

Exc. 1 (a) For an isobaric expansion against p_{ex} :

$$w = -p_{\text{ex}} \Delta V [1.3] = -(30.0 \times 10^3 \text{ Pa}) \times (3.3 \text{ dm}^3) \times \left(\frac{1 \times 10^{-3} \text{ m}^3}{1 \text{ dm}^3} \right) = \boxed{-99 \text{ J}}$$

(b) For an isothermal expansion:

$$n = \frac{4.50 \text{ g}}{16.04 \text{ g mol}^{-1}} = 0.2805 \text{ mol}, V_i = 12.7 \text{ dm}^3, V_f = (12.7 + 3.3) \text{ dm}^3 = 16.0 \text{ dm}^3$$

For an infinitesimal change in volume the amount of work done will be infinitesimally small (i.e., dw). Thus, we write that in the case of mechanical equilibrium ($p_{\text{ex}} = p$, which is valid for a reversible expansion): $dw = -p_{\text{ex}} dV = -pdV$. For a perfect gas $p = nRT/V$ so the work expression becomes $dw = -(nRT/V)dV$. It follows that the total work of an expansion is given by the integrated form of our expression. At constant temperature, T moves outside the integration along with other constants giving:

$$\begin{aligned} w &= -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = -nRT \ln V \Big|_{V_i}^{V_f} \\ &= -nRT \{ \ln V_f - \ln V_i \} \\ &= -nRT \ln \frac{V_f}{V_i} \quad [\text{reversible, isothermal expansion of perfect gas}] \\ &= -(0.2805 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K}) \times \ln \left(\frac{16.0 \text{ dm}^3}{12.7 \text{ dm}^3} \right) = \boxed{-167 \text{ J}} \end{aligned}$$

Exc. 2 We take the room temperature and pressure to be $T = 298 \text{ K}$ and $p = 1.00 \text{ atm}$. The volume is

$$V = (5.5 \text{ m}) \times (6.5 \text{ m}) \times (3.0 \text{ m}) = 1.07 \times 10^5 \text{ dm}^3.$$

The amount of gas in the room is computed with the perfect gas law.

$$n = \frac{pV}{RT} = \frac{(1.00 \text{ atm}) \times (1.07 \times 10^5 \text{ dm}^3)}{(8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 4.38 \times 10^3 \text{ mol}$$

Thus, the energy required to raise the air temperature by 10°C (equivalent to a 10 K change) is

$$\begin{aligned} q &= nC_{p,m} \Delta T \\ &= (4.38 \times 10^3 \text{ mol}) \times (21 \text{ J K}^{-1} \text{ mol}^{-1}) \times (10 \text{ K}) = 9.2 \times 10^5 \text{ J} = \boxed{9.20 \times 10^2 \text{ kJ}}. \end{aligned}$$

Because $q = P \times t$, where P is the power of the heater and t is the time for which it operates,

$$t = \frac{q}{P} = \frac{9.20 \times 10^5 \text{ J}}{1.5 \times 10^3 \text{ J s}^{-1}} = \boxed{6.1 \times 10^2 \text{ s}}.$$

In practice, the walls and furniture of a room are also heated.

Exc. 3 $q = nRT \ln \left(\frac{V_f}{V_i} \right)$ [See derivation of E1.14(b); reversible, isothermal expansion of perfect gas]

$$= (1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \ln \left(\frac{30.0}{22.0} \right) = \boxed{773 \text{ J}}$$

Exc. 4 $w_{\text{lift}} = mgh [1.2] = (0.200 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (1.55 \text{ m}) = 3.04 \text{ J}$

$$w_{\text{animal}} = -w_{\text{lift}} = -3.04 \text{ J}$$

$$\Delta U_{\text{animal}} = w_{\text{animal}} + q_{\text{animal}} [1.6] = (-3.04 \text{ J}) + (-5.0 \text{ J}) = \boxed{-8.04 \text{ J}}$$

Exc.5 (a) The molar internal energy and enthalpy of a perfect gas are related by eqn 1.12b ($H_m = U_m + RT$), which we can write as $H_m - U_m = RT$. When the temperature increases by ΔT , the molar enthalpy increases by ΔH_m and the internal energy increases by ΔU_m , so $\Delta H_m - \Delta U_m = R\Delta T$. Now, divide both sides by ΔT , which gives

$$\frac{\Delta H_m}{\Delta T} - \frac{\Delta U_m}{\Delta T} = R$$

We recognize the first term on the left as the molar constant-pressure heat capacity, $C_{p,m}$, and the second term as the molar constant-volume heat capacity, $C_{v,m}$. Therefore,

$$C_{p,m} - C_{v,m} = R \quad [1.15, \text{perfect gas}]$$

(b) $C_p = \frac{q_p}{\Delta T}$ [1.13 and 1.14a] and division by n gives $C_{p,m} = \frac{q_p}{n\Delta T}$. Thus,

$$C_{p,m} = \frac{q_p}{n\Delta T} = \frac{229 \text{ J}}{(3.00 \text{ mol}) \times (2.06 \text{ K})} = \boxed{37.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$C_{v,m} = C_{p,m} - R [1.15] = (37.1 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{28.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Exc.6

$$C_{v,m} = \frac{dU_m}{dT} \quad [1.9b \text{ after division by } n]$$

$$= \frac{d}{dT}(a + bT + cT^2) = \frac{da}{dT} + \frac{d(bT)}{dT} + \frac{d(cT^2)}{dT} = 0 + b + 2cT = \boxed{b + 2cT}$$

Exc.7 (a) $q = mC_{s,\text{water}}\Delta T$ [1.5b with $C = mC_{s,\text{water}}$ and $C_{s,\text{water}} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$]

$$\Delta T = \frac{q}{mC_s} = \frac{10 \times 10^6 \text{ J}}{(65 \times 10^3 \text{ g}) \times (4.18 \text{ J g}^{-1} \text{ K}^{-1})} = 37 \text{ K} = \boxed{37^\circ\text{C}}$$

(b) Let m_{vap} be the mass of water evaporated by q .

$$q = (m_{\text{vap}}/M)\Delta_{\text{vap}}H^\ominus$$

$$m_{\text{vap}} = \frac{Mq}{\Delta_{\text{vap}}H^\ominus} = \frac{(0.018016 \text{ kg mol}^{-1}) \times (10 \times 10^3 \text{ kJ})}{44 \text{ kJ mol}^{-1}} = \boxed{4.1 \text{ kg}}$$

This estimate ignores both the conduction of heat that occurs from high temperature to low temperature without evaporation and the small amount of heat used to bring ingested water to body temperature.

Exc.8 The electric current provides the heat $q_{\text{heater}} = I\mathcal{V}t$ [1.17], which vaporizes 0.798 g $\text{H}_2\text{O}(\text{l})$ at 373.15 K and 1.0 atm pressure. Under these conditions:

$$\begin{aligned}\Delta_{\text{vap}}H &= \frac{q_{\text{heater}}}{n_{\text{vaporized}}} = \frac{q_{\text{heater}}M}{m_{\text{vaporized}}} = \frac{I\mathcal{V}tM}{m_{\text{vaporized}}} \\ &= \frac{(0.50 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) \times (18.015 \text{ g mol}^{-1})}{0.798 \text{ g}} \\ &= \boxed{40.6 \text{ kJ mol}^{-1}} \quad [1 \text{ A V s} = 1 \text{ J}]\end{aligned}$$

$$\begin{aligned}\Delta_{\text{vap}}U &= \Delta_{\text{vap}}H - p\Delta_{\text{vap}}V_{\text{m}} \quad [1.11\text{b}] \\ &= \Delta_{\text{vap}}H - p\{V_{\text{m}}(\text{water, g}) - V_{\text{m}}(\text{water, l})\} \quad [V_{\text{m}}(\text{water, l}) \ll V_{\text{m}}(\text{water, g})] \\ &= \Delta_{\text{vap}}H - pV_{\text{m}}(\text{water, g}) \\ &= \Delta_{\text{vap}}H - RT \quad [\text{F.8}] \\ &= 40.6 \times 10^3 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373.15 \text{ K}) \\ &= \boxed{37.5 \text{ kJ mol}^{-1}}\end{aligned}$$

Exc.9 We begin by using the data in a computation of the calorimeter heat capacity C .

$$q = I\mathcal{V}t \quad [1.17] = (1.27 \text{ A}) \times (12.5 \text{ V}) \times (157 \text{ s}) = 2.49 \text{ kJ} \quad [1 \text{ A s} = 1 \text{ C}, 1 \text{ C V} = 1 \text{ J}]$$

$$C = \frac{q}{\Delta T} \quad [1.16] = \frac{2.49 \text{ kJ}}{3.88 \text{ K}} = 0.642 \text{ kJ K}^{-1}$$

With the use of an oxygen bomb calorimeter the combustion is at constant volume, giving

$$\Delta U_{\text{calorimeter}} = q_V = C\Delta T = (0.642 \text{ kJ K}^{-1}) \times (2.89 \text{ K}) = \boxed{+1.86 \text{ kJ}}$$

which is the energy released by the combustion reaction.

Exc.10 $\text{C}_3\text{H}_8(\text{l}) \rightarrow \text{C}_3\text{H}_8(\text{g}) \quad \Delta_{\text{vap}}H^\circ = +15 \text{ kJ mol}^{-1}$
 $\text{C}_3\text{H}_8(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l}) \quad \Delta_{\text{c}}H^\circ(\text{propane, g}) = -2220 \text{ kJ mol}^{-1}$

$$\begin{aligned}\text{(a)} \quad \Delta_{\text{c}}H^\circ(\text{propane, l}) &= \Delta_{\text{vap}}H^\circ + \Delta_{\text{c}}H^\circ(\text{propane, g}) \\ &= +15 \text{ kJ mol}^{-1} - 2220 \text{ kJ mol}^{-1} = \boxed{-2205 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad \Delta_{\text{v}}U_{\text{gas}} &= -2[5 \text{ O}_2(\text{g}) \text{ replaced with } 3 \text{ CO}_2(\text{g})] \\ \Delta_{\text{c}}U^\circ(\text{propane, l}) &= \Delta_{\text{c}}H^\circ(\text{propane, l}) - (-2)RT \quad [1.21] \\ &= -2205 \text{ kJ mol}^{-1} + (2 \times 2.5 \text{ kJ mol}^{-1}) = \boxed{-2200 \text{ kJ mol}^{-1}}\end{aligned}$$

Exc.11 $\text{protein}(\text{native}) \rightarrow \text{protein}(\text{denatured}) \quad \Delta_{\text{r}}H^\circ(298 \text{ K}) = +217.6 \text{ kJ mol}^{-1} \quad \Delta_{\text{r}}C_p^\circ = +6.3 \text{ kJ K}^{-1} \text{ mol}^{-1}$

$$\text{(a)} \quad \Delta_{\text{r}}H^\circ(T) = \Delta_{\text{r}}H^\circ(298 \text{ K}) + \Delta_{\text{r}}C_p^\circ \times (T - 298 \text{ K}) \quad [1.24, \text{ temperature-independent heat capacities}]$$

$$\begin{aligned}\text{(i)} \quad \Delta_{\text{r}}H^\circ(351 \text{ K}) &= +217.6 \text{ kJ mol}^{-1} + (+6.3 \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (351 \text{ K} - 298 \text{ K}) \\ &= \boxed{+552 \text{ kJ mol}^{-1}}\end{aligned}$$

$$(ii) \quad \Delta_r H^\circ(263 \text{ K}) = +217.6 \text{ kJ mol}^{-1} + (+6.3 \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (263 \text{ K} - 298 \text{ K}) \\ = \boxed{-2.9 \text{ kJ mol}^{-1}}$$

(b) Answer (i) of part (a) is endothermic while answer (ii) is exothermic. Therefore, there is a temperature T_{zero} between 263 K and 351 K such that below T_{zero} the reaction is exothermic, above T_{zero} it is endothermic, and $\Delta_r H^\circ(T_{\text{zero}}) = 0$. Solving the eqn of part (a) for T_{zero} gives

$$T_{\text{zero}} = 298 \text{ K} - \Delta_r H^\circ(298 \text{ K}) / \Delta_r C_p^\circ \\ = 298 \text{ K} - (+217.6 \text{ kJ mol}^{-1}) / (+6.3 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ = \boxed{263.5 \text{ K}} \quad (\text{slightly greater than } 263 \text{ K})$$

Exc. 12 $\Delta_{\text{vap}} H^\circ(T') = \Delta_{\text{vap}} H^\circ(T) + \Delta_r C_p^\circ \times (T' - T) \quad [1.24]$

$$\Delta_{\text{vap}} H^\circ(373 \text{ K}) = 44.01 \text{ kJ mol}^{-1} + (33.58 \text{ J K}^{-1} \text{ mol}^{-1} - 75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373 \text{ K} - 298 \text{ K}) \\ = \boxed{40.88 \text{ kJ mol}^{-1}}$$