#### 12.1 Ideal solutions

Solutions are among the most important kinds of systems in the chemical and biochemical sciences and technologies, spanning an enormous range of different phenomena and scales. The simplest model of a solution is the so-called ideal one.

An ideal solution is defined by the following properties.

- Components are non-interacting. In other words, there are no explicit energetic interactions between molecules of different species.
- (2) At constant temperature and pressure, an ideal entropy of mixing contributes to the total entropy due to the presence of different species.
- (3) Ideal solutions are usually excellent approximations to real ones in the near-pure limit, in which there is one major component (e.g., a solvent) and the concentrations of all other species (solutes) are very small.

To develop a thermodynamic model of ideal solutions, we first evaluate the entropy of mixing using a simple model. Figure 12.1 illustrates a lattice mixing model for a binary system. Though the lattice certainly does not represent molecular-structural features of actual liquids, the final behavior of the mixing entropy is surprisingly insensitive to its use. Prior to mixing the particles are completely separated into different regions of the system volume. One configuration exists for this state, and thus the entropy is zero. If the particles are then allowed to mix randomly, the number of arrangements of  $N_A$  A particles and  $N_B$  B particles in the  $N=N_A+N_B$  sites is given by the combinations formula

$$\begin{split} &\Omega_{\text{mix}}(N_{\text{A}}, N_{\text{B}}) = \frac{(N_{\text{A}} + N_{\text{B}})!}{N_{\text{A}}! N_{\text{B}}!} \approx \frac{(N_{\text{A}} + N_{\text{B}})^{N_{\text{A}} + N_{\text{B}}}}{N_{\text{A}}^{N_{\text{A}}} N_{\text{B}}^{N_{\text{B}}}} \\ &= \left(\frac{N_{\text{A}}}{N_{\text{A}} + N_{\text{B}}}\right)^{-N_{\text{A}}} \left(\frac{N_{\text{B}}}{N_{\text{A}} + N_{\text{B}}}\right)^{-N_{\text{B}}} \end{split} \tag{12.1}$$

In the second line, we applied Stirling's approximation. By taking the logarithm to obtain the entropy, we find

# Thermodynamics Cambridge University Press Solution Manual

Wilfried Kurz, David J. Fisher, Michel Rappaz

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#### **Table of Contents Thermodynamics Cambridge University Press Solution Manual**

- 1. Understanding the eBook Thermodynamics Cambridge University Press Solution Manual
  - The Rise of Digital Reading Thermodynamics Cambridge University Press Solution Manual
  - Advantages of eBooks Over Traditional Books
- 2. Identifying Thermodynamics Cambridge University Press Solution Manual
  - 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 Thermodynamics Cambridge University Press Solution Manual
  - User-Friendly Interface
- 4. Exploring eBook Recommendations from Thermodynamics Cambridge University Press Solution Manual
  - Personalized Recommendations
  - Thermodynamics Cambridge University Press Solution Manual User Reviews and Ratings
  - Thermodynamics Cambridge University Press Solution Manual and Bestseller Lists
- 5. Accessing Thermodynamics Cambridge University Press Solution Manual Free and Paid eBooks
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- Thermodynamics Cambridge University Press Solution Manual Budget-Friendly Options
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  - Thermodynamics Cambridge University Press Solution Manual Compatibility with Devices
  - Thermodynamics Cambridge University Press Solution Manual Enhanced eBook Features
- 7. Enhancing Your Reading Experience
  - Adjustable Fonts and Text Sizes of Thermodynamics Cambridge University Press Solution Manual
  - Highlighting and Note-Taking Thermodynamics Cambridge University Press Solution Manual
  - Interactive Elements Thermodynamics Cambridge University Press Solution Manual
- 8. Staying Engaged with Thermodynamics Cambridge University Press Solution Manual
  - Joining Online Reading Communities
  - Participating in Virtual Book Clubs
  - Following Authors and Publishers Thermodynamics Cambridge University Press Solution Manual
- 9. Balancing eBooks and Physical Books Thermodynamics Cambridge University Press Solution Manual
  - Benefits of a Digital Library
  - Creating a Diverse Reading Collection Thermodynamics Cambridge University Press Solution Manual
- 10. Overcoming Reading Challenges
  - Dealing with Digital Eye Strain
  - Minimizing Distractions
  - Managing Screen Time
- 11. Cultivating a Reading Routine Thermodynamics Cambridge University Press Solution Manual
  - Setting Reading Goals Thermodynamics Cambridge University Press Solution Manual
  - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Thermodynamics Cambridge University Press Solution Manual
  - Fact-Checking eBook Content of Thermodynamics Cambridge University Press Solution Manual
  - 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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