PHY2201 Summary Sheet 13

Joule-Thompson process: obstructed flow of gas from a uniform high pressure to a uniform low pressure through a semi-permeable "porous plug".

Small mass of gas Δm traverses the obstruction: initial pressure p_0, volume ΔV_0, internal energy u_0; final pressure p_1, volume ΔV_1, internal energy u_1.

Total work done = $p_0 \Delta V_0 - p_1 \Delta V_1$. Since process is adiabatic, 1st law implies:

$u_1 - u_0 = p_0 \Delta V_0 - p_1 \Delta V_1$ hence

$$u_0 + p_0 \Delta V_0 = u_1 + p_1 \Delta V_1$$

define $H = U + pV$

where H is "enthalpy"

Then $h_0 = h_1$ where h_0 is the enthalpy of the small mass of gas Δm before traversing the obstruction, ditto h_1.

Hence enthalpy is conserved in the J-T process, i.e. J-T expansion is *isenthalpic*.

Enthalpy is a function of state, also known as a "thermodynamic potential".

Differentiating :

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

Since $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$

$$\underline{\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p}$$

Hence $H = H(S, p)$

By analogy with $U = U(S, V)$

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

Hence

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

2nd Maxwell relation

n-moles of ideal gas :-

$$U = \frac{3}{2}nRT \quad \& \quad pV = nRT$$

$$\therefore H = \frac{5}{2}nRT$$

Hence $H = H(T)$ for an ideal gas, hence J-T process does NOT cool an ideal gas.

Since $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$, for a reversible isobaric process ($\mathrm{d}p = 0$) $\mathrm{d}H = T\mathrm{d}S = \mathrm{d}'Q$.

Hence H represents the heat flow during a reversible isobaric process i.e.

$\mathrm{d}H = c_\mathrm{p}\,\mathrm{d}T$

c.f. $\mathrm{d}U = c_\mathrm{v}\,\mathrm{d}T$ i.e. U represents the heat flow during an isochoric process.

H is useful when studying processes that occur at constant pressure e.g chemical reactions in an open container.