

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.*

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{\tau, V, N_1, \dots, N_{j-1}, \dots}$$

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

Gerassimos Orkoulas



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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 *Thermal Physics* EduGorilla Prep Experts, 2024-10-25 EduGorilla Publication is a trusted name in the education sector committed to empowering learners with high quality study materials and resources Specializing in competitive exams and academic support EduGorilla provides comprehensive and well structured content tailored to meet the needs of students across various streams and levels *The Physical Chemistry of Electrolytic Solutions* Herbert Spencer Harned, Benton Brooks Owen, 1943

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Separation Process Principles J. D. Seader, Ernest J. Henley, D. Keith Roper, 2016-01-11 *Separation Process Principles with Applications Using Process Simulator* 4th Edition is the most comprehensive and up to date treatment of the major separation operations in the chemical industry The 4th edition focuses on using process simulators to design separation processes and prepares readers for professional practice Completely rewritten to enhance clarity this fourth edition provides engineers with a strong understanding of the field With the help of an additional co author the text presents new information on bioseparations throughout the chapters A new chapter on mechanical separations covers settling filtration and centrifugation including mechanical separations in biotechnology and cell lysis Boxes help highlight fundamental equations Numerous new examples and exercises are integrated throughout as well *The Chemical Engineer*, 2001 **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 **Introduction to Surface Chemistry and Catalysis** Gabor A. Somorjai, 1994-03-18 Among the topics covered are adhesion and tribological properties friction crack formation and lubrication *Numerical Investigations of Phase Transitions* Gerassimos Orkoulas, 1998 *Physics Briefs*, 1989

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