

Chapter 2 – New Exercises and Solutions

E2.1(c) Calculate the work needed for a 65 kg tourist to climb to the top of the great pyramid in Egypt with a height of 159 m. How much work was needed to raise a 1.0 metric ton block of stone to that height?

E2.1(c) The physical definition of work is $dw = -F dz$ [2.4]

In a gravitational field the force is the weight of the object, which is $F = mg$

If g is constant over the distance the mass moves, dw may be integrated to give the total work

$$w = -\int_{z_i}^{z_f} F dz = -\int_{z_i}^{z_f} mg dz = -mg(z_f - z_i) = -mgh \quad \text{where} \quad h = (z_f - z_i)$$

For the tourist: $w = -(65 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (159 \text{ m}) = -1.01 \times 10^5 \text{ J} = \boxed{1.01 \times 10^5 \text{ J needed}}$

For the stone: $w = -(1000 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (159 \text{ m}) = -1.56 \times 10^6 \text{ J} = \boxed{1.56 \text{ MJ needed}}$

E2.3(c) A sample consisting of 1.00 mol of the molecules in air is expanded isothermally at 25°C from 24.2 dm³ to 48.4 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

E2.3(c) For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. (See *Molecular interpretation 2.2* and Section 2.11(b) for a more complete discussion.) From the definition of enthalpy, $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$ (perfect gas). Hence, $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas.

(a) $\boxed{\Delta U = \Delta H = 0}$

$$w = -nRT \ln \left(\frac{V_f}{V_i} \right) \quad [2.11]$$

$$= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{48.4 \text{ dm}^3}{24.2 \text{ dm}^3} \right)$$

$$= -1.72 \times 10^3 \text{ J} = \boxed{-1.72 \text{ kJ}}$$

$$q = \Delta U - w \text{ [First Law]} = 0 + 1.72 \text{ kJ} = \boxed{+1.72 \text{ kJ}}$$

(b) $\boxed{\Delta U = \Delta H = 0}$

$$w = -p_{\text{ex}} \Delta V \quad [2.8] \quad \Delta V = (48.4 - 24.2) \text{ dm}^3 = 24.2 \text{ dm}^3$$

p_{ex} can be computed from the perfect gas law

$$pV = nRT$$

$$\text{so} \quad p_{\text{ex}} = p_f = \frac{nRT}{V_f} = \frac{(1.00 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{48.4 \text{ dm}^3} = 0.505 \text{ atm}$$

$$w = -(0.505 \text{ atm}) \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) \times (24.2 \text{ dm}^3) \times \left(\frac{1 \text{ m}^3}{10^3 \text{ dm}^3} \right)$$

$$= -1.24 \times 10^3 \text{ Pa m}^3 = -1.24 \times 10^3 \text{ J} = \boxed{-1.24 \text{ kJ}}$$

$$q = \Delta U - w = 0 + 1.24 \text{ kJ} = \boxed{+1.24 \text{ kJ}}$$

(c) $\boxed{\Delta U = \Delta H = 0}$

Free expansion is expansion against no force, so $\boxed{w = 0}$ and $q = \Delta U - w = 0 - 0 = \boxed{0}$

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

E2.4(c) A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,m} = \frac{7}{2}R$, initially at $p_1 = 1.00 \text{ bar}$ and $T_1 = 273 \text{ K}$, is heated reversibly to 373 K at constant volume. Calculate the final pressure, ΔU , q , and w .

E2.4(c) For a perfect gas at constant volume

$$\frac{p}{T} = \frac{nR}{V} = \text{constant, hence, } \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$p_2 = \left(\frac{T_2}{T_1} \right) \times p_1 = \left(\frac{373 \text{ K}}{273 \text{ K}} \right) \times (1.00 \text{ bar}) = \boxed{1.37 \text{ bar}}$$

$$\Delta U = nC_{V,m}\Delta T \text{ [2.16b]} = (n) \times \left(\frac{7}{2}R \right) \times (373 \text{ K} - 273 \text{ K})$$

$$= (1.00 \text{ mol}) \times \left(\frac{7}{2} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K})$$

$$= 2.91 \times 10^3 \text{ J} = \boxed{+2.91 \text{ kJ}}$$

$$\boxed{w = 0} \text{ [constant volume]} \quad q = \Delta U - w \text{ [First Law]} = 2.91 \text{ kJ} - 0 = \boxed{+2.91 \text{ kJ}}$$

E2.8(c) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p / (\text{J K}^{-1}) = 20.17 + 0.03665(T/\text{K})$. Calculate q , w , ΔU , and ΔH when the temperature is raised from 25°C to 300°C (a) at constant pressure, (b) at constant volume.

E2.8(c) (a) $q = \Delta H$, since pressure is constant

$$\Delta H = \int_{T_i}^{T_f} dH, \quad dH = nC_{p,m} dT$$

$$d(H/\text{J}) = \{20.17 + 0.3665(T/\text{K})\}d(T/\text{K})$$

$$\begin{aligned}\Delta(H/J) &= \int_{T_i}^{T_f} (H/J) = \int_{298}^{473} \{20.17 + 0.3665(T/K)\} d(T/K) \\ &= (20.17) \times (573 - 298) + \left(\frac{0.3665}{2}\right) \times \left(\frac{T}{K}\right)^2 \Big|_{298}^{473} \\ &= (5.546 \times 10^3) + (2.4725 \times 10^4) = 3.03 \times 10^4\end{aligned}$$

$$q = \Delta H = \boxed{3.03 \times 10^4 \text{ J}} = \boxed{+30.3 \text{ kJ}}$$

$$w = -p_{\text{ex}} \Delta V \quad [2.8] \quad \text{where} \quad p_{\text{ex}} = p$$

$$\begin{aligned}w &= -p\Delta V = -\Delta(pV) \quad [\text{constant pressure}] = -\Delta(nRT) \quad [\text{perfect gas}] = -nR\Delta T \\ &= (-1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (573 \text{ K} - 298 \text{ K}) = \boxed{-2.29 \times 10^3 \text{ J}} = \boxed{-2.29 \text{ kJ}}\end{aligned}$$

$$\Delta U = q + w = (30.3 \text{ kJ}) - (2.29 \text{ kJ}) = \boxed{+28.0 \text{ kJ}}$$

(b) The energy and enthalpy of a perfect gas depend on temperature alone (*Molecular interpretation 2.2* and Exercise 2.3); hence it does not matter whether the temperature change is brought about at constant volume or constant pressure; ΔH and ΔU are the same.

$$\Delta H = \boxed{+30.3 \text{ kJ}}, \quad \Delta U = \boxed{+28.0 \text{ kJ}}$$

Under constant volume, $w = \boxed{0}$.

$$q = \Delta U - w = \boxed{+28.0 \text{ kJ}}$$

E2.10(c) A sample of oxygen of mass 96 g at 25.0°C is allowed to expand reversibly and adiabatically from 5.00 dm³ to 10.00 dm³. What is the work done by the gas?

E2.10(c) Reversible adiabatic work is

$$w = C_V \Delta T \quad [2.27] = n(C_{p,m} - R) \times (T_f - T_i)$$

where the temperatures are related by

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{1/c} \quad [2.28a] \quad \text{where} \quad c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = 2.531$$

$$\text{So } T_f = [(25.0 + 273.15) \text{ K}] \times \left(\frac{5.00 \text{ dm}^3}{10.00 \text{ dm}^3}\right)^{1/2.531} = 227 \text{ K}$$

$$\text{and } w = \left(\frac{96.0 \text{ g}}{32.0 \text{ g mol}^{-1}}\right) \times [(29.355 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}] \times (227 - 298) \text{ K} = \boxed{-4.48 \text{ kJ}}$$

E2.11(c) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 5.7 atm and 50.0 dm³ to a final volume of 100.0 dm³. Take $\gamma = 1.3$.

E2.11(c) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad [2.29] \quad \text{so } p_f = p_i \left(\frac{V_i}{V_f}\right)^\gamma = (5.7 \text{ atm}) \times \left(\frac{50 \text{ dm}^3}{100 \text{ dm}^3}\right)^{1.3} = \boxed{2.9 \text{ atm}}$$

Comment: Note that knowledge of the initial and final temperatures is not needed to solve this exercise.

E2.13(c) When 5.00 mol N₂ is heated at a constant pressure of 3.00 atm, its temperature increases from 298 K to 345 K. Given that the molar heat capacity of N₂ at constant pressure is 29.125 J K⁻¹ mol⁻¹, calculate q , ΔH , and ΔU .

$$\begin{aligned} \text{E2.13(c)} \quad q_p &= C_p \Delta T \text{ [2.24]} = nC_{p,m} \Delta T = (5.00 \text{ mol}) \times (29.1 \text{ J K}^{-1} \text{ mol}^{-1}) \times (47 \text{ K}) = \boxed{+6.8 \text{ kJ}} \\ \Delta H &= q_p \text{ [2.23b]} = \boxed{+6.8 \text{ kJ}} \\ \Delta U &= \Delta H - \Delta(pV) \text{ [From } H \equiv U + pV] = \Delta H - \Delta(nRT) \text{ [perfect gas]} = \Delta H - nR\Delta T \\ &= (6.8 \text{ kJ}) - (5.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (47 \text{ K}) = (6.8 \text{ kJ}) - (1.95 \text{ kJ}) = \boxed{+4.8 \text{ kJ}} \end{aligned}$$

E2.14(c) A sample of 6.0 mol N₂ is originally confined in 30 dm³ at 273 K and then undergoes adiabatic expansion against a constant pressure of 95 kPa until the volume has increased by a factor of 2.0. Calculate q , w , ΔT , ΔU , and ΔH . (The final pressure of the gas is not necessarily 95 kPa.)

E2.14(c) In an adiabatic process, $q = \boxed{0}$. Work against a constant external pressure is

$$w = -p_{\text{ex}} \Delta V = \frac{-(95 \times 10^3 \text{ Pa}) \times (2 \times 30 - 30) \text{ dm}^3}{(10 \text{ dm m}^{-1})^3} = \boxed{-2.85 \times 10^3 \text{ J}}$$

$$\Delta U = q + w = \boxed{-2.85 \times 10^3 \text{ J}}$$

One can also relate adiabatic work to ΔT (eqn 2.27):

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

$$\Delta T = \frac{-2.85 \times 10^3 \text{ J}}{(6.0 \text{ mol}) \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}} = \boxed{-23 \text{ K}}.$$

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

$$= -2.85 \times 10^3 \text{ J} + (6.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-23 \text{ K}) = \boxed{-4.0 \times 10^3 \text{ J}}$$

E2.15(c) A sample consisting of 2.5 mol of perfect gas molecules with $C_{p,m} = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$ is initially at 303 kPa and 335 K. It undergoes reversible adiabatic expansion until its pressure reaches 250 kPa. Calculate the final volume and temperature and the work done.

E2.15(c) In an adiabatic process, the initial and final pressures are related by (eqn 2.29)

$$p_i V_i^\gamma = p_f V_f^\gamma \quad \text{where} \quad \gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{p,m}}{C_{p,m} - R} = \frac{29.4 \text{ J K}^{-1} \text{ mol}^{-1}}{(29.4 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1}} = 1.39$$

Find V_i from the perfect gas law:

$$V_i = \frac{nRT_i}{p_i} = \frac{(2.5 \text{ mol})(8.31 \text{ J K}^{-1} \text{ mol}^{-1})(335 \text{ K})}{303 \times 10^3 \text{ Pa}} = 0.0230 \text{ m}^3$$

$$\text{so } V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma} = (0.0230 \text{ m}^3) \left(\frac{303 \text{ kPa}}{250 \text{ kPa}} \right)^{1/1.394} = \boxed{0.0264 \text{ m}^3}.$$

Find the final temperature from the perfect gas law:

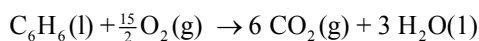
$$T_f = \frac{p_f V_f}{nR} = \frac{(250 \times 10^3 \text{ Pa}) \times (0.0264 \text{ m}^3)}{(2.5 \text{ mol})(8.31 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{318 \text{ K}}$$

Adiabatic work is (eqn 2.27)

$$w = C_V \Delta T = (29.4 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1} \times 2.5 \text{ mol} \times (318 - 335) \text{ K} = \boxed{-9.0 \times 10^2 \text{ J}}$$

E2.17(c) The standard enthalpy of formation of benzene is 49.0 kJ mol^{-1} . Calculate its standard enthalpy of combustion.

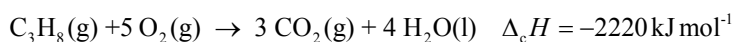
E2.17(a) The reaction is



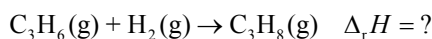
$$\begin{aligned} \Delta_c H^\ominus &= 6\Delta_f H^\ominus(\text{CO}_2, \text{g}) + 3\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\ominus(\text{C}_6\text{H}_6, \text{l}) \\ &= [(6) \times (-393.51) + (3) \times (-285.83) - (49.0)] \text{ kJ mol}^{-1} \\ &= \boxed{-3267.6 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.18(c) The standard enthalpy of combustion of n-propane is $-2220 \text{ kJ mol}^{-1}$ at 25°C . From this information and enthalpy of formation data for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, calculate the enthalpy of formation of n-propane. The enthalpy of formation of propene is $+20.42 \text{ kJ mol}^{-1}$. Calculate the enthalpy of hydrogenation of propene to propane.

E2.18(c) First $\Delta_f H[\text{C}_3\text{H}_8, \text{g}]$ is calculated, and then that result is used to calculate $\Delta_r H$ for the hydrogenation



$$\begin{aligned} \Delta_f H[\text{C}_3\text{H}_8, \text{g}] &= -\Delta_c H + 3\Delta_f H(\text{CO}_2, \text{g}) + 4\Delta_f H(\text{H}_2\text{O}, \text{g}) \\ &= [+2220 + (3) \times (-393.51) + (4) \times (-285.83)] \text{ kJ mol}^{-1} \\ &= \boxed{-103.85 \text{ kJ mol}^{-1}} \end{aligned}$$



$$\begin{aligned} \Delta_r H &= \Delta_f H(\text{C}_3\text{H}_8, \text{g}) - \Delta_f H[\text{C}_3\text{H}_6, \text{g}] \\ &= (-103.85 - 20.42) \text{ kJ mol}^{-1} = \boxed{-124.27 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.20(c) Calculate the standard enthalpy of solution of $\text{AgI}(\text{s})$ in water from the enthalpies of formation of the solid and the aqueous ions.

E2.20(c) The reaction is $\text{AgI}(\text{s}) \rightarrow \text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq})$

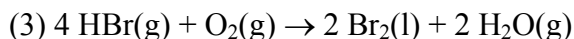
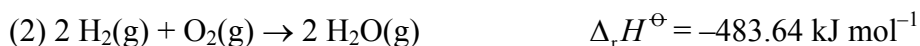
$$\begin{aligned} \Delta_{\text{sol}} H^\ominus &= \Delta_f H^\ominus(\text{Ag}^+, \text{aq}) + \Delta_f H^\ominus(\text{I}^-, \text{aq}) - \Delta_f H^\ominus(\text{AgI}, \text{s}) \\ &= [105.58 + (-55.19) - (-61.8)] \text{ kJ mol}^{-1} = \boxed{+112.19 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.21(c) Given that the standard enthalpy of combustion of graphite is $-393.51 \text{ kJ mol}^{-1}$ and that of buckminsterfullerene, C_{60} , is $-2.589 \times 10^4 \text{ kJ mol}^{-1}$, calculate the enthalpy of the graphite-to-buckminsterfullerene transition.

E2.21(c) The combustion products of graphite and buckminsterfullerene are the same, so the transition $\text{C}(\text{gr}) \rightarrow \text{C}(\text{buck})$ is equivalent to the combustion of graphite plus the reverse of the combustion of buckminsterfullerene. However we need to recognize that a molecular formula of buckminsterfullerene contains 60 C atoms, whereas a molecular formula of graphite is one carbon atom.

$$\Delta_{\text{trans}} H^\ominus = [60 \times (-393.51) - (-2.589 \times 10^4)] \text{ kJ mol}^{-1} = \boxed{+2.279 \text{ MJ mol}^{-1}}$$

E2.22(c) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ for reaction (3), (b) $\Delta_f H^\ominus$ for both $\text{HBr}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ all at 298 K.



E2.22(c) (a) reaction(3) = $(-2) \times$ reaction(1) + reaction(2) and $\Delta n_g = -1$

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

$$\begin{aligned} \Delta_r H^\ominus (3) &= (-2) \times \Delta_r H^\ominus (1) + \Delta_r H^\ominus (2) \\ &= [(-2) \times (-72.80) + (-483.64)] \text{ kJ mol}^{-1} \\ &= \boxed{-338.04 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT [2.21] = (-338.04 \text{ kJ mol}^{-1}) - (-1) \times (2.48 \text{ kJ mol}^{-1}) \\ &= \boxed{-335.56 \text{ kJ mol}^{-1}} \end{aligned}$$

(b) $\Delta_f H^\ominus$ refers to the formation of one mole of the compound, hence

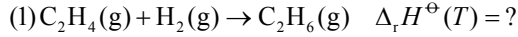
$$\Delta_f H^\ominus (\text{J}) = \frac{\Delta_r H^\ominus (\text{J})}{\nu_j}$$

$$\Delta_f H^\ominus (\text{HBr, g}) = \frac{-72.80}{2} \text{ kJ mol}^{-1} = \boxed{-36.40 \text{ kJ mol}^{-1}}$$

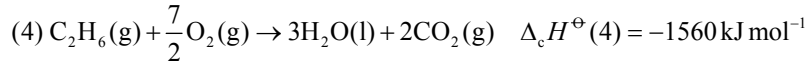
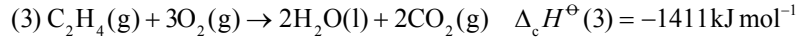
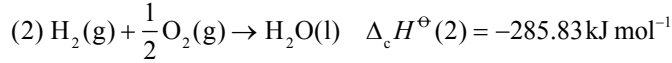
$$\Delta_f H^\ominus (\text{H}_2\text{O, g}) = \frac{-483.64}{2} \text{ kJ mol}^{-1} = \boxed{-241.82 \text{ kJ mol}^{-1}}$$

E2.26(c) Calculate $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ at 298 K and $\Delta_r H^\ominus$ at 348 K for the hydrogenation of ethene (ethylene) to ethane from the enthalpy of combustion and heat capacity data in Tables 2.5 and 2.6. Assume the heat capacities to be constant over the temperature range involved.

E2.26(c) The hydrogenation reaction is



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



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

(a) Hence, at 298 K:

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_c H^\ominus(2) - \Delta_c H^\ominus(4) + \Delta_c H^\ominus(3) \\ &= [(-285.83) - (-1560) + (-1411)] \text{ kJ mol}^{-1} = \boxed{-137 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT \quad [2.21]; \quad \Delta n_g = -1 \\ &= -137 \text{ kJ mol}^{-1} - (-1) \times (2.48 \text{ kJ mol}^{-1}) = \boxed{-135 \text{ kJ mol}^{-1}} \end{aligned}$$

(b) At 348 K:

$$\Delta_r H^\ominus(348 \text{ K}) = \Delta_r H^\ominus(298 \text{ K}) + \Delta_r C_p^\ominus(348 \text{ K} - 298 \text{ K}) \quad [\text{Example 2.6}]$$

$$\begin{aligned} \Delta_r C_p^\ominus &= \sum_j \nu_j C_{p,m}^\ominus(\text{J}) [2.37] = C_{p,m}^\ominus(\text{C}_2\text{H}_6, \text{g}) - C_{p,m}^\ominus(\text{C}_2\text{H}_4, \text{g}) - C_{p,m}^\ominus(\text{H}_2, \text{g}) \\ &= (52.63 - 43.56 - 28.82) \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} = -19.75 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H^\ominus(348 \text{ K}) &= (-137 \text{ kJ mol}^{-1}) - (19.75 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K}) \\ &= \boxed{-138 \text{ kJ mol}^{-1}} \end{aligned}$$

E2.29(c) A vapor at 39 atm and 25°C was allowed to expand adiabatically to a final pressure of 1.00 atm, the temperature fell by 12 K. Calculate the Joule–Thomson coefficient, μ , at 25°C, assuming it remains constant over this temperature range.

E2.29(c) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-12 \text{ K}}{(1.00 - 39) \text{ atm}} = \boxed{0.32 \text{ K atm}^{-1}}$$

E2.30(c) For a van der Waals gas, $\pi_T = a/V_m^2$. Calculate ΔU_m for the isothermal expansion of oxygen gas from an initial volume of 1.00 dm³ to 22.4 dm³ at 273 K. What are the values of q and w ?

E2.30(c) The internal energy is a function of temperature and volume, $U_m = U_m(T, V_m)$, so

$$dU_m = \left(\frac{\partial U_m}{\partial T} \right)_{V_m} dT + \left(\frac{\partial U_m}{\partial V_m} \right)_T dV_m \quad [\pi_T = (\partial U_m / \partial V)_T]$$

For an isothermal expansion $dT = 0$; hence

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

$$\begin{aligned} \Delta U_m &= \int_{V_{m,1}}^{V_{m,2}} dU_m = \int_{V_{m,2}}^{V_{m,1}} \frac{a}{V_m^2} dV_m = a \int_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.4 \text{ dm}^3 \text{ mol}^{-1}} \frac{dV_m}{V_m^2} = -\frac{a}{V_m} \Big|_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.4 \text{ dm}^3 \text{ mol}^{-1}} \\ &= -\frac{a}{22.4 \text{ dm}^3 \text{ mol}^{-1}} + \frac{a}{1.00 \text{ dm}^3 \text{ mol}^{-1}} = \frac{21.4a}{22.4 \text{ dm}^3 \text{ mol}^{-1}} = 0.9553 a \text{ mol dm}^{-3}; \end{aligned}$$

From Table 1.5, $a = 1.364 \text{ dm}^6 \text{ atm mol}^{-1}$

$$\Delta U_m = (0.9553 \text{ mol dm}^{-3}) \times (1.364 \text{ dm}^6 \text{ atm mol}^{-1})$$

$$= (1.30 \text{ dm}^3 \text{ atm mol}^{-1}) \times \left(\frac{1 \text{ m}}{10 \text{ dm}} \right)^3 \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{\text{atm}} \right) = \boxed{+131 \text{ J mol}^{-1}}$$

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

$$w = -\int \left(\frac{RT}{V_m - b} \right) dV_m + \int \frac{a}{V_m^2} dV_m = -q + \Delta U_m$$

Therefore,

$$\begin{aligned} q &= \int_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.4 \text{ dm}^3 \text{ mol}^{-1}} \left(\frac{RT}{V_m - b} \right) dV_m = RT \ln(V_m - b) \Big|_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.4 \text{ dm}^3 \text{ mol}^{-1}} \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) \times \ln \left(\frac{22.4 - 3.2 \times 10^{-2}}{1.00 - 3.2 \times 10^{-2}} \right) = \boxed{+7.13 \times 10^3 \text{ J mol}^{-1}} \end{aligned}$$

$$\text{and} \quad w = -q + \Delta U_m = -(7.13 \times 10^3 \text{ J mol}^{-1}) + (131 \text{ J mol}^{-1}) = \boxed{-7.00 \times 10^3 \text{ J mol}^{-1}}$$

E2.32(c) The isothermal compressibility of diamond at 293 K is $1.87 \times 10^{-7} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

E2.32(c) The isothermal compressibility is

$$\kappa_T = -\left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial p} \right)_T \quad [2.44] \quad \text{so} \quad \left(\frac{\partial V}{\partial p} \right)_T = -\kappa_T V$$

At constant temperature

$$dV = \left(\frac{\partial V}{\partial p} \right)_T dp \quad \text{so} \quad dV = \kappa_T V dp \quad \text{or} \quad \frac{dV}{V} = -\kappa_T dp$$

$$\text{Substituting } V = \frac{m}{\rho} \text{ yields } dV = -\frac{m}{\rho^2} d\rho; \quad \frac{dV}{V} = -\frac{d\rho}{\rho} = -\kappa_T dp$$

$$\text{Therefore, } \frac{\delta\rho}{\rho} \approx \kappa_T \delta p$$

$$\text{For } \frac{\delta\rho}{\rho} = 0.08 \times 10^{-2} = 8 \times 10^{-4}, \quad \delta p \approx \frac{8 \times 10^{-4}}{\kappa_T} = \frac{8 \times 10^{-4}}{1.87 \times 10^{-7} \text{ atm}^{-1}} = \boxed{4.3 \times 10^3 \text{ atm}}$$

E2.33(c) Given that $\mu = -0.062 \text{ K atm}^{-1}$ for helium, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be removed as heat to

maintain constant temperature when 20.0 mol of He flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 100 atm.

E2.33(c) The isothermal Joule-Thomson coefficient is

$$\left(\frac{\partial H_m}{\partial p}\right)_T = -\mu C_{p,m} = (0.062 \text{ K atm}^{-1}) \times (20.8 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{1.29 \text{ J atm}^{-1} \text{ mol}^{-1}}$$

$$dH = n \left(\frac{\partial H_m}{\partial p}\right)_T dp = -n\mu C_{p,m} dp$$

$$\Delta H = \int_{p_1}^{p_2} (-n\mu C_{p,m}) dp = -n\mu C_{p,m} (p_2 - p_1) \quad [\mu \text{ and } C_p \text{ are constant}]$$

$$\Delta H = (20.0 \text{ mol}) \times (+1.29 \text{ J atm}^{-1} \text{ mol}^{-1}) \times (-100 \text{ atm}) = -2.58 \text{ kJ}$$

$$\text{so } q(\text{removed}) = +\Delta H = \boxed{-2.58 \text{ kJ}}$$