Gibbs Free Energy and Chemical Reactions

Michael Brodskiy
Professor: A. Stepanyants

November 14, 2023

- 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 -ΔG
  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:

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

  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

$$\mathrm{v}_1\mathrm{A}_1 + \mathrm{v}_2\mathrm{A}_2 + \ldots + \mathrm{v}_l\mathrm{A}_l = 0$$

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

- Example:

$$2\,\mathrm{H_2} + \mathrm{O_2} \longleftrightarrow 2\,\mathrm{H_2O}\;\; 2\,\mathrm{H_2} + \mathrm{O_2} - 2\,\mathrm{H_2O} = 0$$

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

- 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