

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:
 $dU = \delta q - \delta w$
 $dU = \delta q_{rev} - PdV$ (I)
- 2nd law:
 $dS \geq \frac{\delta q}{T}$
 $dS = \frac{\delta q_{rev}}{T}$
 $\delta q_{rev} = Tds$ (II)
- 3rd law:
 $S = 0$ at 0K
- Enthalpy:
 $H \equiv U + PV$
 $dH = dU + PdV + VdP$ (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 sponteneity
- 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

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