



# Thermodynamics of Polymer Blends

---

YURI S. LIPATOV  
ANATOLY E. NESTEROV

POLYMER THERMODYNAMICS LIBRARY, VOL. 1

0631.2  
L764

9960112

**POLYMER THERMODYNAMICS LIBRARY, VOL. 1**

# **Thermodynamics of Polymer Blends**



**YURI S. LIPATOV**  
**ANATOLY E. NESTEROV**

*Academy of Sciences of Ukraine*



E9960112



LANCASTER • BASEL

## **Polymer Thermodynamics Library—Volume 1**

a **TECHNOMIC**<sup>®</sup> publication

*Published in the Western Hemisphere by*  
Technomic Publishing Company, Inc.  
851 New Holland Avenue, Box 3535  
Lancaster, Pennsylvania 17604 U.S.A.

*Distributed in the Rest of the World by*  
Technomic Publishing AG  
Missionsstrasse 44  
CH-4055 Basel, Switzerland

Copyright © 1997 by ChemTec Publishing

All rights reserved. No part of this publication may be reproduced, stored or transmitted in any form or by any means without written permission of copyright owner. No responsibility is assumed by the Author and the Publisher for any injury or/and damage to persons or properties as a matter of products liability, negligence, use, or operation of any methods, product ideas, or instructions published or suggested in this book.

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Main entry under title:

Polymer Thermodynamics Library—Volume 1: Thermodynamics of Polymer Blends

A Technomic Publishing Company book

Bibliography: p.

Includes index p. 443

Library of Congress Catalog Card No. 97-62285

ISBN No. 1-56676-624-9

This Technomic Publishing Company, Inc. edition is produced under license between Technomic Publishing Company, Inc. and ChemTec Publishing.

# THERMODYNAMICS OF POLYMER BLENDS

#### **HOW TO ORDER THIS BOOK**

BY PHONE: 800-233-9936 or 717-291-5609, 8AM-5PM Eastern Time

BY FAX: 717-295-4538

BY MAIL: Order Department  
Technomic Publishing Company, Inc.  
851 New Holland Avenue, Box 3535  
Lancaster, PA 17604, U.S.A.

BY CREDIT CARD: American Express, VISA, MasterCard

BY WWW SITE: <http://www.techpub.com>

#### **PERMISSION TO PHOTOCOPY-POLICY STATEMENT**

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by Technomic Publishing Co., Inc. provided that the base fee of US \$3.00 per copy, plus US \$ .25 per page is paid directly to Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, USA. For those organizations that have been granted a photocopy license by CCC, a separate system of payment has been arranged. The fee code for users of the Transactional Reporting Service is 1-56676/98 \$5.00 + \$ .25.

Polymer alloys and blends belong to one of the most dynamic sectors of the polymer industry. This explains the great interest in the studies of their physical and mechanical properties, their structure, and the processes of their formation and manufacture. Thermodynamics of polymer blends is based on the classical theories of polymer solutions developed by Flory, Huggins, Prigogine, Patterson, Sanchez, and others as well as on the theories of the phase equilibrium and phase separation in solids developed by Cahn, Prigogine, and other authors. There are many books and reviews on the subject of the thermodynamics of polymer solutions. After the fundamental works by Flory,<sup>1</sup> Huggins,<sup>2</sup> and Tompa,<sup>3</sup> the following publications have been dedicated mainly to the problems discussing excluded volume. Theoretical investigations regarding this subject, performed before 1970, were systematically summarized as the so-called two-parameter theory in the book by Yamakawa<sup>4</sup> and compared with an extensive experimental data. This first stage of research was immediately followed by a new theoretical approach, namely, the renormalization group theory. These developments, achieved until recently, can be found in books by Freed<sup>5</sup> and des Cloizeaux and Jannink.<sup>6</sup> However, the recent experimental data point out to the deficiencies in the two-parameter theory. These data were summarized and discussed by Fujita.<sup>7</sup> There have been published also some reviews.<sup>9,10</sup> The new developments and the fundamental contribution to the theory of polymer solution come from de Gennes<sup>11</sup> discussed in his famous book *Scaling Concepts in Polymer Physics*.

However, if presently there exists a voluminous scientific literature dedicated to various aspects of the physics and chemistry of polymer blends, there are no many books dedicated to the thermodynamics of mixing and thermodynamic behavior of polymer mixtures. This subject was presented in such fundamental works as *Polymer Blends* edited by Paul,<sup>12</sup> books by Olabisi, Robeson, and Shaw,<sup>13</sup> Manson and Sperling,<sup>14</sup> Utracki,<sup>15</sup> and some other authors.<sup>16,17</sup>

Thermodynamic behavior of polymer blends determines the compatibility of the components, their morphological features, rheological behavior, microphase structure, and in such a way the most important physical and mechanical characteristics of blends.

This book is dedicated to the detailed analysis of the thermodynamics of polymer-polymer systems. This book is not intended as an introduction in the field but the knowledge of the main principles of thermodynamics is assumed. We attempted to consider the modern

state of thermodynamics of mixing and phase separation and to discuss both theoretical and experimental aspects of the problem. Chapters 1 and 2 discuss thermodynamics of polymer solutions and the most important theories describing the processes of dissolution and phase separation. These chapters give the reader a fundamental understanding of the present state of knowledge on the thermodynamics of polymer blends. Analyzing the thermodynamic behavior of polymer blends, we pay a special attention to the processes of phase separation and to the formation of an interphase between coexisting phases. The thermodynamic properties of an interphase play a very important role in the mechanical behavior of the blends.<sup>18</sup> One may say that formation of the interphase distinguishes the properties of blends from properties of solution. After all, the rheological and mechanical properties of polymer blends are determined by the compatibility of the components and by the degree of microphase separation that implies the formation of an interphase.

Some words about terminology. Although the concept of "compatibility" is widely used in the literature, we prefer to follow the definition given by Olabisi, Robeson, and Shaw.<sup>13</sup> We cite: "compatibility has been used by many other investigators involving various studies of polymer-polymer blend behavior to describe good adhesion between the constituents, average of mechanical properties, etc. The term "miscibility" has been chosen to describe polymer-polymer blends with behavior similar to that expected of a single-phase system. The term miscibility . . . does not imply ideal molecular mixing but suggests that the level of molecular mixing is adequate to yield macroscopic properties expected of a single-phase material."

Another term that should be defined is: polymer alloys and blends. Both alloys and blends are produced by mixing two polymers in various conditions. Utracki<sup>15</sup> considers all the mixtures as blends that may be either miscible or immiscible. Alloys are formed, after Utracki, only after some modification of immiscible blends which allows to improve the compatibility, i.e., alloy is the result of some compatibilization. This compatibilization does not imply that the system becomes miscible and is only connected with some improvement of interactions at the interface between the two phases of immiscible mixture (a typical example is compatibilization obtained by the introduction in the homopolymer blend of diblock-copolymers composed of blocks corresponding to two homopolymers).

We propose another terminology<sup>18,19</sup> based on the thermodynamic considerations and including the analysis of the phase diagrams of binary mixtures as the basis for differentiation.

It is known that the most common and convenient method of mixing two polymers is by melt blending, which is typical for metallic

alloys. Generally, alloys are macroscopically uniform substances obtained by fusion of two or more metals, nonmetals, and organic compounds. In general, alloys are not obtained by simple mechanical mixing of the components. By fusing, the components may form mixtures of various phases. The phase state of an alloy in equilibrium can be determined from the phase diagram. It is known also that, for linear polymers, the phase diagrams are of two types, with upper and lower critical solution temperatures (UCST and LCST). Taking the phase diagrams as a basis, we give the following definitions:

- Alloys of linear polymers are binary or multicomponent systems that, when mixed in the molten state, they are situated in the region of the phase diagram corresponding to the mutual miscibility of the components and to the formation of one-phase solution. This means that the system is thermodynamically stable (at equilibrium) in the molten state. By cooling the melt, a structure develops which depends on the thermodynamic state at a given temperature. If by cooling, the system with UCST enters the region of unstable states in the phase diagram (immiscibility or thermodynamic incompatibility arises), then the structure becomes the two-phase structure and it is determined by the conditions of phase separation.

The structure depends on the degree of phase separation and on the mechanism of phase separation (nucleation or spinodal decomposition). The ratio and composition of two phases is determined by the kinetics and mechanism of phase separation. For binary systems with UCST, the mixing of the alloy components should be conducted in the region above spinodal and for the systems with LCST – below spinodal, i.e., in the range of one-phase solution. For systems with LCST, one-phase structure is preserved by cooling, i.e., a miscible system is maintained.

- Blends of linear polymers are such binary systems that, by mixing in the molten state, they are not miscible and do not form one-phase system (they are not thermodynamically miscible). The components forming a blend may also have UCST or LCST. For systems with UCST, the formation of blend proceeds at temperatures below the binodal and for systems with LCST above the binodal. The transition from two-phase to one-phase state for systems with LCST is practically impossible by lowering temperature because of the high viscosity of the melt and the slowness of the mutual dissolution process. Thus, the structures of blends are deter-



mined by the degree of dispersion of one or both components achieved during mixing in the melt.

In such a way, depending on the temperature range of mixing, relative to the position of the binodal or spinodal, the same polymer pair may form both alloys and blends. The realization of both possibilities depends on the relationship between the temperature of phase separation for a given composition of a mixture and the glass transition temperatures or melting points of both components. Because the formation of blends or alloys by fusing the components (mixing in the molten state) is always followed by temperature reduction, the definitions given above allow to distinguish between the structural features of polymer alloys and blends. The analysis made above allows to conclude that two-phase or multi-phase blends are typical of systems with UCST, whereas one-phase alloys for systems with LCST.

The principle feature of polymer alloy consists of the incomplete phase separation in the system. By cooling a melt of two polymers the thermodynamic incompatibility of two components arises which causes the incomplete phase separation of the system. This incompleteness of the phase separation causes the development of both the microphase separation regions of various composition and transition or interphase zone between coexisting microregions. The system with incomplete microphase separation is not in the state of thermodynamic equilibrium. A segregated structure develops in the bulk because of these processes with a complex of specific properties: appearance of the regions with different density, composition and mechanical properties, appearance of the internal interphase boundaries, etc.

The same definition may be applied to the reactive mixtures capable of the formation of interpenetrating polymer networks. The transition from the initially one-phase mixture of components to cured two-phase system is connected with the phase separation and the phase-separated system may be attributed to alloy.

However, in the present book, where we consider the thermodynamic behavior of the polymer-polymer systems and do not deal with the peculiarities of their structure in a solid state, we will use the words "blends" and "mixtures" as a general, equivalent, and habitual terms. In reality, when we mix or blend two polymer components we do not know beforehand their thermodynamic behavior.

It is worth noting that there are no either fully miscible or fully immiscible mixtures. All depends on the phase diagram of the system, i.e., on the composition and temperature. At the same time, we fully agree with the statement<sup>13</sup> that "the two-phase system must be defined and contrasted with miscible system to delineate the two

subjects and to establish the criteria." One of the aims of this book is the analysis of conditions of miscibility and immiscibility.

These authors understand that the field of thermodynamics of polymer blends is too extensive to be covered in one book. There are many questions that have not been considered or were considered only briefly. However, we hope that this volume will further stimulate interest in this branch of physical chemistry of polymers.

Authors had worked with full comprehension. Each of us thanks the other for the mutual support and encouragement. We wish also to express our sincere gratitude to Dr. G. Wypych who initiated this work and who waited patiently for its result.

Institute of Macromolecular Chemistry,  
National Academy of Sciences of Ukraine,  
Kiev, June 1997

## REFERENCES

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953.
2. M. L. Huggins, *Physical Chemistry of Polymers*, Interscience, N.Y., 1958.
3. H. Tompa, *Polymer Solutions*, Butterworth, London, 1956.
4. H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, N.Y., 1971.
5. K. F. Freed, *Renormalization Group Theory of Macromolecules*, Wiley-Interscience, N.Y., 1987.
6. J. des Cloizeaux and G. Jannink, *Polymers in Solutions*, Oxford Univ. Press, Oxford, 1990.
7. H. Fujita, *Polymer Solutions*, Elsevier, Amsterdam, 1990.
8. T. Hashimoto, *Current Theories in Polymer Science*, R. M. Ottenbrite, L. A. Utracki, and S. Inoue, Eds., Hanser, N.Y., v. 2, p. 197 (1987).
9. J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, D. Domb and J. L. Lebowitz, Eds., Academic Press, London, v. 8, p. 267 (1983).
10. T. M. Aminabhavi, R. H. Balundgi, and S. S. Joshi. *J. Sci. Ind. Res.*, **47**, 375 (1988).
11. P. de Gennes, *Scaling Concept in Polymer Physics*, Cornell Univ. Press, Ithaca-London, 1979.
12. *Polymer Blends*, D. R. Paul and J. W. Marlow, Eds., Academic Press, N.Y., 1978.
13. O. Olabisi, L. Robeson, and M. Shaw, *Polymer-Polymer Miscibility*, Academic Press, N.Y.-London, 1979.
14. A. Manson and L. Sperling, *Polymer Blends and Composites*, Plenum Press, N.Y., 1976.
15. L. A. Utracki, *Polymer Alloys and Blends*, Hanser Publishers, Munich-Vienna-New York, 1989.
16. *Polymer Alloys-Properties and Application* (in Japanese), Society of Polymer Science Japan, Tokyo, 1981.
17. S. Akiyama, T. Inoue, and T. Nishi, *Polymer Blends* (in Japanese), CMC, Tokyo, 1981.
18. Y. S. Lipatov, *Polymer Reinforcement*, ChemTec Publ., Toronto, 1995.
19. Y. S. Lipatov, *Int. J. Polymer Mater.*, **17**, 91 (1992).

# Table of Contents

<b>Preface</b>	<b>ix</b>
<b>1 Basic Principles of Thermodynamics of Polymer Solutions</b>	<b>1</b>
1.1 The Main Thermodynamic Characteristics of Solution	1
1.2 Regular Solutions. Hildebrand-Scatchard Equation	2
1.3 Phase Equilibrium in Solutions. Binodals and Spinodals	4
1.4 The Flory-Huggins Theory	9
1.4.1 Entropy of Mixing	10
1.4.2 The Heat and Free Energy of Mixing	11
1.5 Dilute Solutions of Polymers	13
1.6 Phase Separation In Polymer Solutions	16
<i>References</i>	30
<b>2 Statistical Theories of Polymer Solutions</b>	<b>33</b>
2.1 The Theory by Prigogine-Patterson	34
2.2 The Role of Various Contributions of the Mixing Parameters	42
2.3 Effect of Solvent Chain Length on the Interaction Parameters	44
2.4 New Flory Theory	48
2.5 Modification of the New Flory Theory	55
2.6 New Huggins Theory	59
2.7 Sanchez-Lacombe Theory	65
2.7.1 Equation of State	65
2.7.2 Mixtures of Liquids	67
2.7.3 Free Energy and Chemical Potential	69
2.7.4 Functions of Mixing	70
2.7.5 Phase Stability and Spinodal	71
2.8 Some Experimental Results of Thermodynamic Properties of Polymer Solutions	73
<i>References</i>	77
<b>3 Thermodynamics of Polymer Mixing</b>	<b>81</b>
3.1 Binary Mixtures	81
3.1.1 Application of the Theory of Regular Solutions to Thermodynamics of Polymer Mixing	83
3.1.2 Application of New Statistical Theories for Describing Thermodynamic Properties of Polymer Mixtures	88
3.1.3 The Application of the New Huggins Theory	98
3.1.4 The Sanchez-Lacombe Theory	101
3.1.4.1 Chemical Potentials	102
3.1.4.2 The Stability of Phase and Spinodal	104
3.1.4.3 Criterion of Miscibility of Polymer-polymer Mixture	107
3.2 Experimental Data on Thermodynamic Properties of Binary Polymer Mixtures	110
3.2.1 Phase Behavior of Binary Polymer Mixtures	117

3.2.2	Concentration and Temperature Dependencies of Parameters of Thermodynamic Interactions in the Mixtures of Oligomers and Polymer Homologues	128
3.2.3	Influence of Various Factors on the Miscibility	143
3.2.3.1	Deuteration and Tacticity of Polymers	143
3.2.3.2	Branching of Chains	144
3.2.3.3	Effect of Pressure	144
3.2.3.4	Asymmetry of the Length of Statistical Segment	148
3.2.4	Possible Errors in Estimating the Miscibility of Mixtures Obtained from Solutions in a Common Solvent	148
3.3	Miscibility of Polymers at the Interface with Solid	151
3.3.1	Phase Diagrams of Filled Polymer Mixtures	151
3.3.2	Phase Separation in Thin Films of Polymer Mixtures at the Interface with Solid	155
3.3.3	Thermodynamic Interaction Parameters in Filled Polymer Mixtures	161
3.3.4	On the Equilibrium and Non-equilibrium Compatibilization of Polymer Mixtures	167
3.4	Ternary Polymer Systems	169
3.4.1	Ternary Systems Polymer-polymer-solvent	169
3.4.2	Ternary Polymer-polymer-polymer Systems	185
3.5	Thermodynamics of Formation of Stable Dispersion in Binary Polymer Mixtures	205
	<i>References</i>	210
<b>4</b>	<b>Homopolymer-copolymer and Copolymer-copolymer Blends</b>	<b>227</b>
4.1	Mean-field Binary Interaction Models	227
4.1.1	Miscibility Windows	230
4.2	Effect of the Sequence Distribution in Copolymer on the Phase Behavior of Homopolymer-copolymer Mixtures	235
4.3	The Dependence of the Phase Behavior of Copolymer Mixtures of Various Compositions on the Sequence Distribution	239
4.4	The Effect of the Sequence Distribution in Copolymer and Its Compatibilizing Effect in Mixture of Two Immiscible Polymers	243
4.4.1	Mixtures of Homopolymers with Homologue Series of Polymers of Another Chemical Nature	251
4.5	Ternary Mixtures	259
4.6	Modified Theories of the Equation-of-state	264
	<i>References</i>	271
<b>5</b>	<b>Mechanism and Kinetics of Phase Separation in Polymer Solutions and Blends</b>	<b>275</b>
5.1	Nucleation and Growth	275
5.2	Spinodal Mechanism of Phase Separation	277
5.3	Application of the Theory of Spinodal Decomposition to Polymeric Systems	283

5.4	Some Experimental Results on Kinetics of Phase Separation in Solutions and Mixtures of Polymers	299
5.5	Factors Influencing the Kinetics of Phase Separation	320
5.5.1	Tacticity	321
5.5.2	Effects of Addition of Diblock-copolymers	323
5.5.3	Spinodal Decomposition Near Solid Surface	328
5.5.4	Shear-induced Phase Separation	329
5.6	Phase Separation Accompanying Reactions of Polymer Blend Formation	334
5.6.1	Spinodal Decomposition in IPNs	334
5.6.2	Nucleation and Growth During IPN Formation	340
5.6.3	Some Features of Microphase Structure of IPNs	351
	<i>References</i>	356
<b>6</b>	<b>Interface in Demixing Solutions and Polymer Mixtures</b>	<b>363</b>
6.1	Vrij-Roebersen Theory	364
6.2	Kammer's Theory	371
6.3	The Theory by Helfand	374
6.4	The Theory by Nose	380
6.5	Sanchez-Lacombe Theory	381
6.6	Other Theories of Polymer-polymer Interface	391
6.7	Scaling Principle in Describing the Interface	397
6.8	Some Experimental Data on the Interfacial Properties of Polymer Blends	400
6.8.1	Interfacial Tension	400
6.8.2	The Interfacial Width and Interfacial Profiles	401
6.9	Surface Segregation in Polymer Mixtures	406
6.9.1	Surface Segregation Near the Interface with Solid	408
6.10	Segregation of Block-copolymers at the Interface Between Homopolymers	412
	<i>References</i>	428
	<b>Nomenclature</b>	<b>435</b>
	<b>Index</b>	<b>443</b>

## BASIC PRINCIPLES OF THERMODYNAMICS OF POLYMER SOLUTIONS

### 1.1 THE MAIN THERMODYNAMIC CHARACTERISTICS OF SOLUTION

The main thermodynamic functions of any solution are the changes in enthalpy of its formation,  $\Delta H$ , entropy changes,  $\Delta S$ , and Gibbs free energy,  $\Delta G = \Delta H - T\Delta S$ . At constant temperature and pressure, the dissolution is a spontaneous process proceeding in the direction of diminishing Gibbs free energy of mixing. The solution has lower free energy as compared with the sum of free energies of solution components (polymer and solvent):

$$G_{\text{solution}} < \sum_i n_i G_i^0 \quad [1.1]$$

where  $G^0$  is the free energy of  $i$ -th component.

The excess free energy determined as

$$\Delta G = G_{\text{solution}} - \sum_i n_i G_i^0 \quad [1.2]$$

by spontaneous dissolution is negative. Correspondingly, the chemical potential of a component in solution,  $\mu_i$ , should be lower than its value before dissolution,  $\mu_i < \mu_i^0$  i.e.,  $\Delta\mu_i < 0$ . Values  $\Delta G < 0$ ,  $\Delta\mu_i < 0$  are the criteria of the affinity between components. Their values are determined by the absolute magnitude of the differences  $\Delta G$  or  $\Delta\mu_i$ .

The solution in which all molecules of components equally interact with each other are considered as ideal solutions. Their properties are the additive sum of the properties of components. Such solutions obey the Henry and Raul laws:

$$p_2 = Kx \quad [1.3]$$

$$p_1 = p_1^0(1 - x) \quad [1.4]$$

where  $p_1$  and  $p_2$  are partial pressure of components,  $x$  is the molar fraction of component in solution. Because

$$\Delta\mu_i = RT \ln p_i/p_i^0 \quad [1.5]$$

we find that

$$\Delta\mu_i = RT \ln x_i \quad [1.6]$$

It means that the chemical potential of any component is only determined by its molar fraction in solution. In the majority of cases, solutions do not obey Eqs 1.3 to 1.6. They are thus considered non-ideal. The deviations from the ideality ( $p_i/p_i^0 = x_i$ ) may be positive ( $p_i/p_i^0 > x_i$ ) or negative ( $p_i/p_i^0 < x_i$ ). To estimate the degree of deviation from the ideality, the concept of excess quantities is introduced as an excess of properties in comparison with the ideal magnitude. These are:

$$\Delta\mu_i^{\text{exc}} = \Delta\mu_i - \Delta\mu_i^{\text{id}} = RT \ln \gamma_i \quad [1.7]$$

$$\Delta\bar{S}_i^{\text{exc}} = \bar{S}_i - S_i^{\text{id}} = -RT \ln \gamma_i - RT \left( \frac{\delta \ln \gamma_i}{\gamma T} \right)_p \quad [1.8]$$

$$\Delta\bar{H}_i^{\text{exc}} = -RT^2 \left( \frac{\delta \ln \gamma_i}{\delta T} \right)_p \quad [1.9]$$

$$\Delta\bar{G}_i^{\text{exc}} = R \ln \gamma_i \quad [1.10]$$

where  $\gamma_i$  is the activity coefficient of component  $i$  in a real solution ( $\gamma_i = a_i/x_i$ ). If the activity is expressed as  $RT \ln a_i = \mu_i - \mu_i^0$ , then we have:

$$\Delta G_i^{\text{exc}} = \sum x_i \Delta\mu_i^{\text{exc}} = RT \sum x_i \ln \gamma_i \quad [1.11]$$

$$\Delta H^{\text{exc}} = \sum x_i \Delta\bar{H}_i^{\text{exc}} = -RT^2 \sum x_i \left( \frac{\delta \ln \gamma_i}{\delta T} \right)_p \quad [1.12]$$

$$\Delta S^{\text{exc}} = \sum x_i \Delta\bar{S}_i^{\text{exc}} = -R \sum x_i \ln \gamma_i - RT \sum x_i \left( \frac{\delta \ln \gamma_i}{\delta T} \right)_p \quad [1.13]$$

## 1.2 REGULAR SOLUTIONS.

### HILDEBRAND-SCATCHARD EQUATION

According to Hildebrand, a solution is called regular if by its formation  $\Delta H \neq 0$ . It is accepted that the distribution of mixed molecules is fully random, i.e., the entropy of mixing equals to the ideal value, whereas mixing proceeds without changing volume. The energy of mixing of pure liquid components,  $\Delta E_{\text{mix}}$ , equals to the difference between inter-

molecular energy of one mole of solution,  $E_{\text{sol}}$ , and the sum of intermolecular energies of pure liquid components,  $E_i^0$ :

$$\Delta E_{\text{mix}} = 2\pi N_0 V \varphi_1 \varphi_2 \left( \frac{2}{V_1 V_2} \int_0^\infty \varepsilon_{12} \rho_{12} r^2 dr - \frac{1}{V_1^2} \int_0^\infty \varepsilon_{11} \rho_{11} r^2 dr - \right. \\ \left. - \frac{1}{V_2^2} \int_0^\infty \varepsilon_{22} \rho_{22} r^2 dr \right) \quad [1.14]$$

where  $V$  is the volume of one mole of solution,  $\varepsilon_{11}$ ,  $\varepsilon_{22}$ , and  $\varepsilon_{12}$  are the interaction energies of two molecules in a pair,  $\rho_{11}$ ,  $\rho_{22}$ , and  $\rho_{12}$  are the probabilities that any arbitrary chosen molecule in the volume unit is the molecule of the 1, 2, etc. kind,  $r$  is the distance from the arbitrary chosen central molecule,  $\varphi_1$  and  $\varphi_2$  are volume fractions of components that are constant in a solution:  $\varphi_1 = V_1(1-x)/[V_1(1-x) + V_2x]$ ;  $\varphi_2 = V_2x/[V_1(1-x) + V_2x]$ . Using expression for  $\varepsilon_{ij}$  as  $-k_{ij}/r^6$ , where  $k_{ij}$  is the interaction constant for molecules of the type  $i$  and  $j$ , and the rule of the geometric average  $k_{12} = (k_{11} k_{22})^{1/2}$ , one can obtain Eq 1.14 in the form:

$$\Delta E_{\text{mix}} = V \varphi_1 \varphi_2 [(E_1^0/V_1)^{1/2} - (E_2^0/V_2)^{1/2}]^2 \quad [1.15]$$

This is the Hildebrand-Scatchard equation for the regular solutions. The ratio  $E_i/V_i$  is called the density of cohesion energy. The value  $\delta = (E_i/V_i)^{1/2}$  was called by Hildebrand the coefficient or solubility parameter of the component. The difference of magnitudes in the square brackets (Eq 1.15) determines a deviation of the solution from the ideal behavior. The shortcoming of the theory of regular solution consists of the assumption that the behavior of molecules in solution does not depend on the heat effect of mixing, or that the entropy of mixing is ideal,  $\Delta H \neq 0$ . This theory is only applicable to solutions containing weakly polar or non-polar components, having the molecular field of spherical symmetry and mixing with a low change in volume.

The non-uniform distribution of molecules is the basis of the theory of strictly regular solutions. The theory uses the lattice model, based on the following assumptions:

- the solution structure is considered quasi-crystalline (short range order) and the particles of the solute and solvent have one and the same coordination number,  $z$
- only the interaction between neighboring molecules is considered



- the potential energy of the system is divided into configurational energy (the energy of the disposition of all the molecules into the lattice site) and acoustic energy (the vibration energy near the equilibrium center). The vibration energy of the molecule does not depend whether the molecule is in solution or in a pure liquid.
- each molecule occupies one lattice cell (therefore molecules should have the same shape and volume).

The potential energy of the molecular exchange of various liquids is taken as:

$$E_{11} + E_{22} - 2E_{12} = -2\Delta w_{12} \quad [1.16]$$

where  $w_{ij}$  is the interaction energy of two molecules. Due to exchange, the number of bonds,  $z$ , of the type 1-1 with energy  $E_{11}$  and  $z$  bonds of the type 2-2 with energy  $E_{22}$  are destroyed and  $2z$  bonds of the type 1-2 are formed with energy  $E_{12}$ . If the exchange energy is zero, the system is athermic, whereas, for the non-zero energy, the system is called non-athermic. The zero approximation of the theory of regular solution gives the relationship:

$$\Delta H = N_0(1-x) \left( \Delta w_{12} - T \frac{\delta \Delta w_{12}}{\delta T} \right) \quad [1.17]$$

and

$$\Delta G = N_0 x(1-x) \Delta w_{12} \quad [1.18]$$

### 1.3 PHASE EQUILIBRIUM IN SOLUTIONS. BINODALS AND SPINODALS

A system of unperturbed equilibrium consists of only one phase. Any perturbation leads to the appearance of some amount of a new phase. The intensive properties of this new phase (partial molar volume, composition, etc.) may differ from the properties of the equilibrium system either by infinitely small or finite value. Various situations may arise:<sup>1</sup>

- the initial phase is stable in the relation to all other phases, independently on the difference in properties is infinitely small, or it has a finite value
- the initial phase is stable in relation to all phases that differ infinitely small from it, but there is at least one phase in the system in relation to which the initial phase is not stable
- the initial phase is not stable in relation to the phases with infinitely small difference.