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.*

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

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

Hans-Georg Elias

Chapter 5 Chemical Potential And Gibbs Distribution 1:

Thermal Physics Charles Kittel,Herbert Kroemer,1980-01-15 CONGRATULATIONS TO HERBERT KROEMER 2000 NOBEL LAUREATE FOR PHYSICS For upper division courses in thermodynamics or statistical mechanics Kittel and Kroemer offers a modern approach to thermal physics that is based on the idea that all physical systems can be described in terms of their discrete quantum states rather than drawing on 19th century classical mechanics concepts Biochemical Energetics and Kinetics Alva Rae Patton,1965 **The Physical Chemistry of Electrolytic Solutions** Herbert Spencer Harned,Benton Brooks Owen,1943 **Phase Equilibria in Chemical Engineering** Stanley M. Walas,1985 *Macromolecules, Volume 3* Hans-Georg Elias,2005 Providing a broad survey of the entire field Macromolecules integrates representations of chemistry physics and technology as well as including precise descriptions of basic phenomena and balanced treatments of facts and theory **Physical Chemistry** Johannes Nicolaus Brønsted,1938 *Macromolecules · 1* Hans-Georg Elias,1984-02-29 The second edition of this textbook is identical with its fourth German edi tion and it thus has the same goals precise definition of basic phenomena a broad survey of the whole field integrated representation of chemistry physics and technology and a balanced treatment of facts and comprehen sion The book thus intends to bridge the gap between the often oversimpli fied introductory textbooks and the highly specialized texts and monographs that cover only parts of macromolecular science The text intends to survey the whole field of macromolecular science Its organization results from the following considerations The chemical structure of macromolecular compounds should be inde pendent of the method of synthesis at least in the ideal case Part I is thus concerned with the chemical and physical structure of polymers Properties depend on structure Solution properties are thus discussed in Part 11 solid state properties in Part Ill There are other reasons for dis cussing 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 *Separation and Preconcentration Methods in Inorganic Trace Analysis* Jerzy Minczewski,Jadwiga Chwastowska,Rajmund Dybczyński,1982 Progress in Liquid Physics Clive Anthony Croxton,1978

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