



DET 05970 Termodinâmica e Transmissão de Calor

Entalpia

Aula 9-10

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Entalpia

$$H(T, p)$$

$$H \equiv U + pV$$

Reações químicas e processos biológicos usualmente ocorrem sob pressão constante e com trabalho pV reversível.

$$\begin{array}{ccc} \text{gas } (p, T_1, V_1) & \xrightarrow[\text{const. } p]{\text{reversible}} & \text{gas } (p, T_2, V_2) \\ U_1 & & U_2 \end{array}$$

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

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

$$\Delta U + \Delta(pV) = q_p \quad \Rightarrow \quad \overbrace{\Delta(U + pV)}^{\text{definido como H}} = q_p$$

$$H \equiv U + pV \quad \Rightarrow \quad \Delta H = q_p \quad (\text{p/ processos reversíveis sob } p \text{ cte})$$

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

$$\left(\frac{\partial H}{\partial T} \right)_p \quad \Rightarrow \quad \text{para processo reversível sob } p \text{ constante } (dp = 0)$$

$$dH = \delta q_p \quad \text{e} \quad dH = \left(\frac{\partial H}{\partial T} \right)_p dT$$

$$\Rightarrow \quad \delta q_p = \left(\frac{\partial H}{\partial T} \right)_p dT \quad \text{mas} \quad \delta q_p = C_p dT \quad \text{logo}$$

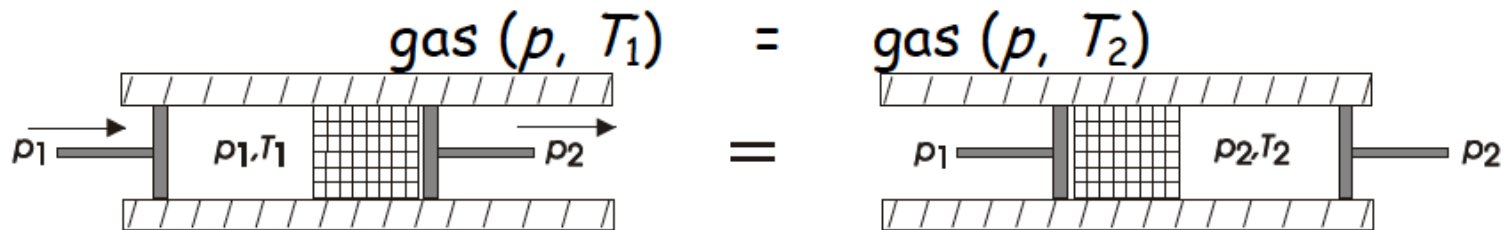
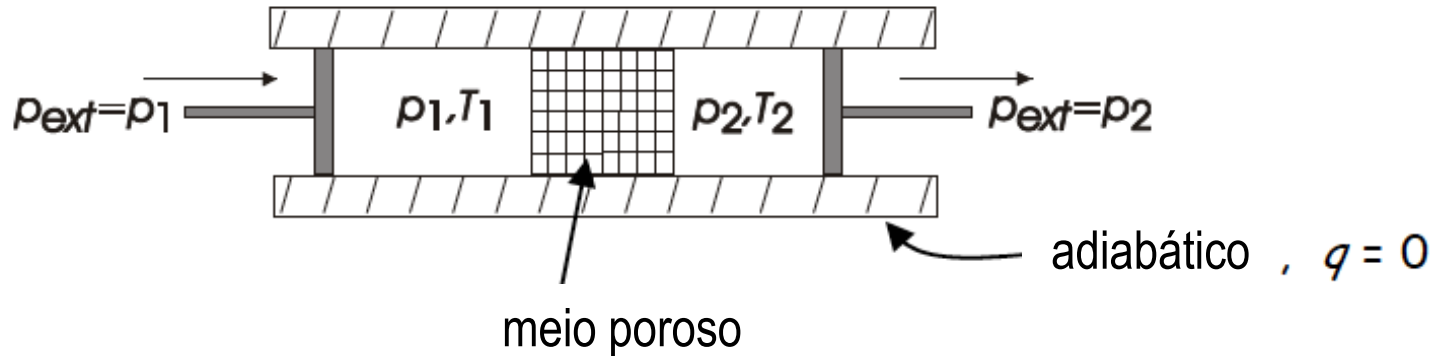
\therefore

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

$$\left(\frac{\partial H}{\partial p} \right)_T$$



Expansão Joule-Thomson



$$w = p_1 V_1 - p_2 V_2 \Rightarrow \Delta U = q + w = p_1 V_1 - p_2 V_2 = -\Delta(pV)$$

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

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

Joule-Thomson é um processo com entalpia constante.

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

$$\Rightarrow \left(\frac{\partial H}{\partial p} \right)_T = -C_p \left(\frac{\partial T}{\partial p} \right)_H \leftarrow \text{pode ser medido} \quad \left(\frac{\Delta T}{\Delta p} \right)_H$$

Definição:

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

$$\therefore \boxed{\left(\frac{\partial H}{\partial p} \right)_T = -C_p \mu_{JT}}$$

e

$$\boxed{dH = C_p dT - C_p \mu_{JT} dp}$$

Para um gás ideal: $U(T), \quad pV=nRT$

$$H \equiv U(T) + pV = \underbrace{U(T) + nRT}_{\text{depende somente de T}}$$

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

Para um gás de Van der Waals:

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

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

então $\left(\frac{\Delta T}{\Delta p}\right)_H < 0$ portanto se $\Delta p < 0$ ($p_2 < p_1$)
então $\Delta T > 0$

gás aquece sobre expansão

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

então $\left(\frac{\Delta T}{\Delta p}\right)_H > 0$ portanto se $\Delta p < 0$
então $\Delta T < 0$

gás resfria sobre expansão

$T_{inv} \gg 300K$ para maioria dos gases reais

\Rightarrow Usual utilizar a expansão J-T para liquefazer gases

Prove que: $\bar{C}_p = \bar{C}_V + R$ para um gás ideal

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

$$\bar{H} = \bar{U} + p\bar{V}, \quad p\bar{V} = RT$$

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

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

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

