

Chapter Four: Enthalpy

Enthalpy

$$H(T, p) \quad H \equiv U + pV$$

Chemical reactions and biological processes usually take place under constant pressure and with reversible pV work. Enthalpy turns out to be an especially useful function of state under those conditions.

$$\text{gas } (p, T_1, V_1) \xrightarrow[\text{const. } p]{\text{reversible}} \text{gas } (p, T_2, V_2)$$

$$U_1 \qquad \qquad \qquad U_2$$

$$\Delta U = q + w = q_p - p\Delta V$$

$$\Delta U + p\Delta V = q_p$$

$$\Delta U + \Delta(pV) = q_p \Rightarrow \Delta(U + pV) = q_p$$

$$H \equiv U + pV$$

$\Rightarrow \Delta H = Q_p$ for a reversible constant p process

$$\text{Choose } H(T, p) \Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

What are $\left(\frac{\partial H}{\partial T}\right)_p$ and $\left(\frac{\partial H}{\partial p}\right)_T$?

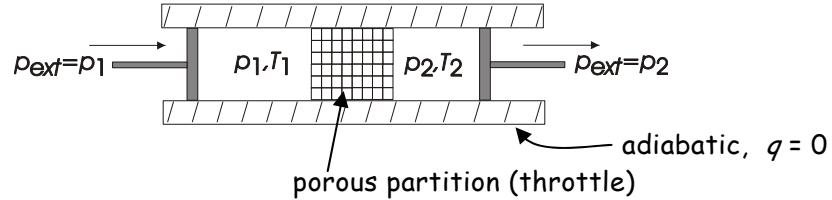
- $\left(\frac{\partial H}{\partial T}\right)_p \Rightarrow \text{for a reversible process at constant } p \ (dp = 0)$

$$dH = dq_p \text{ and } dH = \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$\Rightarrow dq_p = \left(\frac{\partial H}{\partial T}\right)_p dT \quad \text{but} \quad dq_p = C_p dT \quad \text{also}$$

$$\therefore \boxed{\left(\frac{\partial H}{\partial T}\right)_p = C_p}$$

- $\left(\frac{\partial H}{\partial p}\right)_T \Rightarrow \text{Joule-Thomson expansion}$



$$\begin{aligned} \text{gas } (p, T_1) &= \text{gas } (p, T_2) \\ p_1 - p_2 &\Rightarrow \Delta U = q + w = p_1 V_1 - p_2 V_2 = -\Delta(pV) \\ \therefore \Delta U + \Delta(pV) &= 0 \Rightarrow \Delta(U + pV) = 0 \\ \therefore \boxed{\Delta H = 0} \end{aligned}$$

Joule-Thomson is a constant Enthalpy process.

$$\begin{aligned} dH &= C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \Rightarrow C_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp_H \\ \Rightarrow \left(\frac{\partial H}{\partial p}\right)_T &= -C_p \left(\frac{\partial T}{\partial p}\right)_H \leftarrow \text{can measure this } \left(\frac{\Delta T}{\Delta p}\right)_H \end{aligned}$$

Define $\lim_{\Delta p \rightarrow 0} \left(\frac{\Delta T}{\Delta p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_H \equiv \mu_{JT} \leftarrow \text{Joule-Thomson Coefficient}$

$$\therefore \boxed{\left(\frac{\partial H}{\partial p}\right)_T = -C_p \mu_{JT}} \quad \text{and} \quad \boxed{dH = C_p dT - C_p \mu_{JT} dp}$$

For an ideal gas: $U(T)$, $pV=nRT$

$$H \equiv U(T) + pV = \underbrace{U(T) + nRT}_{\text{only depends on } T, \text{ no } p \text{ dependence}}$$

$$H(T) \Rightarrow \left(\frac{\partial H}{\partial p} \right)_T = \mu_{JT} = 0 \quad \text{for an ideal gas}$$

For a van der Waals gas:

$$\left(\frac{\partial H}{\partial p} \right)_T \approx b - \frac{a}{RT} \Rightarrow \mu_{JT} \approx \frac{a}{RT} - b = 0 \quad \text{when } T = T_{inv} = \frac{a}{Rb}$$

$$1. \quad \text{If } \frac{a}{RT} < b \Rightarrow T > \frac{a}{Rb} = T_{inv}$$

then $\left(\frac{\Delta T}{\Delta p} \right)_H < 0$ so if $\Delta p < 0$ ($p_2 < p_1$)
 then $\Delta T > 0$
 gas heats up upon expansion.

$$2. \quad \text{If } \frac{a}{RT} > b \Rightarrow T < \frac{a}{Rb} = T_{inv}$$

then $\left(\frac{\Delta T}{\Delta p} \right)_H > 0$ so if $\Delta p < 0$
 then $\Delta T < 0$
 gas cools upon expansion.

$T_{inv} \gg 300K$ for most real gases.

\Rightarrow Use J-T expansion to liquefy gases

Proof that $\bar{C}_p = \bar{C}_V + R$ for an ideal gas

$$\begin{aligned}\bar{C}_p &= \left(\frac{\partial \bar{H}}{\partial T} \right)_p, & \bar{C}_V &= \left(\frac{\partial \bar{U}}{\partial T} \right)_V \\ \underbrace{\bar{H} = \bar{U} + p\bar{V},}_{\downarrow} & & p\bar{V} &= RT \\ \overbrace{\left(\frac{\partial \bar{H}}{\partial T} \right)_p = \left(\frac{\partial \bar{U}}{\partial T} \right)_p + p \left(\frac{\partial \bar{V}}{\partial T} \right)_p}^{\uparrow} & & & \\ \bar{C}_p &= \bar{C}_V + \cancel{\left(\frac{\partial \bar{U}}{\partial V} \right)}_{=0 \text{ for ideal gas}} \left(\frac{\partial \bar{V}}{\partial T} \right)_p + p \left(\frac{R}{p} \right) \\ \therefore \bar{C}_p &= \bar{C}_V + R\end{aligned}$$