

Chapter 5. Chemical potential and Gibbs distribution

1 Chemical potential

So far we have only considered systems in contact that are allowed to exchange “heat”, *i.e.* systems in thermal contact with one another. In this chapter we consider systems that can also exchange particles with one another, *i.e.* systems that are in *diffusive* contact.

Consider 2 systems \mathcal{S}_1 and \mathcal{S}_2 that are in diffusive contact with one another and in thermal contact with a 3rd system, a reservoir at temperature τ . We have shown that the Helmholtz free energy for the combined system $\mathcal{S}_1 + \mathcal{S}_2$ will be a minimum when it is in equilibrium with the reservoir. We must therefore minimise

$$F = F_1 + F_2$$

with respect to the distribution of the particles between \mathcal{S}_1 and \mathcal{S}_2 to find the equilibrium state of this combined system. The total number of particles in the system is fixed, so that

$$dF = \left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} dN_1 - \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau} dN_1 = 0$$

in equilibrium, *i.e.*

$$\left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} = \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau}.$$

The quantity

$$\mu(\tau, V, N) = \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$$

is known as the *chemical potential*, so that our equilibrium condition is that

$$\mu_1 = \mu_2.$$

Inspecting the expression for dF , we see that when $\mu_1 > \mu_2$ moving particles from \mathcal{S}_1 to \mathcal{S}_2 decreases F , taking the system closer to equilibrium. Thus, particles tend to flow from systems of high chemical potential to systems of lower chemical potential. μ is the (Helmholtz) free energy “per particle” in a system.

If several chemical species are present within a system, then there is chemical potential associated with each distinct species, *e.g.*

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{\tau, V, N_1, N_2, \dots}$$

is the chemical potential for species j .

1.1 Example: the ideal gas

In chapter 3 we showed that the Helmholtz free energy of an ideal monatomic gas is

$$F = -N\tau \ln(n_Q V) + N\tau \ln N - N\tau,$$

so that

$$\mu = -\tau \ln(n_Q V) + \tau \ln N = \tau \ln \left(\frac{n}{n_Q} \right).$$

Chapter 5 Chemical Potential And Gibbs Distribution 1

**John W. Cahn, W. Craig Carter, William
C. Johnson**



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concerned with the chemical and physical structure of polymers Properties depend on structure Solution properties are thus discussed in Part II solid state properties in Part III There are other reasons for discussing properties before synthesis For example it is difficult to understand equilibrium polymerization without knowledge of solution thermodynamics the gel effect without knowledge of the glass transition temperature etc Part IV treats the principles of macromolecular syntheses and reactions

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Comparative Morphology and Behavior Norman R. Joseph,1979

Chemical Thermodynamics of Solid Solutions of Interest in Radioactive Waste Management Organisation for Economic Co-operation and Development,2007 This volume provides a state of the art report on the modelling of aqueous solid solution systems by the combined use of chemical thermodynamics and experimental and computational techniques These systems are ubiquitous in nature and therefore intrinsic to the understanding and quantification of radionuclide containment and retardation processes present in geological repositories of radioactive waste The various approaches are illustrated with case studies from the literature

The Chemical Engineer ,2001

Physics Briefs ,1989

Engineering Thermodynamics Murlin T. Howerton,1962

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