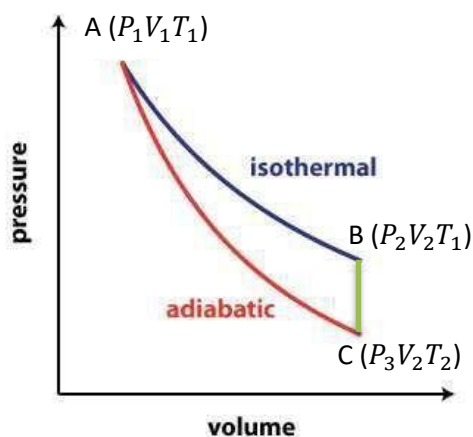## The First Law: Heat and Work

$$\Delta U = q + w$$

State and path functions

$$dU = \delta q + \delta w, \qquad \oint dU = 0$$

Lets consider an example of expansion of an ideal gas. Consider some reversible processes.

Isothermal path (A→B):

$$\Delta U_{AB} = 0 \ \Rightarrow \delta w_{AB} = -\delta q_{AB}$$

$$\delta w = -P_{ext} dV = -PdV \text{ for rev. change}$$

$$w_{AB} = -q_{AB} = -\int_{V_1}^{V_2} PdV$$

$$= -\int_{V_1}^{V_2} \frac{RT_1}{V} dV = -RT_1 \ln\frac{V_2}{V_1} \text{ (for one mole)}$$

Adiabatic path (A→C) + constant volume path (C→B):

Path A→C:

$$q_{AC} = 0 \ \Rightarrow dU_{AC} = \delta w_{AC}$$

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

$$\therefore \Delta U_{AC} = \int_{T_1}^{T_2} C_V(T)dT = w_{AC}$$

Path C→B:

Heat the gas reversibly at constant volume. So $w_{CB} = 0$ and hence,

$$\Delta U_{CB} = q_{CB} = \int_{T_2}^{T_1} C_V(T)dT$$

Total: AC+CB

$$\Delta U_{AC} + \Delta U_{CB} = \int_{T_1}^{T_2} C_V(T)dT + \int_{T_2}^{T_1} C_V(T)dT = 0 = \Delta U_{AB}$$

However, q and w are not the same for the two paths!! Work and heat are path functions

Temperature T_1 or T_2 – which one is greater?

Isotherm: Gas expands and does work, heat is pumped in to maintain temperature at T_1

Adiabat: Gas expands and does work, but no heat pumped in to maintain temperature – gas cools down to T_2

Adiabatic expansion

$$dU = \delta w = dw$$

Work is now a state function

$$dU = C_V(T)dT$$

$$dw = -PdV = -\frac{nRT}{V}dV$$

Equate the two,

$$\overline{C_V}(T)dT = -\frac{RT}{V}dV$$

$$\int_{T_1}^{T_2} \frac{\overline{C_V}(T)}{T}dT = -\int_{V_1}^{V_2} \frac{R}{V}dV$$

For a **monatomic ideal gas**, $\overline{C_V} = \frac{3}{2}R$

$$\frac{3}{2}R\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\frac{3}{2}\ln\frac{T_2}{T_1} = \ln\frac{V_1}{V_2}$$

$$\boxed{\left(\frac{T_2}{T_1}\right)^{3/2} = \left(\frac{V_1}{V_2}\right)}$$

$$\left(\frac{P_2V_2}{P_1V_1}\right)^{3/2} = \left(\frac{V_1}{V_2}\right)$$

Or

$$\boxed{PV^\gamma = constant} \ \ where \ \gamma = \frac{C_p}{C_v} = \frac{5}{3} \ \text{for a monatomic ideal gas}$$

Molecular Interpretation of Work and Heat

Average energy of a macroscopic system

$$\langle U \rangle = \sum_j p_j(N, V, \beta) \, E_j(N, V)$$

$$\text{where } \quad p_j = \frac{e^{-\beta E_j}}{Q(N, V, \beta)}$$

Now, $U = U(p, E)$

$$dU = \sum_j p_j dE_j + \sum_j E_j dp_j$$

Let us not change the number of particles, i.e. we deal with a closed system. $\therefore dE_j$ is the change due to a change in the volume. So,

$$dU = \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV + \sum_j E_j dp_j$$

$$dU = \delta w + \delta q = -PdV + \delta q$$

Now, $\sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV$ is the average change in energy because of a change in the volume of the system. Hence, this is the mechanical **average work, w**.

The other term $\sum_j E_j dp_j$ must therefore be the **average heat exchanged, q**.

Since the processes are carried out infinitesimally, these are reversible and so the work done and heat exchanged are carried out reversibly. We can then write

$$\delta w_{rev} = \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV$$

Reversible work is the result of infinitesimal change of allowed energy states without changing the probability distribution.

$$\delta q_{rev} = \sum_j E_j dp_j$$

Reversible heat is the result of changing the probability distribution of the states. There is no change in the energies per se.

Since,

$$\delta w_{rev} = -PdV$$

$$\therefore \quad P = \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N = -\left\langle\left(\frac{\partial E}{\partial V}\right)_N\right\rangle \text{ (we used this result earlier)}$$

Enthalpy

$$\Delta U = q + w = q - \int_{V_1}^{V_2} P dV$$

At constant volume,

$$\Delta U = q_V$$

Measure experimentally using a closed vessel – bomb calorimeter

Most processes occur at constant pressure

$$q_p = \Delta U + P_{ext} \int_{V_1}^{V_2} dV = \Delta U + P_{ext}\Delta V$$

Define enthalpy: $\quad\quad H = U + PV$

At constant pressure, $\quad\quad \Delta H = \Delta U + P\Delta V = q_p$

Two examples

Melting of ice at 0 °C

$$\Delta \bar{H} = q_p = 6.01 \text{ kJ. mol}^{-1}$$

$$\Delta \bar{U} = \Delta \bar{H} - P\Delta \bar{V} = \Delta \bar{H} - P(\bar{V}_l - \bar{V}_S)$$

$$= 6.01 \text{ kJ. mol}^{-1} - (1 \text{ atm})(0.0180 \text{ L. mol}^{-1} - 0.0196 \text{ L. mol}^{-1})$$

$$= 6.01 \text{ kJ. mol}^{-1} - (1.60 \times 10^{-3} \text{ L. atm. mol}^{-1})\left(\frac{8.314 \text{ J}}{0.08206 \text{ L. atm}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right)$$

$$\approx 6.01 \text{ kJ. mol}^{-1}$$

Vaporization of water at 100 °C: $H_2(l) \rightarrow H_2(g)$

$$\Delta \bar{H} = q_p = 40.7 \text{ kJ. mol}^{-1}$$

$$\Delta \bar{V} = (30.6 - 0.0180) \text{ L. mol}^{-1} \approx 30.6 \text{ L. mol}^{-1}$$

$$\Delta \bar{U} = \Delta \bar{H} - P\Delta \bar{V} = 40.7 \text{ kJ. mol}^{-1} - (1 \text{ atm})(30.6 \text{ L. mol}^{-1})\left(\frac{8.314 \text{ J}}{0.08206 \text{ L.atm}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) = 37.6 \text{ kJ mol}^{-1}$$

$\Delta \bar{U}$: used to overcome the intermolecular forces. $\Delta \bar{H} - \Delta \bar{U} = 3.1 \text{ kJ. mol}^{-1}$ is required to increase the volume of the system against the atmospheric pressure.

Heat capacity is a path function: $C_P - C_v = nR$ for an ideal gas. Prove this.

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$