

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 $f(x) \propto e^{\alpha x}$. 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

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

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

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

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

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

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

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

Mcquarrie Solution Manual

Heather Cox, Carole H. McQuarrie



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Table of Contents Mcquarrie Solution Manual

1. Understanding the eBook Mcquarrie Solution Manual
 - The Rise of Digital Reading Mcquarrie Solution Manual
 - Advantages of eBooks Over Traditional Books
2. Identifying Mcquarrie 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 Solution Manual
 - User-Friendly Interface
4. Exploring eBook Recommendations from Mcquarrie Solution Manual
 - Personalized Recommendations

- Mcquarrie Solution Manual User Reviews and Ratings
- Mcquarrie Solution Manual and Bestseller Lists
- 5. Accessing Mcquarrie Solution Manual Free and Paid eBooks
 - Mcquarrie Solution Manual Public Domain eBooks
 - Mcquarrie Solution Manual eBook Subscription Services
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- 6. Navigating Mcquarrie Solution Manual eBook Formats
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 - Mcquarrie Solution Manual Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Mcquarrie Solution Manual
 - Highlighting and Note-Taking Mcquarrie Solution Manual
 - Interactive Elements Mcquarrie Solution Manual
- 8. Staying Engaged with Mcquarrie Solution Manual
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Mcquarrie Solution Manual
- 9. Balancing eBooks and Physical Books Mcquarrie Solution Manual
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Mcquarrie Solution Manual
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Mcquarrie Solution Manual
 - Setting Reading Goals Mcquarrie Solution Manual
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Mcquarrie Solution Manual
 - Fact-Checking eBook Content of Mcquarrie 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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