Gibbs Free Energy and Chemical Reactions

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- The Gibbs free energy is a function of τ, P, and $N \to G(\tau, P, N)$

- 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:

$$G(N, P, \tau) \to \begin{cases} \left(\dfrac{\partial G}{\partial N}\right)_{P,\tau} = \mu \\[2mm] \left(\dfrac{\partial G}{\partial P}\right)_{N,\tau} = V \\[2mm] \left(\dfrac{\partial G}{\partial \tau}\right)_{N,P} = -\sigma \end{cases}$$

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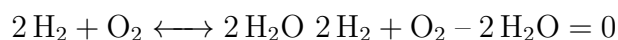
$$\mu(P, \tau) = \tau \ln\left(\frac{P}{\tau n_Q}\right)$$

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

- Chemical reactions at τ, P — constant

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

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

- Example:

$$2\,H_2 + O_2 \longleftrightarrow 2\,H_2O \quad 2\,H_2 + O_2 - 2\,H_2O = 0$$

  - We can find $v_1 = 2$, $v_2 = 1$, $v_3 = -2$ and $A_1 = H_2$, $A_2 = O_2$, $A_3 = H_2O$

- 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
  - For this particle, we may write:

$$\varepsilon_{n,1} = \varepsilon_n + \varepsilon_{int}$$

* Where ε_n is the translational energy and ε_{int} is the rotational and vibrational energy
* In the classical limit, we may write:

$$\mathfrak{z}_n = 1 + \sum_i e^{\frac{\mu - \varepsilon_{int}}{\tau}}$$

$$\mathfrak{z}_n = 1 + \lambda e^{\frac{-\varepsilon_n}{\tau}} \underbrace{\sum_i e^{-\frac{\varepsilon_{int}}{\tau}}}_{z_{int}}$$

$$\mathfrak{z}_n = 1 + \lambda e^{-\frac{\varepsilon_n}{\tau}}$$

$$N = \lambda z_{int} z_1$$

$$\mu = \tau \ln\left(\frac{n}{n_Q z_{int}}\right)$$

- Rotational degrees may be accounted for as:

$$\varepsilon_{int}^l = \frac{\hbar^2}{2I} l(l+1)$$

* Where l is the angular momentum quantum number, and I is the rotational moment of inertia about the center of mass

- Vibrational degrees may be accounted for as:

$$\varepsilon_{int}^n = \hbar\omega\left(n + \frac{1}{2}\right)$$

* Where n is the quantum number, and $\omega = \sqrt{\dfrac{k(m_1 + m_2)}{m_1 m_2}}$

- We may introduce a dummy variable to the chemical potential defined above to get:

$$\mu = \tau\left(\ln\left(\frac{n}{n_o}\right) - \ln\left(\frac{n_Q z_{int}}{n_o}\right)\right)$$

$$\mu = \tau \ln\left(\frac{n}{n_o}\right) + \mu^o(\tau)$$

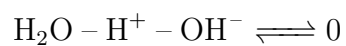- n_o is the reference concentration. For reactions in aqueous solutions:

$$n_o = 1M = 1\left[\frac{\text{mol}}{\text{L}}\right]$$

* For gasses, $n_o = \frac{1}{22}M$
* $\mu^o(\tau)$ is the standard chemical potential, and it depends on τ and $|n_o$

- The Law of Mass Action may be written as:

$$\prod_{i=1}^{l} [A_i]^{-v_i} = e^{-\frac{\Delta G^\circ}{\tau}} = K_{eq}$$

  - This gives us the key-equilibrium constant for a certain reaction
  - For example, for the following reaction, we could find K_{eq}:

$$H_2O - H^+ - OH^- \rightleftharpoons 0$$

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$