

The Boltzmann Factor and Partition Functions

PROBLEMS AND SOLUTIONS

3-1. How would you describe an ensemble whose systems are one-liter containers of water at 25°C?

An unlimited number of one-liter containers of water in an essentially infinite heat bath at 298 K.

3-2. Show that Equation 3.8 is equivalent to $f(x + y) = f(x)f(y)$. In this problem, we will prove that $f(x) \propto e^{ax}$. First, take the logarithm of the above equation to obtain

$$\ln f(x + y) = \ln f(x) + \ln f(y)$$

Differentiate both sides with respect to x (keeping y fixed) to get

$$\begin{aligned} \left[\frac{\partial \ln f(x + y)}{\partial x} \right]_y &= \frac{d \ln f(x + y)}{d(x + y)} \left[\frac{\partial(x + y)}{\partial x} \right]_y = \frac{d \ln f(x + y)}{d(x + y)} \\ &= \frac{d \ln f(x)}{d x} \end{aligned}$$

Now differentiate with respect to y (keeping x fixed) and show that

$$\frac{d \ln f(x)}{d x} = \frac{d \ln f(y)}{d y}$$

For this relation to be true for all x and y , each side must equal a constant, say a . Show that

$$f(x) \propto e^{ax} \quad \text{and} \quad f(y) \propto e^{ay}$$

Let $x = E_1 - E_2$ and $y = E_2 - E_3$. Then $x + y = E_1 - E_3$, and we can write Equation 3.8 as $f(x + y) = f(x)f(y)$. Taking the logarithm of this equation gives

$$\begin{aligned} \ln f(x + y) &= \ln [f(x)f(y)] \\ &= \ln f(x) + \ln f(y) \end{aligned}$$

We then differentiate with respect to x and find

$$\begin{aligned} \left[\frac{\partial \ln f(x + y)}{\partial x} \right]_y &= \left[\frac{\partial \ln f(x)}{\partial x} \right]_y + 0 \\ \frac{d \ln f(x + y)}{d(x + y)} \left[\frac{\partial(x + y)}{\partial x} \right]_y &= \frac{d \ln f(x)}{d x} \\ \frac{d \ln f(x + y)}{d(x + y)} &= \frac{d \ln f(x)}{d x} \end{aligned} \tag{1}$$

Mcquarrie And Simon Solution Manual

Heather Cox,Carole H. McQuarrie

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1. Understanding the eBook Mcquarrie And Simon Solution Manual
 - The Rise of Digital Reading Mcquarrie And Simon Solution Manual
 - Advantages of eBooks Over Traditional Books
2. Identifying Mcquarrie And Simon 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 Mcquarrie And Simon Solution Manual
 - User-Friendly Interface
4. Exploring eBook Recommendations from Mcquarrie And Simon Solution Manual
 - Personalized Recommendations
 - Mcquarrie And Simon Solution Manual User Reviews and Ratings
 - Mcquarrie And Simon Solution Manual and Bestseller Lists
5. Accessing Mcquarrie And Simon Solution Manual Free and Paid eBooks
 - Mcquarrie And Simon Solution Manual Public Domain eBooks
 - Mcquarrie And Simon Solution Manual eBook Subscription Services
 - Mcquarrie And Simon Solution Manual Budget-Friendly Options
6. Navigating Mcquarrie And Simon Solution Manual eBook Formats

- ePub, PDF, MOBI, and More
- Mcquarrie And Simon Solution Manual Compatibility with Devices
- Mcquarrie And Simon Solution Manual Enhanced eBook Features

7. Enhancing Your Reading Experience

- Adjustable Fonts and Text Sizes of Mcquarrie And Simon Solution Manual
- Highlighting and Note-Taking Mcquarrie And Simon Solution Manual
- Interactive Elements Mcquarrie And Simon Solution Manual

8. Staying Engaged with Mcquarrie And Simon Solution Manual

- Joining Online Reading Communities
- Participating in Virtual Book Clubs
- Following Authors and Publishers Mcquarrie And Simon Solution Manual

9. Balancing eBooks and Physical Books Mcquarrie And Simon Solution Manual

- Benefits of a Digital Library
- Creating a Diverse Reading Collection Mcquarrie And Simon Solution Manual

10. Overcoming Reading Challenges

- Dealing with Digital Eye Strain
- Minimizing Distractions
- Managing Screen Time

11. Cultivating a Reading Routine Mcquarrie And Simon Solution Manual

- Setting Reading Goals Mcquarrie And Simon Solution Manual
- Carving Out Dedicated Reading Time

12. Sourcing Reliable Information of Mcquarrie And Simon Solution Manual

- Fact-Checking eBook Content of Mcquarrie And Simon 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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