

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

M Lipman



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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 Fundamentals of Interface and Colloid Science J. Lyklema,1991

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Table of Contents Chapter 5 Chemical Potential And Gibbs Distribution 1

1. Understanding the eBook Chapter 5 Chemical Potential And Gibbs Distribution 1
 - The Rise of Digital Reading Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Advantages of eBooks Over Traditional Books
2. Identifying Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Chapter 5 Chemical Potential And Gibbs Distribution 1
 - User-Friendly Interface
4. Exploring eBook Recommendations from Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Personalized Recommendations
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 User Reviews and Ratings
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 and Bestseller Lists

5. Accessing Chapter 5 Chemical Potential And Gibbs Distribution 1 Free and Paid eBooks
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 Public Domain eBooks
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 eBook Subscription Services
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 Budget-Friendly Options
6. Navigating Chapter 5 Chemical Potential And Gibbs Distribution 1 eBook Formats
 - ePub, PDF, MOBI, and More
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 Compatibility with Devices
 - Chapter 5 Chemical Potential And Gibbs Distribution 1 Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Highlighting and Note-Taking Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Interactive Elements Chapter 5 Chemical Potential And Gibbs Distribution 1
8. Staying Engaged with Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Chapter 5 Chemical Potential And Gibbs Distribution 1
9. Balancing eBooks and Physical Books Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Chapter 5 Chemical Potential And Gibbs Distribution 1
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Setting Reading Goals Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Fact-Checking eBook Content of Chapter 5 Chemical Potential And Gibbs Distribution 1
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning

- Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
- Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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