

Gibbs Free Energy and Chemical Reactions

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- The Gibbs free energy is a function of τ , P , and $N \rightarrow G(\tau, P, N)$
- If S is brought in thermal and mechanical contact with large R (at constant P and τ), then G_s will decrease and S will come to an equilibrium state in which G_s is minimal
 1. Maximum effective work done by the system in a reversible process is equal to $-\Delta G$
 2. $G = U + PV - \tau\sigma$

$$dG = dU + P dV + V dP - \tau d\sigma - \sigma d\tau$$

– From the first law for a reversible process:

$$dG = \mu dN + v dP - \sigma d\tau$$

3. From this, we can find:

$$G(N, P, \tau) \rightarrow \begin{cases} \left(\frac{\partial G}{\partial N}\right)_{P, \tau} = \mu \\ \left(\frac{\partial G}{\partial P}\right)_{N, \tau} = V \\ \left(\frac{\partial G}{\partial \tau}\right)_{N, P} = -\sigma \end{cases}$$

4. $U = U(\sigma, V, N) = Nf\left(\frac{\sigma}{N}, \frac{V}{N}\right)$ — this is an extensive function

$$G(N, P, \tau) = N\mu(P, \tau)$$

– We can see that μ is the Gibbs free energy per particle

5. For an ideal gas ($S = 0$, monatomic) we know that $\mu\tau \ln(n/n_Q)$; this can be rewritten as:

$$\mu(P, \tau) = \tau \ln \left(\frac{P}{\tau n_Q} \right)$$

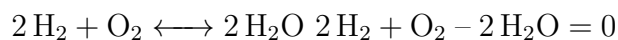
$$G(N, P, \tau) = N\tau \ln \left(\frac{P}{\tau n_Q} \right)$$

- Chemical reactions at τ, P — constant

$$v_1 A_1 + v_2 A_2 + \dots + v_l A_l = 0$$

- Where v_i are the reaction coefficients
- A_i are the reaction species

- Example:



- We can find $v_1 = 2$, $v_2 = 1$, $v_3 = -2$ and $A_1 = \text{H}_2$, $A_2 = \text{O}_2$, $A_3 = \text{H}_2\text{O}$

- In equilibrium, $G(N, P, \tau)$ will be at its minimum and $dG = 0$

$$dG = \sum_{i=1}^l \mu_i dN_i = 0$$

$$dN_i = -\Delta N v_i = 0 \quad \text{in equilibrium}$$

$$\Delta G = -\Delta N \sum_{i=1}^l \mu_i v_i$$

- Moving away from equilibrium:

$$\Delta G = -\Delta N \sum \mu_i v_i < 0 \quad (2^{\text{nd}} \text{ law})$$

- If $\sum \mu_i v_i > 0$, then $\Delta N > 0$, and the reaction will move to the right
- Ideal Gas with internal degrees of freedom

- Spin (S)
- Vibrations
- Rotations