Criteria For Spontaneous Change

$$(dA)_{T,V} \leq 0$$

$$(dG)_{T,p} \leq 0$$

Closed system

$$dA(T,V) = -p\,dV - S\,dT \qquad \text{(Closed system)}$$

$$dG(T,p) = V\,dp - S\,dT$$

$$-p = \left(\frac{\partial A}{\partial V}\right)_T \; ; \quad -S = \left(\frac{\partial A}{\partial T}\right)_V$$

$$V = \left(\frac{\partial G}{\partial p}\right)_T \; ; \quad -S = \left(\frac{\partial G}{\partial T}\right)_p$$

Maxwell Relations (properties of state functions)

$$dG(T,p) = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

Maxwell Relations

$$\frac{\partial^2 G(T,p)}{\partial T\,\partial p} = \frac{\partial^2 G(T,p)}{\partial p\,\partial T}$$

$$\frac{\partial}{\partial T}\left(\left(\frac{\partial G(T,p)}{\partial p}\right)_T\right)_p = \frac{\partial}{\partial p}\left(\left(\frac{\partial G(T,p)}{\partial T}\right)_p\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

E.O.S.

Application :

$$dH(S,p) = dU + d(pV) = TdS - pdV + pdV + Vdp$$

$$dH(S,p) = TdS + Vdp$$

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

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V\left(\frac{\partial p}{\partial p}\right)_T$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$$

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

I.G. E.O.S.

$$pV = nRT$$

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

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$$

$$\left(\frac{\partial H}{\partial p}\right)_T^{I.G.} = \frac{-nRT}{p} + \frac{nRT}{p} = 0$$

$$U^{I.G} = U^{I.G}(T) \text{ only}$$

Maxwell Relations for $A(T, V)$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = ?$$

$$\left(\frac{\partial U^{I.G.}}{\partial V}\right)_T = 0 \quad \text{I.G.}$$

U, S, G, A ← List Maxwell Relations.

Thermochemistry

Goal: ΔH°_{rxn} (298.15 K, P = 1 bar) ← ° = 1 bar

P = 1 bar standard pressure

$q_p = \Delta H_{rxn}$

T = 298.15 K ; P = 1 bar

ΔH°_{rxn}

$CH_4(g, T, 1\,bar) + 2O_2(g, T, 1\,bar) \rightarrow CO_2(g, T, 1\,bar) + 2H_2O(l, T, 1\,bar)$

$-\Delta H^\circ_{f,CH_4}$; $-2\Delta H^\circ_{f,O_2}$; $\Delta H^\circ_{f,CO_2}$; $2\Delta H^\circ_{f,H_2O}$

Some reservoir of "building blocks"

most stable forms of the elements at standard conditions

$O_2(g)$, $H_2(g)$, $C_{graphite}$ ⟸ H = O

$$C_{graphite} + 2H_2(g) \rightarrow CH_4(g)$$

Formation Reaction

$$\Delta H^\circ_{f,CH_4}$$

$$\Delta H^\circ_{rxn} = -\Delta H^\circ_{f,CH_4} - 2\Delta H^\circ_{f,O_2} + \Delta H^\circ_{f,CO_2} + 2\Delta H^\circ_{f,H_2O}$$

$$\Delta H^\circ_{rxn} = \sum_{i=1}^{reactants} \nu_i \Delta H^\circ_{f,i} + \sum_{j=1}^{products} \nu_j \Delta H^\circ_{f,j}$$

$\nu_i < 0$ Reactant

$\nu_j > 0$ Product

$$\Delta H^\circ_{rxn} = \sum_{k=1}^{species} \nu_k \Delta H^\circ_{f,k}$$

Temperature Dependence of ΔH_{rxn}

P = constant

ΔH_{rxn} ($T \neq 298.15$ K)