

Criteria For Spontaneous Change

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

closed
system

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

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

$$dG(T,P) = V dp + S dT$$

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

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

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

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

$$\frac{\partial}{\partial T} \left(\left(\frac{\partial G(T, P)}{\partial P} \right)_{T, P} \right) = \frac{\partial}{\partial P} \left(\left(\frac{\partial G(T, P)}{\partial T} \right)_{P, T} \right)$$

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

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. $E=0, S,$

$$pV = nRT$$

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

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

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

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

Maxwell Relations for $A(T, V)$

$$dU = TdS - pdV$$

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

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

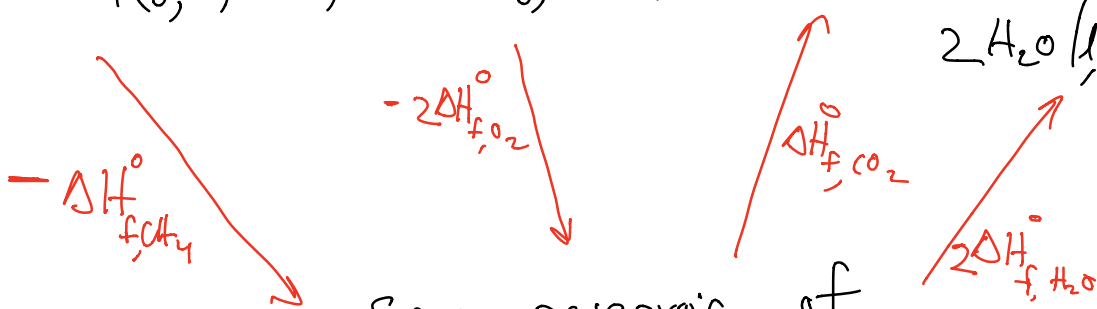
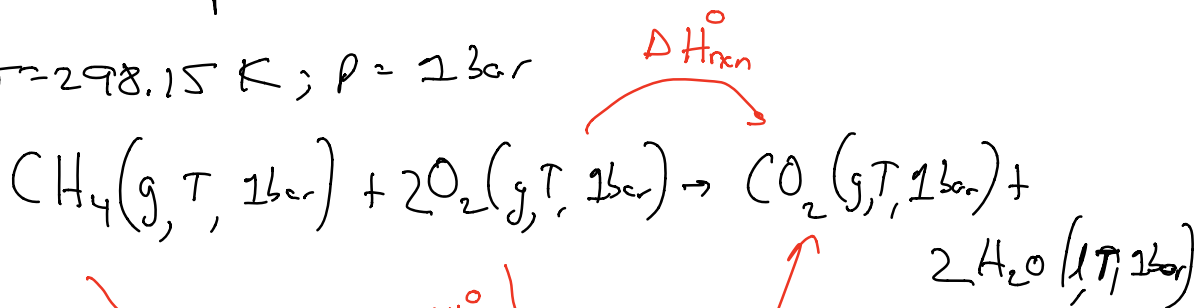
U.S.G.A ← List Maxwell Relations

Thermochemistry

Goal: ΔH_{rxn}° (298.15 K, $P = 1 \text{ bar}$)
 $P = 1 \text{ bar}$ standard pressure

$$Q_p = \Delta H_{rxn}$$

$T = 298.15 \text{ K}; P = 1 \text{ bar}$



Some reservoir of
"building blocks"
most stable forms of the elements
at standard conditions





Formation Reaction

$$\Delta H_{f, \text{C}_2\text{H}_4}^\circ$$

$$\Delta H_{\text{rxn}}^\circ = -\Delta H_{f, \text{C}_2\text{H}_4}^\circ - 2\Delta H_{f, \text{O}_2}^\circ + \Delta H_{f, \text{CO}_2}^\circ + 2\Delta H_{f, \text{H}_2\text{O}}^\circ$$

$$\Delta H_{\text{rxn}}^\circ = \sum_{i=1}^{\text{reactants}} \nu_i \Delta H_{f,i}^\circ + \sum_{j=1}^{\text{products}} \nu_j \Delta H_{f,j}^\circ$$

$\nu_i < 0$ Reactant

$\nu_j > 0$ Product

$$\Delta H_{\text{rxn}}^\circ = \sum_{k=1}^{\text{species}} \nu_k \Delta H_{f,k}^\circ$$

Temperature Dependence of ΔH_{rxn}

$p = \text{constant}$

$$\Delta H_{\text{rxn}} (T \neq 298.15 \text{ K})$$

