Our aim, in writing this two volume textbook, is to provide a simple yet logical treatment of the bases of Chemical Thermodynamics. It is our experience that the level of understanding improves when appropriate justifications are generously provided. In the many years that this course has been taught, we have endeavored to find the most easily grasped explanations or justifications.

Volume 1 presents the fundamental aspects of thermodynamics. It is designed to be appropriate for a first contact with the topic of thermodynamics. We illustrate the first and second laws of thermodynamics, the need to define the thermodynamic temperature scale, and the nature of entropy. We show how spontaneous processes always correspond to an increase of the global entropy. We explore the meaning of auxiliary thermodynamics functions, the origin and usefulness of partial molar quantities. We look into the description of gaseous systems and phase equilibria in systems where chemical reactions do not take place.

Volume 2 contains the tools that are necessary to deal with systems where chemical reactions take place. The variables of reaction are a key to this understanding. Criteria for chemical equilibrium and spontaneity of reactions are established. We illustrate how chemical reactions can provide work as, for example, in batteries. We analyze the effect of external factors on chemical equilibria.

We finally present the more complex situation of solutions, going from ideal to real solutions. The statistical aspect of thermodynamics
and its importance are stretched and examined in the last chapter with many illustrative problems.

Most of the specific mathematical tools are presented either directly in the text if they are used mostly in one chapter, while material needed in several chapters is included in an appendix.

We have purposely kept intermediate steps in the derivations to enhance the clarity of the presentation.

To keep the topic easily accessible to beginners, we selected a primarily phenomenological approach.

Teachers may wish to include some of the problems provided as part of their lectures to illustrate points that they consider particularly important.

Students will definitely appreciate the problem sections where full solutions to the problems are provided to enhance the pedagogical value of this book.

Finally, it is a pleasure to thank here our colleagues who have contributed to improve this work by their varied comments and suggestions, Dr. G. Rothenberger and Dr. D. B. Matthews. Professor A. Wohlhauser provided invaluable help in the treatment of independent reactions. In the course of time, students and assistants have contributed to improve this book by their comments, suggestions and constructive criticisms. Finally, we thank the many individuals who read the final version of the manuscript helping to remove so many unaesthetic details.

Michael Graetzel       Pierre Infelta

Department of Chemistry,  
Swiss Federal Institute of Technology  
Lausanne, Switzerland
Table of Contents

Volume 1

1 Thermodynamic Systems: Definitions ----------------------- 1
  1.1 Introduction ------------------------------------------- 1
  1.2 Interactions of Thermodynamic Systems with their
      Environment ------------------------------------------- 2
  1.3 System in a State of Equilibrium ---------------------- 3
  1.4 Thermal reservoir. Heat Source. ------------------------ 4
  1.5 Diathermal and Adiabatic Enclosures ------------------- 4
  1.6 State Function and State Variables. Intensive and
      Extensive Variables. ---------------------------------- 4
      1.6.1 Definitions and Properties ---------------------- 4
      1.6.2 Isobaric Coefficient of Thermal Expansion.
          Isothermal Compressibility Coefficient -------------- 6
  1.7 Change of a State Variable as the Result of a
      Thermodynamic Process --------------------------------- 7
      1.7.1 General Process --------------------------------- 7
      1.7.2 Cyclic Process ---------------------------------- 8
      1.7.3 Expansion and Compression of a Gas -------------- 9
      1.7.4 Mathematical Properties of a State Function ----- 10
  1.8 Reversible and Irreversible Processes ------------------ 11
  1.9 Equation of State -------------------------------------- 11

2 Work --------------------------------------------------------- 13
  2.1 Introduction ------------------------------------------- 13
  2.2 Sign Convention ---------------------------------------- 13
  2.3 Mechanical Work ---------------------------------------- 14
      2.3.1 Definition -------------------------------------- 14
      2.3.2 Work and Volume Change ------------------------- 15
      2.3.3 Examples --------------------------------------- 16
  2.4 Electrical Work ---------------------------------------- 18
  2.5 Various Forms of Energy ------------------------------- 19
  2.6 Various Expressions for Work --------------------------- 20

3 First Law of Thermodynamics ------------------------------- 21
  3.1 Introduction ------------------------------------------- 21
  3.2 The Joule Experiment ---------------------------------- 22
  3.3 Internal Energy. First Law ----------------------------- 22
      3.3.1 General Aspects. Expression of the First Law
          of Thermodynamics ---------------------------------- 22
      3.3.2 Application to a Closed System ------------------ 23
  3.4 Internal Energy – A Look at the Molecular Scale....... 25

4 Second Law of Thermodynamics ----------------------------- 27
  4.1 Spontaneous Processes. Illustration at the Molecular
      Scale ----------------------------------------------- 27
      4.1.1 Spatial rearrangement ----------------------------- 27
4.1.2 Heat Transfer  ...............................................................28
4.1.3 A First Glance at Entropy  ..............................................29
4.2 First Formulation of the Second Law  ....................................31
4.3 Carnot Cycle. Heat Engine. Thermodynamic Temperature  ..........32
   4.3.1 Carnot Cycle. Operation of an Engine  ........................32
   4.3.2 Reversible Cycles of Two Distinct Systems  ......................33
   4.3.3 Definition of the Thermodynamic Temperature  ......................34
4.4 Entropy. Reversible and Irreversible Processes  ......................35
   4.4.1 Definition  ...............................................................35
   4.4.2 Entropy is a State Function  ........................................36
   4.4.3 Implications of the Second Law towards Entropy and Spontaneity of Processes  ...............38
   4.4.4 System in Contact with a Single Thermal Reservoir  ...............39
   4.4.5 System in Contact with Several Thermal Reservoirs  ...............41
   4.4.6 Other Formulations of the Second Law. Equilibrium Condition  ...............43
   4.4.7 Thermal Equilibrium  ..................................................43
   4.4.8 Differential Expression for the Internal Energy of a Closed System  ...............45
   4.4.9 Maximum Usable Work during a Process  .........................46
   4.4.10 Entropy Change during a Monothermal Expansion of an Ideal Gas  ...............47
4.5 Carnot Cycle of an Ideal Gas  ............................................50
   4.5.1 Isothermal (Reversible) Process of an Ideal Gas  ..................50
   4.5.2 Reversible Adiabatic Process of an Ideal Gas  ......................51
   4.5.3 Properties of the Cycle  ..............................................52
4.6 Heat Engines, Refrigerators, Heat Pumps  ............................55
   4.6.1 Thermal Machines  ....................................................55
   4.6.2 Efficiency of an Engine  .............................................55
   4.6.3 Refrigerator, Air Conditioner, Heat Pump  ..........................56
4.7 Internal Combustion Engine  ..............................................58
   4.7.1 The Otto Cycle or Beau de Rochas Cycle  ..........................58
   4.7.2 Efficiency of an Engine  .............................................59
4.8 Other Examples  ..................................................................60
   4.8.1 Stirling Cycle  .............................................................60
   4.8.2 Joule Cycle  ...............................................................63
5 Auxiliary Functions : Enthalpy, Helmholtz Energy, Gibbs Energy  .............65
   5.1 Introduction  .................................................................65
   5.2 Closed Systems  .............................................................66
      5.2.1 Constant Volume Process (Isochoric Process) .....................66
      5.2.2 Constant Pressure Process (Isobaric Process) .....................67
   5.3 Characteristic Variables. Fundamental Equations. Open Systems  .............68
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>5.3.1</td>
<td>Generalities</td>
<td>68</td>
</tr>
<tr>
<td>5.3</td>
<td>5.3.2</td>
<td>Internal Energy</td>
<td>69</td>
</tr>
<tr>
<td>5.3</td>
<td>5.3.3</td>
<td>Enthalpy</td>
<td>70</td>
</tr>
<tr>
<td>5.3</td>
<td>5.3.4</td>
<td>Helmholtz Function (Helmholtz Energy)</td>
<td>70</td>
</tr>
<tr>
<td>5.3</td>
<td>5.3.5</td>
<td>Gibbs Function (Gibbs Energy, Free Enthalpy)</td>
<td>71</td>
</tr>
<tr>
<td>5.3</td>
<td>5.3.6</td>
<td>Chemical Potential. Summary</td>
<td>72</td>
</tr>
<tr>
<td>5.4</td>
<td></td>
<td>Maxwell’s Relations</td>
<td>73</td>
</tr>
<tr>
<td>5.5</td>
<td></td>
<td>Thermodynamic Equation of State</td>
<td>75</td>
</tr>
<tr>
<td>5.5</td>
<td>5.5.1</td>
<td>General Case</td>
<td>75</td>
</tr>
<tr>
<td>5.5</td>
<td>5.5.2</td>
<td>Equation of State for an Ideal Gas</td>
<td>77</td>
</tr>
<tr>
<td>5.6</td>
<td></td>
<td>Properties of $C_p$ and $C_V$</td>
<td>78</td>
</tr>
<tr>
<td>5.6</td>
<td>5.6.1</td>
<td>Relation between $C_p$ and $C_V$</td>
<td>78</td>
</tr>
<tr>
<td>5.6</td>
<td>5.6.2</td>
<td>Variation of $C_V$ with Volume and of $C_p$ with Pressure</td>
<td>80</td>
</tr>
<tr>
<td>5.7</td>
<td>5.7.1</td>
<td>Physical Meaning of the Auxiliary Functions</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>6.1</td>
<td>Pure Substances and Mixtures : Molar Quantities and Partial Molar Quantities</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>6.2</td>
<td>Homogeneous Functions and their Properties</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>6.3</td>
<td>Extensive Variables : Essential Property</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>6.4</td>
<td>Intensive Variables</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>6.5</td>
<td>Gibbs-Duhem Equation</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>6.6</td>
<td>Partial Molar Quantities</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>6.6.1</td>
<td>Definition</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>6.6.2</td>
<td>Relation between Partial Molar Quantities</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>6.6.3</td>
<td>Pure Substance</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>6.6.4</td>
<td>Other Relations</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>6.7</td>
<td>Measurement of Partial Molar Volumes</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>7.1</td>
<td>Thermodynamics of Gases</td>
<td>105</td>
</tr>
<tr>
<td>7</td>
<td>7.1.1</td>
<td>Pure Ideal Gas</td>
<td>105</td>
</tr>
<tr>
<td>7</td>
<td>7.1.2</td>
<td>Selection of the Standard State Pressure</td>
<td>106</td>
</tr>
<tr>
<td>7</td>
<td>7.1.3</td>
<td>Mathematical Expressions of other Thermodynamic Functions of Ideal Gases</td>
<td>106</td>
</tr>
<tr>
<td>7</td>
<td>7.1.4</td>
<td>Entropy Change of an Ideal Gas due to a Change of State</td>
<td>107</td>
</tr>
<tr>
<td>7</td>
<td>7.2</td>
<td>Mixtures of Ideal Gases</td>
<td>108</td>
</tr>
<tr>
<td>7</td>
<td>7.2.1</td>
<td>Basic Properties, Ideal Gas Mixture</td>
<td>108</td>
</tr>
<tr>
<td>7</td>
<td>7.2.2</td>
<td>Entropy of Mixing, Gibbs and Helmholtz Energy of Mixing of Two Ideal Gases Forming an Ideal Gas Mixture</td>
<td>110</td>
</tr>
</tbody>
</table>
Volume 2

9 Energetics of Chemical Reactions ---------------------------- 271
  9.1 Introduction ----------------------------------------------- 271
  9.2 The Extent of Reaction -------------------------------------- 272
  9.3 Variables of Reaction ---------------------------------------- 273
    9.3.1 Gibbs Energy of Reaction (Free Enthalpy of Reaction) -------------- 273
    9.3.2 Spontaneous Reaction. Equilibrium ------------------------ 274
    9.3.3 Systems where Several Reactions can Take Place Simultaneously ------------------ 274
    9.3.4 Other Variables of Reaction ----------------------------- 276
    9.3.5 Standard Variables of Reaction ------------------------- 276
    9.3.6 Standard Variables of Formation ------------------------ 278
  9.4 Hess's Law ------------------------------------------------- 280
    9.4.1 Content ------------------------------------------------- 280
    9.4.2 Application --------------------------------------------- 280
    9.4.3 Generalization ------------------------------------------ 282
    9.4.4 Example ------------------------------------------------- 282
  9.5 Kirchoff's Equation ---------------------------------------- 284
  9.6 Effect of Temperature on the Entropy of Reaction and the Gibbs Energy of Reaction ------------------ 286
  9.7 Conversion of Chemical Energy into Work --------------------- 288
    9.7.1 Any Form of Work ---------------------------------------- 288
    9.7.2 Work other than Work due to Volume Change ------------- 289
    9.7.3 Batteries ----------------------------------------------- 290
    9.7.4 Lead Storage Battery ----------------------------------- 291
  9.8 Effect of the Choice of the Standard State Pressure on the Tabulated Thermodynamic Values ------------------ 293
    9.8.1 Justification of the Choice ------------------------------ 293
    9.8.2 Useful Relations ---------------------------------------- 294
    9.8.3 Ideal Gases --------------------------------------------- 294
    9.8.4 Real Gases --------------------------------------------- 296
    9.8.5 Condensed Phase ---------------------------------------- 296
    9.8.6 System with one Gas Phase and Several Condensed Phases ---------------------------------- 296
  9.9 Variables of Combustion ------------------------------------ 297

10 Chemical Equilibria--------------------------------------------- 299
  10.1 Introduction ----------------------------------------------- 299
  10.2 Spontaneous Reaction and Equilibrium Condition ----------- 299
  10.3 Change in G(ξ) with the Extent of Reaction ---------------- 300
    10.3.1 General Expression for a Mixture of Reacting Ideal Gases ---------------------------------------- 300
    10.3.2 Schematic Representation ---------------------------------- 302
  10.4 Affinity --------------------------------------------------- 303
  10.5 Law of Mass Action for a Mixture of Gases ------------------ 304
    10.5.1 General Case --------------------------------------------- 304
10.5.2 Other Forms of the Law of Mass Action 305
10.6 Chemical Equilibrium in the Presence of Pure Condensed Phases 307
  10.6.1 Chemical Potential of a Pure Condensed Phase. Activity 307
  10.6.2 Law of Mass Action for Heterogeneous Systems 307
10.6.1 Chemical Potential of a Pure Condensed Phase. Activity 307
10.6.2 Law of Mass Action for Heterogeneous Systems 308
10.7 Independent Reactions 310
  10.7.1 General Remarks 310
  10.7.2 Number and Nature of Independent Reactions 311
  10.7.3 Verifying the Independence of Reactions 315
  10.7.4 Consequences on Equilibrium and the Law of Mass Action 317
10.8 Phase Rule for Systems with Chemical Reactions 317
  10.8.1 Demonstration 317
  10.8.2 Examples of the Use of the Phase Rule 318
10.9 Effect of Temperature on the Equilibrium Constant 319
10.10 Displacement Laws of Equilibria 321
  10.10.1 Effect of Temperature 321
  10.10.2 Effect of Pressure 322
  10.10.3 Effect of Volume 323
  10.10.4 Effect of the Addition of an Inert Gas 323
  10.10.5 Effect of an Excess in One of the Reacting Species at Constant Pressure 324
10.11 Reduction of Iron Oxides 327
  10.11.1 Introduction and Method 327
  10.11.2 Reduction by Carbon Monoxide 328
  10.11.3 Reduction by Hydrogen 333
11 Thermodynamics of Perfect and Ideal Solutions 337
  11.1 Introduction 337
  11.2 Perfect Solution 340
    11.2.1 Isothermal Diagram 340
    11.2.2 Isobaric Representation 342
  11.3 Mixing Properties of Ideal Solutions 343
  11.4 Effect of Pressure and Temperature on Liquid Vapor Equilibria 344
  11.5 Depression of the Freezing Temperature of a Solvent in the Presence of a Solute 345
  11.6 Elevation of the Boiling Temperature of a Solvent in the Presence of a Solute 347
  11.7 Osmotic Pressure 348
12 Thermodynamics of Non Ideal Solutions 351
  12.1 Introduction 351
  12.2 Variables and Excess Variables of Mixing 352
  12.3 Effect of Temperature and Pressure on the Activity Coefficient 353
12.4 Standard State – Convention I for the Activity Coefficient 354
12.5 Applications of the Gibbs–Duhem Equation 356
12.5.1 Relation between Activity Coefficients in Binary Systems 356
12.5.2 Equilibrium Shift. Azeotropy 357
12.6 Isothermal Diagram 360
12.7 Isobaric Diagram 361
12.8 Standard State – Convention II for the Activity Coefficient 362
12.9 Liquid – Liquid Extraction 366
12.10 Other Composition Scales and Standard States 367
12.10.1 Molality 367
12.10.2 Concentration 369
12.11 Law of Mass Action for Liquid Phase Systems 369
12.12 Electrolytes 371
12.12.1 General Considerations 371
12.12.2 Chemical Potential of Ions in Solution 372
12.12.3 Dissociation Equilibrium 373
12.12.4 Hydrogen Ion Convention for Aqueous Solutions 374
12.12.5 Electrode Potential 376

13 Statistical Mechanics 377
13.1 Introduction 377
13.2 Statistical Models 379
13.2.1 Maxwell–Boltzmann Statistics 379
13.2.2 Bose–Einstein Statistics 380
13.2.3 Fermi–Dirac Statistics 381
13.2.4 Illustration of the Different Statistics in a Simple Case 381
13.2.5 Dilute Systems. Corrected Boltzons 382
13.3 Stirling’s Approximations 383
13.4 Microcanonical Ensemble 384
13.5 Thermodynamic Functions for a System of Corrected Boltzons 386
13.6 A Simple System 388
13.6.1 Energy Levels for a Particle in a Box 388
13.6.2 Expression for the Partition Function 389
13.6.3 Expressions for the Thermodynamic Functions 390
13.7 Internal Degrees of Freedom 391
13.8 Microcanonical Partition Functions 392
13.8.1 Translational Partition Function 392
13.8.2 Vibrational Partition Function 392
13.8.3 Rotational Partition Function for Diatomic Molecules 394
13.8.4 Rotational Partition Function for Polyatomic Molecules 395
13.8.5 Electronic Partition Function 395
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.9</td>
<td>Canonical Ensemble</td>
<td>396</td>
</tr>
<tr>
<td>13.10</td>
<td>Canonical Partition Function for Independent Particles</td>
<td>400</td>
</tr>
<tr>
<td>13.10.1</td>
<td>Independent Distinguishable Particles</td>
<td>400</td>
</tr>
<tr>
<td>13.10.2</td>
<td>Independent Indistinguishable Particles</td>
<td>401</td>
</tr>
<tr>
<td>13.11</td>
<td>Heat Capacities of a Crystal</td>
<td>401</td>
</tr>
<tr>
<td>13.11.1</td>
<td>Introduction</td>
<td>401</td>
</tr>
<tr>
<td>13.11.2</td>
<td>Einstein Model</td>
<td>401</td>
</tr>
<tr>
<td>13.11.3</td>
<td>Debye Model</td>
<td>403</td>
</tr>
<tr>
<td>13.12</td>
<td>Evaluation of Entropies</td>
<td>405</td>
</tr>
<tr>
<td>13.13</td>
<td>Third Law of Thermodynamics</td>
<td>406</td>
</tr>
<tr>
<td>13.14</td>
<td>Implications of the Third Law</td>
<td>407</td>
</tr>
<tr>
<td>13.14.1</td>
<td>Heat Capacities</td>
<td>407</td>
</tr>
<tr>
<td>13.14.2</td>
<td>Effect of Pressure and Volume on Entropy at 0 K</td>
<td>407</td>
</tr>
<tr>
<td>13.14.3</td>
<td>Helmholtz Energy and Gibbs Energy at 0 K</td>
<td>407</td>
</tr>
<tr>
<td>13.14.4</td>
<td>Agreement with Statistical Thermodynamics</td>
<td>408</td>
</tr>
</tbody>
</table>

Problems and Solutions Chapters 9 through 13

Appendix

A.1 Legendre Transform
A.1.1 Mathematical Considerations
A.1.2 Application to Thermodynamic Functions
A.2 Lagrange Multipliers
A.2.1 Single Constraint
A.2.2 Multiple Constraints

Bibliography

Textbooks
Handbooks and Tables
Articles

Index
9 Energetics of Chemical Reactions

9.1 Introduction

We now focus our attention on a closed system in which a chemical reaction can take place. The reaction is written as:

$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$ \hspace{1cm} (9.1)

Conventionally, species on the left hand side of equation 9.1 are designated as the reactants, while species on the right hand side are known as products, indicating our potential interest in the reaction when it takes place from left to right. The $|\nu|$ are the stoichiometric coefficients of the reaction. They are positive integers or simple fractional numbers. The stoichiometric coefficients originate in the conservation of atoms in the reactants ($A, B$) and products ($C, D$). We will frequently use this reaction as our typical reaction. We also use another formal representation of chemical reactions which lends itself better to mathematical use. We write reaction 9.1 as:

$\nu_C C + \nu_D D + \nu_A A + \nu_B B = 0$ \hspace{1cm} (9.2)

In equation 9.2, the stoichiometric coefficients are algebraic. The coefficients of the products $C$ and $D$ are conventionally taken as positive, while those of the reactants $A$ and $B$, are negative. This convention has the same implication as equation 9.1, since it indicates that, when
\( \nu_C \) moles of C and \( \nu_D \) moles of D are formed, \( \nu_A \) moles of A have reacted with \( \nu_B \) moles of B. A general reaction can be written:

\[
\sum_i \nu_i M_i = 0 \quad i = 1, 2, \ldots, n \quad (9.3)
\]

where the \( M_i \) refer to chemical species \( i \), and \( n \) is the number of species present in the system. If a species present in the system does not take part in the reaction, its stoichiometric coefficient is simply zero. When several reactions may take place simultaneously, they will be represented by:

\[
\sum_i \nu_{i,k} M_i = 0 \quad \begin{cases} 
  i = 1, 2, \ldots, n \\
  k = 1, 2, \ldots, r 
\end{cases} \quad (9.4)
\]

Each of the \( r \) reactions written in this way implies that atoms are conserved during a chemical reaction.

### 9.2 The Extent of Reaction

We now consider a closed system where only one reaction can take place. We write the equations for both the typical reaction 9.1 and the general formalism (equation 9.3). Let \( n_i^0 \) be the number of moles of species \( i \) in the initial state of the system. When the reaction occurs, the variations of the number of moles of each species, \( n_i \), are not independent, as indicated by the stoichiometric coefficients. This fact can be written:

\[
\begin{aligned}
\frac{dn_1}{\nu_1} &= \cdots = \frac{dn_i}{\nu_i} = \cdots = \frac{d\xi}{\nu_i} \\
\frac{dn_A}{\nu_A} &= \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} = \frac{d\xi}{\nu_D} & \text{for the typical reaction 9.1}
\end{aligned} \quad (9.5)
\]

where the variable \( \xi \) (units of mol) relates the changes in the amount of the chemical species present. By integrating the system of differential equations 9.5 and taking \( \xi = 0 \) as the initial state of the system, we get:

\[
\begin{aligned}
  n_1 &= n_1^0 + \nu_1 \xi, \ldots \quad n_i &= n_i^0 + \nu_i \xi, \ldots \\
  n_A &= n_A^0 + \nu_A \xi \\
  n_B &= n_B^0 + \nu_B \xi \\
  n_C &= n_C^0 + \nu_C \xi \\
  n_D &= n_D^0 + \nu_D \xi
\end{aligned} \quad (9.6)
\]
where we should recall that \( \nu_A \) and \( \nu_B \) are negative numbers. Since all the numbers of moles are always positive (or zero), the range of valid \( \xi \) values is limited. When the variable \( \xi \) spans the entire range of valid values, we cover all of the possible states of the system linked to the chemical reaction, \( \xi \) is called the \textit{extent of the reaction}. This variable is an extensive variable like the number of moles. If the \( n_i^0 \) for the reactants are sufficiently large such that \( \xi = 1 \text{ mol} \) is an allowed value, then this value of \( \xi \) corresponds to the conversion of a number of moles equal to the stoichiometric coefficients.

\[ \text{An increase of } \xi \text{ by } 1 \text{ mol corresponds to the conversion of numbers of moles of reactants to numbers of moles of products corresponding to the stoichiometric coefficients of the reaction.} \]

### 9.3 Variables of Reaction

#### 9.3.1 Gibbs Energy of Reaction (Free Enthalpy of Reaction)

We consider a \textit{closed system}, in which only a single chemical reaction can take place. Let us write the expression of the differential of its Gibbs energy for an \textit{isothermal and isobaric process}. Using 5.26 and 9.5, we have:

\[
dG = \sum_i \mu_i \, dn_i
\]

\[
= \sum_i \mu_i \, v_i \, d\xi = \Delta_r G \, d\xi
\]

\[ \text{with } \Delta_r G = \sum_i \nu_i \mu_i \]

The quantity \( \Delta_r G \) is referred to as the \textit{Gibbs energy of reaction} or the \textit{free enthalpy of reaction}. It is an \textit{intensive variable}. Like chemical potentials, it \textit{depends on the composition of the system}. It corresponds to what the change of the Gibbs energy of the system would be, if, \textit{at constant composition}, the extent of reaction \( \xi \) increased by 1 mol. A number of moles of reactants equal to the stoichiometric coefficients is then transformed into the number of moles equal to the stoichiometric coefficients of products of the reaction.

For a general process, where \( p, T \) as well as the extent of reaction can vary, the differential of the Gibbs energy is:
\[ dG = V \, dp - S \, dT + \left( \frac{\partial G}{\partial \xi} \right)_{p, T} \, d\xi \]
\[ \left( \frac{\partial G}{\partial \xi} \right)_{p, T} = \sum_i v_i \mu_i = \Delta_r G \]

The extensive variable \( \xi \) is associated to the intensive variable \( \Delta_r G \). For a closed system, the changes in the numbers of moles of the various species present are all linked to the change in the reaction extent \( \xi \).

### 9.3.2 Spontaneous Reaction. Equilibrium

We consider again a closed system in which a single chemical reaction can take place. Moreover, we assume that the system can only exchange work due to volume change with its surroundings. An infinitesimal isothermal and isobaric change can take place spontaneously if the corresponding change in the Gibbs energy is such that \( dG < 0 \) (relation 5.82). Equation 9.7 shows that:

- If \( \Delta_r G > 0 \), then the reaction takes place spontaneously from right to left since \( dG < 0 \) implies that \( d\xi < 0 \).
- If \( \Delta_r G < 0 \), then the reaction takes place spontaneously from left to right since \( dG < 0 \) implies that \( d\xi > 0 \).
- If \( \Delta_r G = 0 \), then the system is at equilibrium.

The equilibrium condition is that the enthalpy of reaction be zero and it can also be written:

\[ \Delta_r G = \sum_i v_i \mu_i = 0 \quad \Rightarrow \quad \text{Chemical equilibrium is reached} \]
\[ G \text{ has reached a minimum} \]

### 9.3.3 Systems where Several Reactions can Take Place Simultaneously

In the case of a system with \( n \) chemical species where \( r \) independent reactions\(^\dagger\) can occur, we can write, for each reaction, an equation corresponding to equation 9.5.

\(^\dagger\) We will see in detail in chapter 10 what independent reactions are, and how to determine their number for a given chemical system.
where $\xi_k$ is the extent of the $k^{th}$ reaction. The differential of the Gibbs energy can be expressed in terms of the extents of reaction of the $r$ independent reactions and of their Gibbs energy of reaction. Using 5.26, we obtain:

$$dG = V \, dp - S \, dT + \sum_i \mu_i \sum_k v_{i,k} \, d\xi_k$$

$$\Rightarrow \quad dG = V \, dp - S \, dT + \sum_k \Delta_r G_k \, d\xi_k$$

where $\Delta_r G_k$ is the Gibbs energy of reaction $k$. A spontaneous change can take place until $G$ has reached its minimum value. The equilibrium of the system is obtained when $dG = 0$. Since the process is isothermal, isobaric and the $\xi_k$ are independent, this is achieved when:

$$\Delta_r G_k = \sum_k v_{i,k} \mu_i = 0 \quad \text{for} \quad (k = 1, 2, \ldots, r)$$

At equilibrium, a system where $r$ independent reactions can take place implies the existence of $r$ independent relations between the chemical potentials of the species it contains.

The simultaneous evolution of the reactions affects the chemical potentials of the species. The essential difference here with the case of a single reaction is that the change in Gibbs energy of the system due to one particular reaction can be positive while the system evolution still corresponds to a decrease of its Gibbs energy. Some reactions, that would not take place if carried out alone, can occur if other reactions can take place simultaneously to make the whole process spontaneous. The reactions are said to be coupled.
9.3.4 Other Variables of Reaction

While the Gibbs energy of reaction plays a special role in chemistry since isothermal and isobaric conditions are frequently encountered, other variables of reaction must be considered and are useful to obtain many properties of the Gibbs energy of reaction. Let us consider any extensive variable, \( X \), such as \( U \), \( H \), \( S \), \( A \), \( V \), \( Cp \), or \( CV \), as functions of \( p \), \( T \) and the \( n_i \), the numbers of moles of each species of the system. In a system where a single reaction can take place, under isothermal and isobaric condition, the expression for the differential of the variable is (equation 6.25):

\[
dX = \left( \frac{\partial X}{\partial p} \right)_T, n_i \ dp + \left( \frac{\partial X}{\partial T} \right)_p, n_i \ dT + \sum_i X_i \ dn_i = \Delta_r X \ d\xi
\]

where \( \Delta_r X \) is the variable of reaction corresponding to \( X \). The variables of reaction have therefore simple expressions in terms of the partial molar quantities. We have:

\[
\Delta_r U = \sum_i v_i U_i \quad \Delta_r S = \sum_i v_i S_i \quad \Delta_r A = \sum_i v_i A_i \quad \Delta_r V = \sum_i v_i V_i \quad \Delta_r Cp = \sum_i v_i Cp_i\]

(9.14)

9.3.5 Standard Variables of Reaction

The chemical potentials or the partial molar quantities that are part of the expressions for variables of reaction depend on the composition of the system. Thermodynamic tables contain numerical values of molar quantities for numerous systems for a state of the system known as the standard state. From the values found in the tables, it is subsequently possible to evaluate the variables of interest to various degrees of approximation. The standard state can be selected in various ways as we already saw in chapter 7. In the tables, the standard states as well as the units used can vary. In general, the tables contain, as well as the physical
state of the species, solid (with the crystalline form for solids if several exist), liquid or gas, the pertinent information needed to fully characterize the standard state that has been selected for the tabulation.

- The standard state pressure $p^o$ selected has always a value 1. It can be 1 atm (old convention) or 1 bar (most recent convention).
- The selected temperature is often 298.15 K, which corresponds to $25^oC$.
- The standard state for a species that is gaseous under standard conditions, corresponds to the pure substance behaving as an ideal gas under the standard pressure (Equation 7.60).
- The standard state for a solvent or a pure solid or a liquid, corresponds to the pure substance under the standard pressure $p^o$.
- For solutes, several different standard states can be used. The various possible choices as well as the reasons that motivate their selection will be presented in chapter 12.

To evaluate a standard variable of reaction, we consider a system which in its initial state contains the number of moles of reactants corresponding to their stoichiometric coefficients, taken (pure) in their standard state (for gases, the standard state is a hypothetical state where the gas behaves as an ideal gas). The final state corresponds to the number of moles of products present in the stoichiometric equation again in their standard state. In the stoichiometric equation, the physical state of the species, reactants or products, are mentioned. This is illustrated in Table 9.1 for the reaction 9.1 when all the species participating in the reaction are gaseous.

The variables of reaction thus evaluated are referred to as: $\Delta_r G^o_T$, $\Delta_r H^o_T$, $\Delta_r S^o_T$, etc...

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p = 1$ atm or 1 bar, $T$</td>
<td>$p = 1$ atm or 1 bar, $T$</td>
</tr>
<tr>
<td>$\nu_A$ moles of pure $A$</td>
<td>$\nu_C$ moles of pure $C$</td>
</tr>
<tr>
<td>ideal gas behavior</td>
<td>ideal gas behavior</td>
</tr>
<tr>
<td>$p = 1$ atm or 1 bar, $T$</td>
<td>$p = 1$ atm or 1 bar, $T$</td>
</tr>
<tr>
<td>$\nu_B$ moles of pure $B$</td>
<td>$\nu_D$ moles of pure $D$</td>
</tr>
<tr>
<td>ideal gas behavior</td>
<td>ideal gas behavior</td>
</tr>
</tbody>
</table>

Table 9.1 Chemical process from an initial standard state of the reactants to a final standard state of the products, for reaction 9.1. The gases behave as ideal gases.
The *standard variables of reaction* can be expressed using the result of equation 9.14. Since all of the species are in their standard state, the partial molar quantities are simply the standard molar quantities. We obtain:

\[
\begin{align*}
\Delta_r U^o &= \sum_i v_i U_i^o \\
\Delta_r A^o &= \sum_i v_i A_i^o \\
\Delta_r H^o &= \sum_i v_i H_i^o \\
\Delta_r G^o &= \sum_i v_i \mu_i^o \\
\Delta_r S^o &= \sum_i v_i S_i^o \\
\Delta_r C_p^o &= \sum_i v_i C_{p,i}^o \\
\Delta_r V^o &= \sum_i v_i V_i^o
\end{align*}
\] (9.15)

We should note here that standard molar entropy, standard molar heat capacity and standard molar volume are the only standard extensive variables that are known in an absolute way. The other standard molar quantities in equation 9.15 are not known absolutely and their values depend on the selection of a reference for the energy scale.

### 9.3.6 Standard Variables of Formation

In order to be able to prepare consistent tables of thermodynamic data, it is convenient to introduce the *standard variables of formation* of chemical species which are just a special case of the standard variables of reaction. These are usually found in chemical thermodynamic data tables.

The standard variable of formation of a species corresponds to the change in the corresponding extensive variable when *one mole of substance is formed* in its standard state from the appropriate number of moles of the most stable state of each element it contains taken in its standard state.

- The initial state corresponds to the elements present in the substance, taken in their standard state at the same temperature in the physical state of interest mentioned in the reaction (usually their most stable state at the chosen temperature and standard pressure), the number of moles being equal to the stoichiometric coefficients.
• The final state is one mole of the species of interest in its standard state, at the temperature of interest and in the appropriate physical state as mentioned in the reaction.

• The standard variables of formation of an element in its most stable state at temperature \( T \) and standard state pressure \( p^0 \) are zero, by definition. The reaction of formation of the elements from themselves corresponds to no change.

The standard variables of formation of a species at a temperature \( T \) are represented by:

\[
\Delta_f G^o_T, \Delta_f H^o_T, \Delta_f S^o_T, \Delta_f U^o_T, \Delta_f C_p^o_T, \Delta_f A^o_T, \ldots
\]

Using equation 9.15, the standard variables of formation can be related to standard molar quantities. Let us consider, as an example, the formation of ammonia at 25°C.

\[
\frac{1}{2} \text{N}_2 (g) + \frac{3}{2} \text{H}_2 (g) \rightarrow \text{NH}_3 (g) \quad (9.16)
\]

Under 1 bar at 298.15 K, the elements that constitute ammonia, nitrogen and hydrogen, are stable as molecules. The standard enthalpy of formation of ammonia that is found in the tables, corresponds to (equation 9.15):

\[
\Delta_f H_{298.15}^o (\text{NH}_3) = H_{298.15}^o (\text{NH}_3) - \frac{1}{2} H_{298.15}^o (\text{N}_2) - \frac{3}{2} H_{298.15}^o (\text{H}_2) \quad (9.17)
\]

In thermodynamic tables, data can be found on a number of chemicals. The data found most frequently are:

\[
\begin{align*}
\Delta_f G_{298.15}^o & \quad \text{Standard Gibbs energy of formation} \\
\Delta_f H_{298.15}^o & \quad \text{Standard enthalpy of formation} \\
S_{298.15}^o & \quad \text{Standard entropy} \\
C_p^{o,298.15} & \quad \text{Standard molar heat capacity at constant pressure}
\end{align*}
\]

Only the first two are standard variables of formation. They always refer to one mole of the species that is been formed. The other two are standard molar quantities. The last three can be used to obtain the first one and to calculate other standard formation or reaction variables (for example at different temperatures). The standard Gibbs energies of formation allow the calculations of standard Gibbs energy of a reaction, \( \Delta_f G_{298.15}^o \), which leads to the knowledge of the equilibrium constant of a reaction (as we will see in chapter 10).
9.4 Hess’s Law

9.4.1 Content

Hess’s Law is a direct consequence of the fact that the change of a state function during a thermodynamic change is independent of the path selected to effect the change. It applies to reaction enthalpies and can be stated in the following way:

*The enthalpy of a reaction is equal to the sum of the enthalpies of other reactions into which it can be formally decomposed.*

Since variables of reactions are evaluated from the change of some extensive variable between two well defined states, this law can be generalized to any variable of reaction.

9.4.2 Application

This law can be used to obtain the standard enthalpy of a reaction from standard enthalpies of formation. Let us consider as an example, the oxidation of ammonia by oxygen:

\[
2 \text{NH}_3(g) + \frac{5}{2} \text{O}_2(g) \rightarrow 2 \text{NO}(g) + 3 \text{H}_2\text{O}(g) \quad (9.18)
\]

The standard enthalpy of reaction can be computed from the initial and final states of a system as presented in Table 9.2.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p = 1 \text{ atm or 1 bar}, \ T )</td>
<td>( p = 1 \text{ atm or 1 bar}, \ T )</td>
</tr>
<tr>
<td>2 moles of pure ( \text{NH}_3 ) ideal gas</td>
<td>2 moles of pure ( \text{NO} ) ideal gas</td>
</tr>
<tr>
<td>( p = 1 \text{ atm or 1 bar}, \ T )</td>
<td>( p = 1 \text{ atm or 1 bar}, \ T )</td>
</tr>
<tr>
<td>( \frac{5}{2} ) moles of pure ( \text{O}_2 ) ideal gas</td>
<td>3 moles of pure ( \text{H}_2\text{O} ) ideal gas</td>
</tr>
</tbody>
</table>

**Table 9.2** Initial and final standard state of the oxidation of gaseous ammonia according to reaction 9.18. The gases behave as ideal gases.
Using Hess’s law, we can consider an intermediate state of the system made of the elements of the reactants. We write:

\[
2 \text{NH}_3 (g) + \frac{5}{2} \text{O}_2 (g) \rightarrow \text{N}_2 (g) + 3 \text{H}_2 (g) + \frac{5}{2} \text{O}_2 (g) \quad (9.19)
\]

\[
\text{N}_2 (g) + 3 \text{H}_2 (g) + \frac{5}{2} \text{O}_2 (g) \rightarrow 2 \text{NO} (g) + 3 \text{H}_2\text{O} (g) \quad (9.20)
\]

Let us write the standard enthalpies of reactions for the reactions 9.19 and 9.20 in terms of the standard variables of formation. Taking into account the fact that the standard enthalpy of formation of the elements are conventionally taken as zero, we have:

\[
\begin{align*}
\Delta H^\circ_T (9.19) &= -2 \Delta H^\circ_T (\text{NH}_3 (g)) \\
\Delta H^\circ_T (9.20) &= 2 \Delta H^\circ_T (\text{NO} (g)) + 3 \Delta H^\circ_T (\text{H}_2\text{O} (g))
\end{align*}
\]

(9.21)

Enthalpies of formation of \text{N}_2, \text{H}_2 and \text{O}_2 are not in equation 9.21 since they are zero. For reaction 9.18, we obtain:

\[
\begin{align*}
\Delta H^\circ_T (9.18) &= \Delta H^\circ_T (9.19) + \Delta H^\circ_T (9.20) \\
&= 2 \Delta H^\circ_T (\text{NO} (g)) + 3 \Delta H^\circ_T (\text{H}_2\text{O} (g)) \\
&\quad - 2 \Delta H^\circ_T (\text{NH}_3 (g))
\end{align*}
\]

(9.22)

Using directly equations 9.15 for reaction 9.18, we would have found:

\[
\begin{align*}
\Delta H^\circ_T (9.18) &= 2 H^\circ_T (\text{NO} (g)) + 3 H^\circ_T (\text{H}_2\text{O} (g)) \\
&\quad - 2 H^\circ_T (\text{NH}_3 (g)) - \frac{5}{2} H^\circ_T (\text{O}_2 (g))
\end{align*}
\]

(9.23)

which corresponds to what we would obtain using equation 9.15 in equation 9.22.
9.4.3 Generalization

The result obtained for $\Delta_H^o_T$ can be generalized to any standard variable of reaction. We have:

$$\Delta_X^o_T = \sum_i v_i X_i^o_T = \sum_i v_i \Delta_f X_i^o_T$$

(9.24)

and a standard variable of reaction may be obtained from the standard variables of formation. In view of Hess’s law and equations 9.15, we can write the following relations for some of the standard variables of reaction:

$$\Delta G^o_T = \sum_i v_i \mu_i^o_T = \sum_i v_i \Delta_f G_i^o_T$$

$$\Delta H^o_T = \sum_i v_i H_i^o_T = \sum_i v_i \Delta_f H_i^o_T$$

$$\Delta U^o_T = \sum_i v_i U_i^o_T = \sum_i v_i \Delta_f U_i^o_T$$

$$\Delta S^o_T = \sum_i v_i S_i^o_T = \sum_i v_i \Delta_f S_i^o_T$$

(9.25)

For a reaction taking place at temperature $T$, we can write, using 5.1, 5.2 and 5.3:

$$\Delta_f A = \Delta_f U - T \Delta_f S$$

$$\Delta_f G = \Delta_f H - T \Delta_f S$$

(9.26)

While these relations are of course valid for the variables of reactions in general, they can be applied to standard variables of reaction to relate the various values found in the tables of thermodynamic data.

9.4.4 Example

To illustrate our findings, let us calculate the standard enthalpy and the standard Gibbs energy (standard free enthalpy) of reaction for the complete oxidation of ethanol by oxygen at 298.15 K. The reaction is:

$$\text{C}_2\text{H}_5\text{OH (l)} + 3 \text{O}_2 (g) \rightarrow 2 \text{CO}_2 (g) + 3 \text{H}_2\text{O (l)}$$

(9.27)
In table 9.3, we have gathered the thermodynamic data concerning the species of this system. We have included two different standard pressures and different energy units. Selecting the standard pressure as 1 bar, let us write the expressions for the standard enthalpy of reaction for reaction 9.27:

\[
\Delta H^\circ_{298.15} = \sum_i v_i \Delta H^\circ_{1,298.15}
\]

\[
= 2 \Delta H^\circ_{298.15} (CO_2 (g)) + 3 \Delta H^\circ_{298.15} (H_2O (l)) - \Delta H^\circ_{298.15} (C_2H_5OH (l))
\]

\[
= 2 (-393.51) + 3 (-285.830) - (-277.69)
\]

\[
= -1366.82 \text{ kJ mol}^{-1}
\]

The standard enthalpy of reaction obtained is negative. During this process, the system delivers heat to the surroundings. In such a case, the reaction is said to be **exothermic**. If the standard enthalpy of a reaction is positive, then the reaction is said to be **endothermic**.

In a similar way, we can calculate the standard reaction entropy, using 9.14 or 9.15.
Index

Pages 1 through 270 are in Volume 1.
Pages 271 through 542 are in Volume 2.

Italic page numbers refer to problems.

Activity
coefficient and molality, 368, 489
coefficient in the concentration scale, 369
coefficient of a species in a real solution, 351
coefficient using convention I, 355, 489
coefficient using convention II, 362, 489
effect of temperature and pressure on the — coefficient, 353
of a condensed phase, 308
of a pure condensed phase, 307
of a species in a real solution, 351
relation between convention I and II in solutions, 364

Adiabatic
change of a van der Waals gas, 169
closed — system, 38, 237
enclosure, 4, 23
irreversible — process, 171
open — system, 172
process, 23, 169, 182
reversible process of an ideal gas, 51, 108, 185
reversible process, 33

Affinity
definition, 303
of a reaction, 303

Air conditioner, 56

Auxiliary
functions, 65, 205
state variable, 4

Avogadro’s number, 31
Azeotropy, 357-360

Batteries
lead storage —, 291
—, 290

Beau de Rochas cycle, 58

Binary
mixture, 337, 340, 342, 463, 464, 467, 486
system, 356, 486, 487

Boiling
elevation of the — point of a solvent in the presence of a solute, 347, 467
point curve, 340, 463, 464

Boltzmann constant, 30
Boltzons
—, 380
corrected —, 382
thermodynamic functions for a system of corrected —, 386

Bose-Einstein Statistics, 379, 380
Bosons, 381

Canonical
ensemble, 396-399
partition function, 398, 401, 511

Carbon monoxide
reduction of iron oxides by —, 328

Carnot
cycle, 32, 50
reverse — cycle, 34

Change
isothermal reversible — of a gas, 17
of a state variable, 7
of the Gibbs energy in a mixture of chemical species, 300, 431
of the Gibbs energy with the extent of reaction, 300, 302, 431
The Bases of Chemical Thermodynamics

Characteristic variables, 68-73, 536
Châtelier
Le —'s principle, 321-326, 432
Chemical
condition for — equilibrium, 274
conversion of — energy into work, 288, 289, 414
equilibrium, 299-335, See also
Chemical equilibrium
independent — reactions, 310
reaction, 271
spontaneous — reaction, 299
Chemical equilibrium
effect of an inert gas on a —, 431
effect of pressure on a —, 322
effect of species in excess on a —, 324
effect of temperature on a —, 321
effect of volume on a —, 323
reduction of iron oxides, 327
—, 274, 299-335, 427
Chemical potential
definition, 70
intensive property, 92
of a multiphase system at equilibrium, 135
of a pure condensed phase, 307
of a pure real gas, 118
of a real gas in a mixture, 127
of a species in a real solution, 351
of an ideal component, 338
of an ideal gas in a mixture, 113-114
of ions in solution, 372
relations, 72
standard —, 106
Chemical reaction
isothermal and isobaric —, 273
system with several —s, 274
volume work for a —, 17
Chloroform
liquid state study of —, 208
Choice
of the standard state pressure, 293

Clapeyron equation, 139, 255
Clausius inequality, 42
Clausius-Clapeyron equation, 142
Closed
adiabatic system, 40, 43, 237
system with one chemical reaction, 271
system, 2
Coefficient
activity — and molality, 368, 489
activity — and the concentration scale, 369
fugacity — of a pure real gas, 119, 238
fugacity — of a real gas in a mixture, 128
fugacity —, 118, 238
isobaric — of thermal expansion, 7
isothermal compressibility —, 6, 7, 155
Joule-Thomson —, 125
of performance, 55, 57
partition —, 366
stoichiometric —s, 271, 428, 429, 433
thermal expansion —, 6
van der Waals —, 121
Combustion
internal — engine, 58
variables of —, 297
Complex
van der Waals —, 118
Components
Number of —s in a system, 318
Composition
molality and —, 367
mole fraction scale, 351
of the vapor phase of a binary solution, 340, 342, 361, 362, 464
Compressibility
factor, 119, 237
isothermal — coefficient of an ideal
gas, 156
isothermal — coefficient, 6, 7, 155
Index

Compression
  isothermal — of an ideal gas, 47
  monothermal — of an ideal gas, 47
  of a gas, 9, 16
  ratio, 60, 64
Concentration
  and composition, 369
  scale, 369
Condensation
  curve, 340, 342, 359, 361, 464
  —, 141
Condensed phase
  choice of the standard state of a —, 296
Constant
  critical —s, 122, 236
  Henry’s —, 364, 365
  Raoult’s —, 339, 365
  standard equilibrium —, 305, 489
  thermodynamic equilibrium —, 305
  volume thermal expansion coefficient, 7
Constant pressure
  process at —, 67, 164
Constant volume
  process at —, 66
Continuity of the fluid state, 148
Convention
  for aqueous systems, 374
  I for the standard state and activity coefficient, 354, 486
  II for the standard state and activity coefficient, 362, 489
  relation between — I and II, 364
  relation between — II and the molality scale, 368, 489
  sign — for energy exchanges, 13
  — for activity coefficients in solutions, 352-369, 485
Conversion of chemical energy into work, 288-289, 414
Corrected boltzons, 382
Corresponding states of real gases, 123
Creation of entropy, 41
Critical
  constants, 122, 236
  point, 122, 148, 236
  temperature, 121
Crystallization, 141
Curve
  condensation —, 342
  inversion —, 126
  vaporization —, 340, 342, 463, 464
Cycle
  Beau de Rochas —, 58
  Carnot — of an ideal gas, 50
  Carnot —, 32
  dithermal —, 32
  engine —, 33
  Joule —, 63
  Otto —, 58
  reverse Carnot —, 34
  reversible — of two systems, 33
  Stirling —, 60
Cyclic
  process of a gas, 207
  process, 8, 24, 185
Dalton’s law, 110
Debye
  model, 403
  temperature, 404
Debye-Hückel theory, 373
Degrees of freedom
  number of —, 138
  —, 391
Delay
  phase change —s, 150
Depression
  of the freezing point in the presence of
  a solute, 345, 465
Dew point curve, 340, 342, 359, 361, 464
Diagram
  isobaric — for a perfect binary
  solution, 342, 464
isothermal — for a perfect binary solution, 340
phase —, 146
Diamond
   equilibrium of — and graphite, 431
Diathermal enclosure, 4
Differential
   exact —, 9-10
Differential expression
   for state functions (multiple phases), 134
   — for the enthalpy, 70
   — for the entropy, 206
   — for the free energy, 71
   — for the free enthalpy, 71
   — for the Gibbs energy, 71
   — for the Gibbs function, 71
   — for the Helmholtz function, 71
   — for the internal energy, 69
   —, 155
   — for open systems, 72
Dilute solutions, 355, 363, 368, 369
Dilute systems, 382
Dissociation equilibrium, 373
Distribution
   laws in statistical mechanics, 379
   most probable —, 397
Diathermal cycle, 32
Dulong and Petit’s law, 401
Effect
   Joule–Thomson —, 124, 239
   of an inert gas on chemical equilibria, 323, 431
   of an inert gas on vapor pressure, 144, 256
   of pressure on chemical equilibria, 322, 432
   of pressure on phase equilibrium, 255
   of species in excess on chemical equilibria, 324, 433
   of temperature and pressure on the activity coefficient, 353
The Bases of Chemical Thermodynamics
   of temperature on chemical equilibria, 321, 427, 432
   of temperature on the entropy of reaction, 286, 412, 413
   of temperature on the Gibbs energy of reaction, 286, 412, 413
   of temperature on the latent heat, 145, 256
   of temperature on vapor pressure, 145, 255, 256
   of volume on chemical equilibria, 323
Efficiency of an engine, 55, 59
Einstein
   model, 401
   temperature, 402
Electrical work, 18
Electrode potential
   and standard entropy, 376
   definition, 376
Electrolyte
   chemical potential of ions in solution, 372
   dissociation, 371
Electroneutrality of a solution, 371
Electronic partition function, 395
Elevation of the boiling point of solvent in the presence of a solute, 347, 467
Enclosure
   adiabatic —, 4, 23
   diathermal —, 4
Endothermic reaction, 283
Energetics of chemical reactions, 271-297, 411
Energy
   free —, 70
   Gibbs —, 66
   Helmholtz —, 66
   internal —, 22, 69
   levels for a particle in a box, 389
   sign convention for — exchanges, 13
   various forms of —, 19
Index

Engine cycle, 33
Ensemble
  canonical —, 396-399
  microcanonical —, 384, 396
Enthalpy
  explicit expression for the —, 94
  free — of reaction, 273
  of a phase change, 257
  of an ideal mixture of gases, 131
  of mixing, 112, 129, 344
  of phase change, 141
  of reaction, 276
  standard — of formation, 279
  —, 6, 65
Entropy
  a first glance at —, 29
  and irreversible adiabatic process of an ideal gas, 185
  and probability, 378
  change during freezing, 182
  change of — of an ideal gas due to a change of state, 107, 235
  created, 41
  definition, 35
  effect of temperature on the — of reaction, 286, 412, 413
  evaluating —, 405
  global —, 42, 81, 82, 112, 182, 206, 207, 258, 288, 290
  of a gas mixture and statistical mechanics, 512
  of an ideal gas, 106, 206
  of mixing, 110, 235, 344, 353, 514
  of reaction, 276, 376
  standard —, 279, 514
  state function, 36-38
  variation at 0 K with volume and pressure, 407
Equation
  Clapeyron —, 139, 255
  Clausius-Clapeyron —, 142
  Gibbs-Duhem —, 95
  Kirchoff’s —, 284-286, 413, 437
  van der Waals — of state, 120, 236, 237
  van’t Hoff’s —, 320
  virial —, 119, 236
Equation of state
  for a gas when internal energy is independent of volume, 206
  of a pure liquid, 156, 307
  thermodynamic, 75-77
  van der Waals —, 120, 236, 237
  — of an ideal gas, 77
Equilibria
  simultaneous —, 428
Equilibrium
  condition for chemical —, 274
  condition, 43, 86, 300
  constant in the liquid phase, 370
  constant, 305
  displacement laws, 321, 432
  dissociation —, 373
  effect of an inert gas on a chemical —, 323, 431
  effect of pressure on a chemical —, 322
  effect of pressure on phase —, 255, 431
  effect of species in excess on a chemical —, 324
  effect of temperature and pressure on liquid vapor —, 344
  effect of temperature on a chemical —, 321
  effect of temperature on the — constant, 319, 427
  effect of volume on a chemical —, 323
  gas and condensed phase, 141
  liquid vapor —, 340, 466
  mechanical —, 3
  of a chemical system, 3
  of two phases, 139-146, 255
  reaction extent at —, 429, 430, 433
  reduction of iron oxides, 327-335
  solid liquid —, 255, 467, 468
  standard — constant, 305, 489
  system in a state of —, 3
  thermal —, 3, 43
  thermodynamic — constant, 305
Equilibrium constant
  in heterogeneous systems, 308
  in solutions, 370
  in the gas phase, 306
  in the liquid phase, 370
  standard —, 305
Euler’s identity, 90, 93
Eutectic
  mixture, 467
  temperature, 467
Evaluation of entropies, 405
Evaporation, 141
Exact differential, 9-10, 155, 157
Excess
  entropy of mixing (gases), 129
  entropy of mixing, 353
  Gibbs energy of mixing (gases), 129
  Gibbs energy of mixing, 353, 486
  variable of mixing (gases), 129
  variable of mixing, 352, 486
Exothermic reaction, 283
Expansion
  isobaric coefficient of thermal — of an ideal gas, 156
  isobaric coefficient of thermal —, 6, 155
  isothermal — of an ideal gas, 47
  monothermal — of an ideal gas, 47, 49-50
  of a gas, 9
Explicit expression
  for enthalpy, 94
  for internal energy, 93
  for the Gibbs energy, 94
  for the Helmholtz energy, 94
Expression
  explicit — for the Gibbs energy, 94
  explicit — for the Helmholtz energy, 94
  for partial molar volumes, 225, 226
  general — of state functions for multiphase systems, 136
  of the molar entropy of an ideal gas, 106

Extensive
  properties of — variables, 90
  variable, 5, 93
Extent
  Change of the Gibbs energy with the — of reaction, 300, 431
  change of the Gibbs energy with the — of reaction, 302
  effect of temperature on the — of reaction, 430, 432
  maximum value of the — of reaction, 301
  of reaction and expression of enthalpy, 285
  of reaction and maximum work, 292
  of reaction and work, 288, 289
  of reaction for independent reactions, 275
  of reaction, 411, 429
Extraction
  liquid-liquid —, 366
Factor
  integrating —, 157
Fermi-Dirac Statistics, 379, 381
Fermions, 381
Field
  magnetic —, 20
First law
  about the —, 21-25
  of thermodynamics, 169
Fluid
  continuity of the — state, 148
Force
  external —, 14
  van der Waals —, 116
  work of an external —, 14
Formation
  standard enthalpy of —, 279
  standard Gibbs energy of —, 279
  standard Helmholtz energy of —, 279
  standard variables of —, 278
Forward
  Carnot cycle, 33
  reaction, 304
Free
energy, 66, 70, See also Helmholtz
enthalpy, 6, 66, 71, See also Gibbs
energy
Freedom
degrees of —, 391, See also Variance
Freezing
point depression by a solute, 345, 465
spontaneous — of water, 205
temperature of sea water, 467
—, 141
Fugacity
and the law of mass action, 305
coefficient of a pure real gas, 119, 238
coefficient, 118, 238
definition, 118
of a real gas in a mixture, 128
Function
auxiliary state —, 65, 205
canonical partition —, 401
homogeneous —s, 89-90
microcanonical partition —, 386, 392, 511, 513, 515
of mixing, 114-116
properties of homogeneous —s, 89-90
rotational partition —, 394
state —, 10
thermodynamic —s for a system of
corrected boltzons, 386
thermodynamic —s in the
microcanonical ensemble, 390
translational partition —, 392
Fundamental state variables, 4
Fusion
curve, 146
latent heat of —, 346, 466
—, 141
Gas
constant, 11
Effect of an inert — on vapor pressure, 144, 256
Equation of state of an ideal —, 11
ideal — mixture, 108
real —es, 116
thermodynamics of —es, 105-132
Gauss elimination, 314
General process, 7, 23
Generalization of Hess’s law, 282
Gibbs
change of the — energy with the extent
of reaction, 411
effect of temperature on the — energy, 286, 412, 413
excess — energy of mixing (gases), 129
excess — energy of mixing (solutions), 353, 486
explicit expression for the — energy, 94
function, 6, 66
Gibbs energy
and extent of reaction, 411
and vaporization, 257
at 0 K, 407
minimum and equilibrium, 300
of a mixture of reactants, 300, 431
of formation of hydrogen ions, 374
of mixing in solutions, 344, 463
of mixing of an ideal gas mixture, 110, 235
of mixing of real gases, 129
of mixing, 112, 344, 352, 463
of reaction, 273, 276
—, 66
Gibbs-Duhem
application of the — equation, 356, 486, 487
equation, 95
Gibbs-Helmholtz equations, 73
Global
entropy and spontaneity, 49, 182, 184, 258
entropy change during vaporization,
257
entropy, 42, 81, 82, 112, 182, 206, 207, 258, 288, 290
Graphite
- equilibrium of — and diamond, 431

Half-cell standard potential, 376

Heat
- about —, 21-22
- engine, 32, 55
- pump, 55, 57, 186
- source, 4
- system in contact with several — sources, 42
- system in contact with two — sources, 32
- transfer, 28, 182

Heat capacity
- at constant pressure, 68
- at constant volume, 67
- molar —, 52
- of a crystal at constant volume, 401-405
- of reaction, 276
- statistical studies, 401

Helmholtz energy
- at 0 K, 407
- explicit expression for the —, 94
- of mixing, 110, 235
- of reaction, 276
- —, 66

Helmholtz function, 6, 66, 70

Henry’s
- constant, 364, 365
- law, 363, 488, 489

Hess’s law, 280

Heterogeneous
- example of — system, 328
- system and equilibrium, 429, 431
- system, 3
- systems and the law of mass action, 308

Homogeneous
- functions, 89-90
- system, 3

Hydrogen
- ion convention for aqueous solutions, 374
- reduction of iron oxides by —, 333

The Bases of Chemical Thermodynamics

Ideal
- component, 338
- enthalpy of an — mixture of gases, 131
- internal energy of an — mixture of gases, 132
- Mixture of gases, 130-132
- mixture of ideal gases, 108
- perfect and — solutions, 337-350
- species, 338

Ideal gas
- definition, 77
- equation of state of an —, 11
- law of mass action for —es, 305
- mixture of —es, 108
- partial pressure of an —, 109

Identity
- Euler’s —, 90, 93

Implications
- of the first law, 23
- of the second law, 38
- of the third law, 407

Independent reactions
- and the law of mass action, 317
- number of —, 311, 314, 428, 429
- —, 310, 315, 329

Inert
- effect of an — gas on chemical equilibria, 323, 431
- effect of an — gas on vapor pressure, 144, 256

Infinitesimal process, 24

Integrating factor, 157

Intensive
- properties of — variables, 91
- variable, 5, 92

Internal energy
- differential expression for the —, 45
- explicit expression for the —, 93
- expression for the —, 45
- of an ideal mixture of gases, 132
- of mixing, 111, 129
- of reaction, 276
- of van der Waals gas, 156
- —, 22, 25, 69
Invariant system, 148
Inversion curve and temperature, 126, 239
Ionic strength, 373
Ions
   chemical potential of — in solutions, 372
   law of mass action for —, 374
Irreversible
   (real) process, 11
   adiabatic change of an ideal gas, 171
   mixing, 206
   mixture of ice and water, 256
   process in an open system, 186, 187
   process, 35, 163
   vaporization, 257
Isenthalpic process, 125, 240
Isentropic process, 38, 52
Isobaric
   and isothermal process, 86, 87
   coefficient of thermal expansion of an ideal gas, 156
   coefficient of thermal expansion, 6, 155
   diagram for a perfect binary solution, 342, 464
   diagram, 361
   expansivity, 7
   phase change, 147
   process, 67, 169
   representation, 361
Isochoric process, 66, 169, 181
Isolated system, 2
Isothermal
   compressibility coefficient of an ideal gas, 156
   compressibility coefficient, 6, 7, 155
   compression of an ideal gas, 47
   diagram, 360
   expansion of an ideal gas, 47
   phase change, 146
   process of an ideal gas, 50
   process, 181
   representation of perfect solution
   liquid vapor equilibrium, 340
   reversible process, 33, 163
Isotope
   entropy of an — mixture, 512
Joule
   cycle, 63
   energy unit, 22
   the — experiment, 22, 169, 182
Joule-Thomson
   coefficient, 125
   effect, 124, 239
Justification of the choice of the standard state pressure, 293
Kirchoff’s equation, 284-286, 413, 437
Lagrange multipliers, 136, 385, 397, 433, 512, 514, 537
Latent heat
   and triple point, 255
   effect of temperature on the —, 145, 256
   of fusion, 346, 466
   of phase change, 141
   of vaporization, 347
   variation of the — of vaporization with temperature, 257
Law
   Dalton’s —, 110
   displacement —s of equilibria, 321, 432
   Henry’s —, 363, 488, 489
   Hess’s —, 280
   of mass action for a heterogeneous system, 308, 310
   of mass action for ideal gases, 305
   of mass action for ions, 374
   of mass action in a liquid phase, 369
   of mass action in solutions, 369
   of mass action, 304
   Raoult’s —, 339, 340, 366
Law of thermodynamics
   first —, 21-25
   second —, 27-64
   third —, 406-408
Le Châtelier’s principle, 321-326, 432
Lead storage batteries, 291
Legendre transform, 535
Lennard-Jones interaction, 117
Lever rule, 342, 343
Lewis-Randall rule, 132
Liquid
  process at constant volume or pressure
  in a —, 208
Loss
  small —es, 11
Magnetic field, 20
Mass action
  law of —, 304-310
Maximum
  efficiency, 56
  entropy, 43
  of the extent of reaction, 301
  usable work, 46-47
Maxwell
  —’s relations, 73-75
Maxwell-Boltzmann statistics, 379
Measurement
  of partial molar volumes, 100-103
Mechanical equilibrium, 3
Mechanics
  statistical —, 25, 377, 511
Metastable state, 43, 431
Microcanonical
  ensemble, 384, 396
  partition function, 386, 392, 515
Microstate
  number of —s, 384
Mixing
  enthalpy of —, 112, 129, 344
  entropy of —, 110, 235, 344, 463, 514
  excess entropy of —, 353
  excess variable of — (gases), 129
  function of —, 114
Gibbs energy of — of real gases, 129
Gibbs energy of —, 110, 235, 344, 463
The Bases of Chemical Thermodynamics

Helmholtz energy of —, 110, 235
internal energy of —, 111, 129
irreversible — of two ideal gases, 113
process, 27
properties of ideal solutions, 343
variable of — for ideal gases, 110
variable of — for real gases, 128
variable of —, 114, 352, 486
volume of — of real gases, 128
volume of —, 101, 232, 344
Mixture
  azeotropic —, 359
  binary —, 463
  binary, 337, 340, 342, 464, 467, 486
  chemical potential of an ideal gas in a —, 113
  fugacity of a real gas in a —, 128
  ideal — of gases, 130-132
  ideal —s of ideal gases, 108
  law of mass action for a — of gases, 304
  standard state of a real gas in a —, 128
  water-acetic acid —, 226
  water-ethanol —, 100, 225
  water-glycerol —, 226
  —s of ideal gases, 108
  —s of real gases, 127
Model
  Debye — for heat capacity, 403
  Einstein — for heat capacity, 401
Molality
  definition, 367
  scale, 367
Molar
  heat capacity, 52
  partial — entropy, 353
  partial — quantities, 89-103, 225, 226
  partial — volume, 100-103
  properties, 98
  quantities, 96, 98
  volume of a mixture, 226
Molarity, 369
Index

Mole fraction
  in an ideal gas mixture, 112
  intensive property, 93
  of a species in a solution, 338
Molecular
  interactions in real gases, 116
  partition function, 386
Moment of inertia, 394
Monobaric
  monothermal process, 84
Monothermal
  change of a van der Waals gas, 170
  irreversible process, 163, 205
  monobaric process, 84
  process, 31, 169
Multiple step process, 170
Multipliers
  Lagrange —, 136, 385, 397, 433, 512, 514, 537
Natural variables, 68, 536
Number
  of chemical species in a system, 138, 318
  of components of a system, 318
  of independent species in a system, 318
  of independent reactions, 311, 314, 428, 429
  of phases in a system, 138
Open system
  and irreversible process, 186, 187
  change, 172
  —, 2, 68, 136
Osmotic pressure, 348, 467, 491
Otto cycle, 58
Oxidation of ethanol, 283
Partial
  molar entropy, 353
  molar quantities of pure substances, 98
  molar quantities, 89, 96-103, 225, 226
  molar volume, 100-103, 225, 226
  pressure of an ideal gas, 109
Particle
  energy levels for a — in a box, 389
  in a box, 388-391, 511, 513, 515
Particles
  distinguishable and independent —,
  400
  distinguishable —, 379
  independent and indistinguishable —,
  401
  indistinguishable —, 379
Partition
  canonical — function, 398, 511
  coefficient, 366
  function for a crystalline solid, 401
  function for a particle in a box, 389, 515
  function, 386
Perfect
  and ideal solutions, 337-350
  solution, 340
Phase
  activity of a pure condensed —, 308
  chemical potential of a condensed —,
  307
  condensed —, 296
  definition, 133
  diagram, 146
  law of mass action in the liquid —, 369
  number of —s in a system, 138
  rule and electrolytes, 372
  rule and examples, 318
  rule, 5, 138-139, 317-319
Phase change
  and thermodynamic functions, 142
  delays, 150
  isobaric —, 147
  isothermal —, 146
Physical meaning of
  free energy, 81-84
  free enthalpy, 84-86
  Gibbs function, 84-86
  Helmholtz function, 81-84
Point
  critical —, 148
  triple —, 35, 147
Potential
half-cell standard —, 376
reduction —, 376

Pressure
effect of — on chemical equilibria, 322, 432
effect of — on the activity coefficient, 353
intensive variable, 92
osmotic —, 348, 467, 491
standard state —, 106, 277

Principle
Le Châtelier’s —, 321-326, 432

Probability and entropy, 378

Probable
most — distribution, 397

Process
adiabatic —, 23
at constant external pressure, 16
at constant pressure, 67
at constant volume, 66
chemical —, 271
cyclic —, 8, 24
irreversible —, 11, 35
isenthalpic —, 125, 240
isobaric —, 67, 163, 169
isochoric —, 66, 163, 169
isothermal and isobaric —, 86, 87
isothermal —, 86, 163, 181
mixing —, 27
monothermal —, 31
multiple step —, 170
reverse — and work, 18
reversible adiabatic — of an ideal gas, 51, 185
reversible —, 11, 35
spontaneous —, 38, 43, 113

Properties
of a state function, 10
of extensive variables, 90
of homogeneous functions, 89-90
of intensive variables, 91

The Bases of Chemical Thermodynamics

Pure
chemical potential of a — real gas, 118
real gas, 116

Quantum number
rotation —, 394
vibration —, 393
—s, 391

Rank of a matrix, 312, 314, 316, 329, 428, 429

Raoult’s
constant, 339, 365
law, 339, 340, 366

Rare gas
standard entropy of —es, 511

Real
mixtures of — gases, 127
solution, 351, 485
volume of mixing of — gases, 128

Real gas
fugacity of a — in a mixture, 128
partial molar volume of a —, 128
pure —, 116

Reduced variables, 122

Reduction
of iron oxides, 327-335
potential, 376

Reference state for entropy, 406

Refrigerator, 55, 56

Relation
between activity coefficients in binary systems, 356, 486, 487
between $C_p$ and $C_V$, 78-79
between partial molar quantities, 97, 98

Reverse
Carnot cycle, 34
process and the sign of work, 18
reaction, 304
Reversible
  adiabatic process of an ideal gas, 51, 185
  approximation of a — process, 170
  isothermal expansion or compression of an ideal gas, 47
  process, 11, 35, 163, 170
Rotational partition function, 394
Rule
  lever —, 342, 343
  Lewis-Randall —, 132
  phase — and electrolytes, 372
  phase —, 5, 138-139
Schwarz theorem, 10, 73, 74, 80
Second law of thermodynamics
  First form of the —, 31
  molecular scale, 27
  —, 43
Selection of the standard state pressure, 106
SI units, 163
Sign convention for energy exchange, 13
Simultaneous
  independent — reactions, 310
  reactions, 274, 428
Solid
  as one crystalline form, 146
  liquid equilibrium, 255
  with several crystalline forms, 150
Solidification, 141
Solubility
  in a binary mixture, 467
  in an perfect binary mixture, 468
Solute
  effect of a — on the boiling temperature, 347, 467
  freezing point depression by a —, 345 —, 345, 362
Solution
  ideal —, 338
  isothermal diagram, 340
  non ideal —, 351, 485
  perfect and ideal —s, 337-350
  perfect —, 340
  real —, 351, 485
Solvent
  depression of the freezing point of a — by a solute, 345, 465
  elevation of the boiling temperature of a — by a solute, 347, 467
  —, 345, 362
Source voltage, 19
Species in excess
  effect of — on chemical equilibria, 324, 433
Spontaneous
  evolution of a system, 86, 205
  freezing of water, 205
  process at constant Gibbs energy, 257
  process, 43, 113
  reaction, 274, 299
  transfer of species between phases, 137
  vaporization of ethanol, 257
Standard
  chemical potential in liquids, 355
  chemical potential using convention I, 355
  chemical potential using convention II, 363
  chemical potential, 106
  electrochemical cell potential, 293, 414
  entropy of the electron, 376
  entropy, 279, 514
  equilibrium constant, 305, 489
  Gibbs energy of formation, 279
  heat capacity at constant pressure, 279
  Helmholtz energy of formation, 279
  molar heat capacity at constant pressure, 279
  quantity, 106
  state on the molality scale, 368, 489
  state pressure, 106
  state, 277
thermodynamic functions of oxygen, 515
variable of combustion, 297
variable of reaction, 276, 411, 412, 413

Standard state
and convention I, 486
and convention II, 489
choice of the — for a condensed phase, 296
effect of the choice of the — on the
thermodynamic tables, 293
effect of the choice of the — of a real
gas, 296
effect of the choice of the — of an ideal
gas, 294
of a real gas in a mixture, 128
of a real gas, 118, 296
of an ideal gas, 294
pressure, 106, 277
temperature, 277

State
(corresponding —s of real gases, 123
effect of the choice of the standard —
for an ideal gas, 294
equation of —, 11
function, 4, 6, 10, 38
metastable —, 43, 431
standard — and convention I for the
activity coefficient, 354, 486
standard — and convention II for the
activity coefficient, 362, 489
standard —, 277
variable of —, 4, 6

Statistical
mechanics of a gas mixture, 512
mechanics, 25, 377, 511
models, 379

Statistical thermodynamics
agreement of the third law with —, 408

Statistics
Bose-Einstein —, 379, 380
Fermi-Dirac —, 379, 381, 514
Maxwell-Boltzmann —, 379

The Bases of Chemical Thermodynamics

Stirling
cycle, 60
design, 62
—’s approximation, 383

Stoichiometric coefficients, 271, 428, 429,
433

Sublimation, 141
Symmetry factor, 395

System
at equilibrium, 3
binary —, 356, 486, 487
closed adiabatic —, 237
closed —, 2, 66-68, 299
dilute —, 382
divariant and trivariant —, 318
heterogeneous — and the law of mass
action, 308
heterogeneous —, 3
homogeneous —, 3
in contact with one thermal reservoir, 31, 41
in contact with several thermal
reservoirs, 42
in contact with two heat sources, 32, 207
interaction with environment, 2
invariant —, 148
irreversible process in a —, 38, 237
open —, 2, 68-73, 136
simple — in statistical
thermodynamics, 388
thermodynamic —, 1
univariant —, 139
with a gas phase and condensed
phases, 296
without chemical reaction, 133-151

Temperature
critical —, 121
Debye —, 404
effect of — on chemical equilibria, 321,
427, 432
effect of — on the activity coefficient,
353
Index XV

effect of — on the equilibrium constant, 319, 427
effect of — on the extent of reaction, 430, 432
Einstein —, 402
in statistical thermodynamics, 387, 512
in the canonical ensemble, 399
inversion —, 126, 239
standard state —, 277
Thermal
equilibrium and entropy, 43
equilibrium, 3
expansion coefficient, 6, 7
machines, 55, 207
Thermal reservoir
definition of a —, 4
entropy change of a —, 48, 49, 112, 113, 290
system in contact with one —, 31, 41
system in contact with several —s, 42
Thermodynamic
equilibrium constant, 305
functions in the canonical ensemble, 398, 511, 515
system, 1
Thermodynamic tables
effect of the choice of the standard state on values in the —, 293
Third Law
implications of the —, 407
of thermodynamics, 406
Transfer
heat —, 28
Transform
Legendre —, 535
Translational
partition function, 392
Triple point
and latent heat, 255
—, 147
Units
SI —, 163
Univariant
system, 139
Usable
maximum — work, 46
Van der Waals
adiabatic change of a — gas, 169
coefficient, 121
complex, 118
equation of state, 120, 236, 237
forces, 116
Internal energy of a — gas, 156
Van’t Hoff’s
equation, 320
Vapor
phase composition of an ideal binary solution, 464
Vapor pressure
effect of an inert gas on —, 144, 256
effect of temperature on —, 145, 256
of an ideal solution, 340
temperature dependence of —, 255
—, 141, 339
Vaporization
curve, 340, 342, 463, 464
in the presence of a gas, 256
latent heat of —, 347
—, 141
Variable
auxiliary state —, 4, 6
auxiliary —, 65, 205
excess — of mixing, 352, 486
extensive —, 5, 65
intensive —, 5, 65
of mixing for ideal gases, 110
of mixing for real gases, 128
of mixing, 352, 486
of reaction, 273, 276
of state, 5, 6
reduced —s, 122
standard — of formation, 278
standard — of reaction, 276, 411, 412, 413
Variables
characteristic —, 536
natural —, 68, 536

Variance
example of the use of —, 329, 331, 332
of a system, 138
—, 318

Variation
of entropy at 0 K with volume and temperature, 407
of Gibbs function with temperature, 73
of heat capacities with pressure, 80
of heat capacities with volume, 80
of Helmholtz function with temperature, 73

Vibrational
characteristic — temperature, 393
partition function, 392

Virial
coefficients, 119, 236
equation, 119, 236

Volume
effect of — on chemical equilibria, 323
molar — of a pure liquid, 339
of mixing, 101, 344
of reaction, 276
partial molar — of a real gas, 128
partial molar — of an ideal gas, 110
partial — of an ideal gas, 110
work due to — change, 47, 181, 299
Water-acetic acid mixture, 226
Water-ethanol mixture, 100, 225
Water-glycerol mixture, 226
Wave function for a particle in a box, 388

Work
and irreversible adiabatic process of an ideal gas, 183
any form of —, 288
due to volume change, 47, 181, 299
electrical —, 18
in an irreversible process, 205
maximum usable —, 46-47

mechanical —, 14
notions, 13-20
other than volume —, 289
sign convention for —, 13
various expressions for —, 20