partial y} (3x^2 y^2) = 6x^2 y \quad \text{and} \quad \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial x} (2x^3 y) = 6x^2 y$$

$$(d) \quad \frac{\partial}{\partial t} \left( \frac{\partial f}{\partial s} \right) = \frac{\partial}{\partial t} (te^s + 1) = e^s \quad \text{and} \quad \frac{\partial}{\partial s} \left( \frac{\partial f}{\partial t} \right) = \frac{\partial}{\partial s} (2t + e^s) = e^s$$

**P2.22**

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$$\boxed{\left( \frac{\partial C_V}{\partial V} \right)_T = \left( \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_V \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V} \quad [\text{derivatives may be taken in any order}]$$

$$\left( \frac{\partial U}{\partial V} \right)_T = 0 \text{ for a perfect gas [Section 2.11(b)]}$$

$$\text{Hence, } \boxed{\left( \frac{\partial C_V}{\partial V} \right)_T = 0}$$

$$\text{Likewise } C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \text{so} \quad \boxed{\left( \frac{\partial C_p}{\partial p} \right)_T = \left( \frac{\partial}{\partial p} \left( \frac{\partial H}{\partial T} \right)_p \right)_T = \left( \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial p} \right)_T \right)_p}$$

$$\left( \frac{\partial H}{\partial p} \right)_T = 0 \text{ for a perfect gas.}$$

$$\text{Hence, } \left( \frac{\partial C_p}{\partial p} \right)_T = 0.$$