5.60 Thermodynamics & Kinetics
Spring 2008

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

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.

$$\text{gas }(p,\ T_1,\ V_1) \underset{const.p}{\overset{reversible}{=}} \text{gas }(p,\ T_2,\ V_2)$$

$$U_1 \qquad\qquad U_2$$

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

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

$$\Delta U + \Delta\left(pV\right) = q_p \quad \Rightarrow \quad \Delta\underbrace{\left(U + pV\right)}_{\text{define as } H} = q_p$$

$H \equiv U + pV \quad \Rightarrow \quad \Delta H = q_p$ for a reversible constant p process

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

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

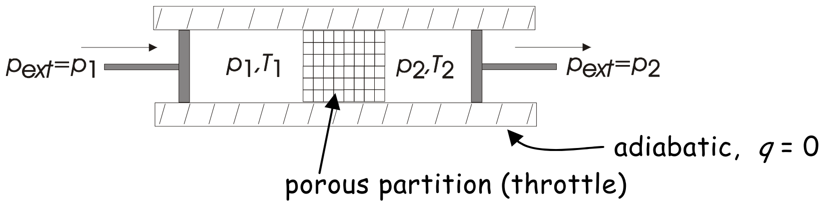
- $\left(\frac{\partial H}{\partial T}\right)_p \quad \Rightarrow$ for a reversible process at constant p ($dp = 0$)

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

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

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

- $\left(\frac{\partial H}{\partial p}\right)_T \qquad \Rightarrow$ <u>Joule-Thomson</u> <u>expansion</u>



gas (p, T_1) = gas (p, T_2)

$$w = p_1V_1 - p_2V_2 \quad \Rightarrow \quad \Delta U = q + w = p_1V_1 - p_2V_2 = -\Delta\left(pV\right)$$

$$\therefore \quad \Delta U + \Delta\left(pV\right) = 0 \quad \Rightarrow \quad \Delta\left(U + pV\right) = 0$$

$$\therefore \quad \boxed{\Delta H = 0}$$

Joule-Thomson is a constant Enthalpy process.

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad \Rightarrow \quad C_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp_H$$

$$\Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = -C_p\left(\frac{\partial T}{\partial p}\right)_H \quad \leftarrow \text{ can measure this } \left(\frac{\Delta T}{\Delta p}\right)_H$$

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

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

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

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

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

For a van der Waals gas:

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

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

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

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

$T_{inv}>>300K$ 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

$$\bar{C}_p = \left(\frac{\partial \bar{H}}{\partial T}\right)_p, \qquad \bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

$$\underbrace{\bar{H} = \bar{U} + p\bar{V}}_{\downarrow}, \qquad p\bar{V} = RT$$

$$\overbrace{\left(\frac{\partial \bar{H}}{\partial T}\right)_p = \left(\frac{\partial \bar{U}}{\partial T}\right)_p + p\left(\frac{\partial \bar{V}}{\partial T}\right)_p}^{\uparrow}$$

$$\bar{C}_p = \overbrace{\bar{C}_V + \underbrace{\cancel{\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T}}_{=0\text{ for ideal gas}}\left(\frac{\partial \bar{V}}{\partial T}\right)_p}^{\uparrow} + \cancel{p}\left(\frac{R}{\cancel{p}}\right)$$

$$\therefore \quad \bar{C}_p = \bar{C}_V + R$$