Clase 7   12 Agosto 2014

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Forma alterna de obtener entalpía

$Q = \Delta U + W$ $\Delta U = Q - W$

$W = p \, \Delta V$

$Q_V = n \bar{C_V} \Delta T$

$p \Delta V = nR\Delta T$

$Q_P = n\bar{C_V}\Delta T + nR\Delta T$ Q_p = Calor a presión constante

$Q_P = n(\bar{C_V} + R)\Delta T$

$$Q_p = \Delta H$$

$$\Delta H = n \bar{C}_p \Delta T$$

Forma diferencial

$$dH = n \bar{C}_p \, dT$$

Entalpía es función de T y P

$$\bar{H} = f(T, P)$$

$$d\bar{H} = \left(\frac{\partial \bar{H}}{\partial T}\right)_P dT + \left(\frac{\partial \bar{H}}{\partial P}\right)_T dT$$

si el proceso es a T = cte

$$d\bar{H} = \left(\frac{\partial \bar{H}}{\partial T}\right)_P dT \qquad \left(\frac{\partial \bar{H}}{\partial T}\right)_P = \bar{C}_p$$

$$dH = n\left(\frac{\partial \bar{H}}{\partial T}\right)_P dT = n\,\bar{C}_p\,dT$$

Relaciones de Maxwell (Revisar)

$$z = f(x,y) = cte$$

$$dz = 0 \quad \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dx$$

$$0 = M\,dx + N\,dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y\,\partial x} \qquad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x\,\partial y}$$

de esta forma

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Ejemplo

$$du = T\,ds - p\,dv \quad \text{- - - - - -} \quad (1)$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad \text{- - - - -} \quad (2)$$

para entalpía

$$dH = Tds + vdp \quad \cdots\cdots \quad (3)$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \quad \cdots\cdots \quad (4)$$

Sustituyendo (2) y (4)

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Comprobar porque en un proceso Isotérmico $\Delta H = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad \text{y de} \quad V = \frac{nRT}{P}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$ sustituyendo

$$\left(\frac{\partial H}{\partial T}\right)_P = \cancel{\frac{nRT}{P}} - T\left(\cancel{\frac{nR}{P}}\right) = 0$$

comprobado $\Delta H = 0$ gas perfecto y gas ideal

Ejercicio (Realizar la misma comprobación con ΔU para proceso isotérmico)

$$dU = T\,dS - P\,dV$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$dA = -P\,dV - S\,dT$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$P = \frac{nRT}{V}$$

$$V = \frac{nRT}{P}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$ de esta folma

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{nR}{V}\right) - \frac{nRT}{V} = 0$$

Comprobado $\Delta U = 0$ proceso isotérmico gas ideal y pefecto