

1. We used the thermodynamic equation of state to show the internal energy of an isothermal ideal gas is constant. Use $(\partial U/\partial V)_T = 0$ for an ideal gas to show the enthalpy of an isothermal ideal gas is also constant. (Hints: $H \equiv U + pV$ and for an ideal gas $pV = nRT$)

[2]

2. 75.0 moles of argon (assumed to be an ideal gas) are compressed isothermally from an initial pressure of 2.00 bar to a final pressure of 5.00 bar at 300 K.

a) Calculate ΔU , ΔH , w and q if the compression is reversible ($p_{\text{external}} = p$).

[8]

b) Calculate ΔU , ΔH , w and q if the compression is irreversible with $p_{\text{external}} = p_{\text{final}} = 5.00$ bar.

c) Use the results from **a** and **b** to illustrate that U and H are **state functions**.

d) Use the results from **a** and **b** to illustrate that w and q are **path-dependent**.

3. a) The compression factor $Z = pV/nRT = pV_m/RT$ is a useful and convenient indicator of the nonideal behavior of real gases. Why? Explain briefly.

[3]

b) The compression factor is also useful for calculating compression/expansion work. Show the work done for the reversible isothermal expansion or compression of a real gas is

$$w = -nRT \int \frac{Z}{V} dV$$

c) Methane is reversibly compressed from 5.00 bar to 100 bar at 25 °C. For methane under these conditions, $Z > 1$ (see the graph in the course notes). Do intermolecular forces increase the work required to compress the gas, or decrease it? Justify your answer.

4. 28.0 moles of liquid water (about 500 mL) are heated from 20 °C to 100 °C at 1.00 bar.

a) Use $C_{pm} = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$ for the molar heat capacity of liquid water to calculate q .

b) The heat calculation in **a** also gives ΔH for the process. Why?

c) Suppose the water is heated in an electric kettle to make tea. Nova Scotia Power charges \$0.153 per kilowatt-hour of electrical energy. Calculate the cost of electrically heating 28.0 moles of liquid water from 20 to 100 °C. (Hint: $1 \text{ kW-hr} = 1000 \text{ J s}^{-1} \times 3600 \text{ s} = 3.6 \times 10^6 \text{ J}$).

[7]

d) The actual cost of heating the water in an electric kettle is significantly larger than the value calculated in **c**. Why?

$$\text{or: } \left(\frac{\partial H}{\partial V} \right)_T = \left[\frac{\partial (U + pV)}{\partial V} \right]_T = \left(\frac{\partial U}{\partial V} \right)_T + \left(\frac{\partial nRT}{\partial V} \right)_T = 0$$

(Q1) The internal energy U of an isothermal ideal gas is constant.

The enthalpy is defined as $H = U + pV$

For an ideal gas $H = U + pV = U + nRT$
($pV = nRT$)

For an isothermal ideal gas, U and nRT are constants, so $H = U + pV$ is also constant

(Q2) 75.0 moles of ideal gas are compressed from 2.00 bar to 5.00 bar at 300 K (isothermal process).

a) reversible compression ($P_{\text{external}} = P$)

$\Delta U = 0$	$\Delta H = 0$
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(isothermal ideal gas)

$$dw = -P_{\text{external}} dp = -pdV = -\frac{nRT}{V} dV$$

$$w = \int dw = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV \quad (\text{isothermal})$$

$$= -nRT \ln(V_f/V_i)$$

$$= -nRT \ln\left(\frac{nRT/P_f}{nRT/P_i}\right) = -nRT \ln(P_i/P_f)$$

$$w = -(75.0 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln\left(\frac{2.00 \text{ bar}}{5.00 \text{ bar}}\right) = \boxed{17,400 \text{ J}}$$

$$\Delta U = q + w = 0$$

$$\boxed{q = -w = -17,400 \text{ J}}$$

(Q2 cont.)

b) irreversible compression

$$P_{\text{external}} = 5.00 \text{ bar}$$

$$\Delta U = 0 \quad \Delta H = 0$$

(isothermal ideal gas)

$$w = - \int_{V_i}^{V_f} P_{\text{external}} dV = - (5.00 \text{ bar}) \int_{V_i}^{V_f} dV$$
$$= - (5.00 \text{ bar}) (V_f - V_i)$$

$$= - 5.00 \text{ bar} \left(\frac{nRT}{P_f} - \frac{nRT}{P_i} \right) = - 5.00 \text{ bar} \left(\frac{nRT}{5.00 \text{ bar}} - \frac{nRT}{2.00 \text{ bar}} \right)$$

$$= - nRT \left(\frac{5.00 \text{ bar}}{5.00 \text{ bar}} - \frac{5.00 \text{ bar}}{2.00 \text{ bar}} \right) = - nRT (1 - 2.5)$$

$$= \frac{3}{2} nRT = \frac{3}{2} (75.0 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K})$$

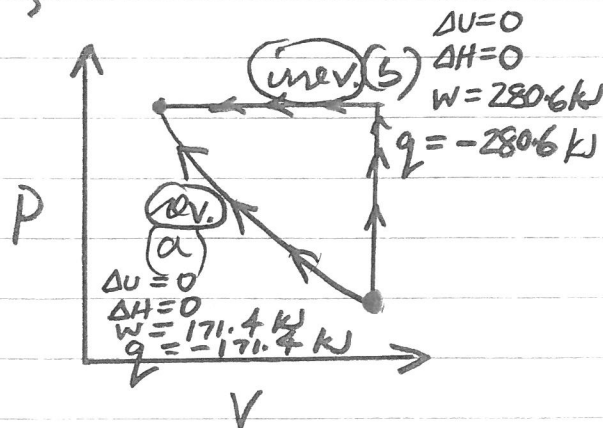
$$w = 280,600 \text{ J}$$
$$q = -280,600 \text{ J}$$

$$\Delta U = 0 = w + q \quad q = -w$$

notice:
irreversible compression
requires more work

c) different paths, reversible or irreversible connecting the initial and final states give the same differences $\Delta U = 0$, $\Delta H = 0$ for state functions U and H

d) different paths give different values of w and q
 $w_{\text{rev}} \neq w_{\text{irrev}}$
 $q_{\text{rev}} \neq q_{\text{irrev}}$ } path dependent



Q3 a) compression factor $Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$ dimensionless
(no units)

Why useful and convenient for describing real gases?

- $Z > 1$ repulsive intermolecular forces dominate
 - $Z < 1$ attractive " " " " " "
 - $Z \rightarrow 1$ as $p \rightarrow 0$ ($V_m \rightarrow \infty$) for all gases
 - $Z = 1$ at all p, V, T values for ideal gases
- } easy to use "index" of gas behavior

Z data are used in practice to calculate compression/expansion work for real gases

b) compression/expansion work for reversible processes ($p = p_{\text{external}}$) at constant T (isothermal)

$$dw = -p_{\text{external}} dV = -pdV$$

for a real gas $Z = \frac{PV}{nRT}$

gives $p = Z \frac{nRT}{V}$

$$dw = -pdV = -Z \frac{nRT}{V} dV$$

$$w = \int dw = - \int \frac{nRT}{V} Z dV \quad (\text{isothermal})$$

$$w = -nRT \int \frac{Z}{V} dV$$

used to calculate work for real gases

c) ideal gas $w_{\text{ideal}} = -nRT \int \frac{1}{V} dV$ real gas (methane) $w = -nRT \int \frac{Z}{V} dV$

w larger for methane (more negative) than w_{ideal} ($Z > 1$)

$$C_p = n C_{pm} \quad \text{per mole}$$

Q4) 28.0 moles of liquid water heated from 20°C to 100°C at 1.00 bar (constant pressure)

a) heat required?

$$C_p = n C_{pm} = \frac{dq_p}{dT} \quad \text{multiply by } dT$$

$$dq_p = n C_{pm} dT \quad \text{integrate}$$

$$q_p = \int dq_p = \int n C_{pm} dT$$

$$\left(\begin{array}{l} C_{pm} = 75.4 \text{ J K}^{-1} \text{ mol}^{-1} \\ n = 28.0 \text{ mol} \\ \text{(constants)} \end{array} \right)$$

$$q_p = n C_{pm} \int_{T_i}^{T_f} dT = n C_{pm} (T_f - T_i)$$

$$q_p = (28.0 \text{ mol}) (75.4 \text{ J K}^{-1} \text{ mol}^{-1}) (100 - 20) \text{ K}$$

$$q_p = 168900 \text{ J}$$

b) $\Delta H = q_p$ at constant pressure

c) cost of electricity to heat the water:

$$\left(\frac{\$0.153}{3.6 \times 10^6 \text{ J}} \right) (168,900 \text{ J}) = \$0.00718$$

d) If the water is heated in an electric kettle, the water is heated, but also the kettle and some of the surrounding air, requiring $q_p > 168900 \text{ J}$