

1 review

Boltzmann probability:

$$S = -k \sum p_i \ln p_i$$

Entropy of mixing:

$$S = R \sum x_i \ln x_i$$

Standard Entropy:

$$S^\circ = \int_0^{298} \frac{C_p}{T} dT$$

2 Section 4A - Gibbs and Auxillary functions

Gibbs:

$$dG = dH - Tds$$

2.1 Gibbs derivation

All systems tend toward a lower "Energy state". This process acquires entropy (maximizes configuration). Consider the three laws applied to a reversible process:

- 1st law:

$$dU = \delta q - \delta w$$

$$dU = \delta q_{rev} - PdV \text{ (I)}$$

- 2nd law:

$$dS \geq \frac{\delta q}{T}$$

$$dS = \frac{\delta q_{rev}}{T}$$

$$\delta q_{rev} = Tds \text{ (II)}$$

- 3rd law:

$$S = 0 \text{ at } 0\text{K}$$

- Enthalpy:

$$H \equiv U + PV$$

$$dH = dU + PdV + vdP \text{ (III)}$$

2.2 cont.

$$(II) \circ (I): dU = Tds - PdV \text{ (IV)}$$

$$(IV) \circ (III): dH = (Tds - PdV) + PdV + VdP$$

$$dH = TdS + VdP \text{ (IV)}$$

2.3 For a process at constant T and P

$$(IV) \Big|_{P,T}: dH = Tds$$

- This equation is a criteria for spontaneity
- It displays an equilibrium which can be used to predict the direction of a reaction
- This equation balances both:
 - enthalpy (naturally lower energy state is preferred)
 - entropy (naturally tends towards a statistically favored state)

2.4 Gibbs Free Energy

$$G \equiv H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$dG = dU + VdP + PdV - SdT - TdS$$

$$dG = \delta q - \delta w + VdP + PdV - SdT - TdS$$

$$dG = TdS - PdV + VdP + PdV - SdT - TdS$$

$$dG = VdP - SdT$$

The final line indicates that the equilibrium criteria varies with temperature and pressure

$$\boxed{\left. \frac{\delta G}{\delta T} \right|_P = -S \quad \left. \frac{\delta G}{\delta P} \right|_T = V \quad \left. \frac{\delta H}{\delta P} \right|_S = V \quad \left. \frac{\delta H}{\delta S} \right|_P = T}$$