Thermo

$dU = \delta W + Q$

Monobare $dH = Q_p + \delta W'$ (autre que les force de P)

$dU = m C_v dT$, $dH = m C_p dT$

$\Delta S = S^e + S^c$

$\delta S^c \geq 0$ $\delta S^e = \frac{\delta Q}{T}$ (source)

Identité thermo $dU = TdS - pdV$

$dH = TdS + Vdp$

Remarques

▷ S°_m gaz # $200 J.K^{-1}mol^{-1}$. $S^\circ_m(H^+) = 0$

▷ • $\Delta_r G = \Delta_r H - T\Delta_r S$ < à T ↗↗ Réaction sous l'influence de S ; à T ↘↘ de H

• $\frac{d\Delta_r G^\circ}{dT} = -\Delta_r S^\circ$

• $\frac{d}{dT}\left(\frac{\Delta_r G^\circ}{T}\right) = -\frac{\Delta_r H^\circ}{T^2}$ (Kirchhoff like)

Laplace Isentropique ⟹ $PV^\gamma = cte$

Thermochimie

$\Delta_r Z(T) = \sum_i \nu_i Z^\circ_{m,i}$

$\Delta H^\circ = \sum_i \nu_i \Delta_f H^\circ_i(T)$ (Hess)

$\frac{d\Delta_r S^\circ}{dT} = \frac{\Delta_r C_p^\circ}{T}$; $\frac{d\Delta_r H^\circ}{dT} = \Delta_r C^\circ_p$ (Kirchhoff)

→ Mélange idéal : $H_{m,i} = H^\circ_{m,i}$, $\Delta H = \Delta_r H^\circ(T)$ ind de ξ

→ Gaz parfait ; phase condensée $\Delta_r H \approx \Delta_r H^\circ$

$\Delta H = \Delta\xi \, \Delta_r H^\circ(T)$

→ Il faut penser à faire des cycles

G, T, Pext fixées $G = U - TS + PV = H - TS$

$dG = -SdT + Vdp$

$\Rightarrow S = -\left.\frac{\partial G}{\partial T}\right)_p$ $V = \left.\frac{\partial G}{\partial p}\right)_T$ $\Rightarrow$ $\left.\frac{\partial \mu_i}{\partial T}\right|_p = -S_{m,i}$; $\left.\frac{\partial \mu_i}{\partial p}\right|_T = V_{m,i}$

$H = -T^2 \left.\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p$

$\mu_i = \frac{\partial G}{\partial n_i}$; $G = \sum_i \mu_i n_i$; $\Delta_r G = \sum_i \nu_i \mu_i$

$\mu_i = \mu_i^\circ + RT\ln(a_i)$

- → Gaz : $a_i = \frac{p_i}{p^\circ}$
- → Φ condensée non miscible : $a = 1$
- → Mélange cond. : $a_i = x_i$
- → solvant : $a = 1$
- → soluté : $a_i = \frac{C_i}{C^\circ}$