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The Miscibility of Water and Non-polar Substances at High Temperatures

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Data on the phase equilibria in water-non-polar substance systems at high temperatures and on the relations between the volume, pressure, and composition of the phases involved in these equilibria are considered. The characteristics of the phase equilibria are analysed.
The bibliography includes 66 references.

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I. INTRODUCTION

At normal temperatures the miscibility of water and non-polar substances is very low. With increase of temperature, the miscibility undergoes complex changes and under certain conditions can actually become infinite.

Fairly extensive experimental data have now accumulated on the phase equilibria in water–non-polar substance systems at high temperatures (see the relevant reviews[1-3]). Evidently the available data cannot exhaust the possible wide variety of such mixtures particularly when one takes into account mixtures of several non-polar components with water and mixtures with water containing dissolved salts. It is therefore necessary to formulate general ideas concerning the properties of mixtures of water and non-polar substances which determine the phase equilibria. Such properties are in the first place relations between the chemical potentials (fugacities) of the components and their concentrations, as well as the partial volumes and enthalpies of the components. It is also important to establish to what extent the experimental data obtained are consistent with the existing ideas concerning the molecular nature of the mixtures investigated.

After the description of the phase equilibria in water–non-polar substance systems, this review deals with the characteristics of the variation of the chemical potentials of the components in different phases with pressure, temperature, and composition. In conclusion the phase behaviour in water–non-polar substance systems is explained on the basis of the observed features.

II. GENERAL DESCRIPTION OF THE PHASE EQUILIBRIA IN WATER–NON-POLAR SUBSTANCE SYSTEMS

Two main types of phase behaviour are known for water–non-polar substance systems. The liquid–gas critical curve on the pressure–temperature diagram for the first type consists of two branches. The first branch begins at the critical point of water and either passes through a temperature minimum (Fig. 1*a*) or increases continuously with temperature (Fig. 1*b*) and is directed towards the region of high pressures. This branch probably terminates at very high pressures where the substance solidifies. The second branch begins at the critical point of the non-polar substance and terminates at the critical end point where the critical phase is in equilibrium with some other phase (a second liquid phase, ice, or a clathrate hydrate. For systems of the second type (Fig. 2), the liquid–gas critical curve joins together the critical points of the two components, without splitting into branches. At the same time there exists a liquid–liquid critical curve.

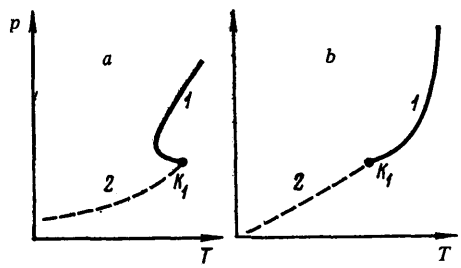


Figure 1. 1) The branch of the critical curve originating at the critical point of water for a water–non-polar substance system (system of type I) (K_1 is the critical point of water); 2) water vapour pressure curve.

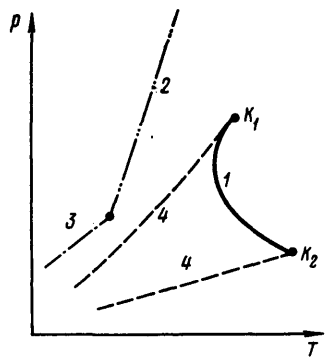


Figure 2. Critical curves for the water–naphthalene system (system of type II) (K_1 and K_2 are the critical points of water and naphthalene respectively): 1) and 2) liquid–gas and liquid–liquid critical curves; 3) liquid–liquid–gas three-phase curve; 4) vapour pressure of the pure substance.

The majority of the water–non-polar substance systems investigated belong to the first type. If the treatment is confined to systems for which the second branch of the critical curve is observed at temperatures where the formation of ice or clathrate hydrates is ruled out, then the pressure–composition diagrams shown in Figs.3–6 are characteristic of equilibria of this type. In Fig.3, which corresponds to a comparatively low temperature, *A* is the region of equilibrium between the solution in the non-polar liquid (henceforth the non-polar or specifically the hydrocarbon liquid) and gas and *B* is the region of equilibrium between the solution of the non-polar substance in water (henceforth the aqueous liquid) and gas. With increase of temperature, there is an increase in the vapour pressures of water and the non-polar substance, of the solubility of water in the non-polar liquid, and of the three-phase equilibrium pressure, and the properties of the non-polar liquid and the gaseous phase involved in the three-phase equilibrium become more similar. This increase in the similarity of the properties terminates with the establishment of the critical state.

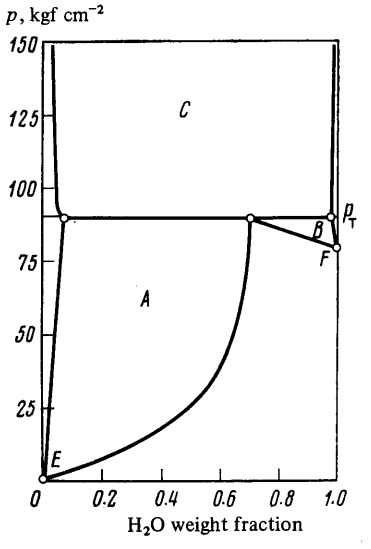


Figure 3. The pressure–composition diagram for a water–non-polar substance system at a temperature below that of the critical end point; *A*, *B*, and *C*—the regions corresponding to non-polar liquid–gas, aqueous liquid–gas, and liquid–liquid equilibria; *E*—vapour pressure of non-polar liquid; *F*—vapour pressure of water; P_T—liquid–liquid–gas three-phase equilibrium pressure.

Fig.4 presents the phase diagram for the same system as in Fig.3 but at a higher temperature, where the properties of the hydrocarbon liquid are the same as those of the gas phase and a critical point *K* appears in the region of the three-phase equilibrium. Since the substance at the critical point is in a region of three-phase equilibrium, it is involved in a phase equilibrium with the aqueous liquid. In this case the critical point is referred to as the critical end point. The equilibrium regions *A* and *B* are in contact at the critical end point.

Fig.5 presents the same system at a temperature exceeding that of the critical end point. At this temperature the three-phase equilibrium no longer exists and regions *A* and *B* are no longer in contact with one another and the critical point *K* is not in equilibrium with the aqueous liquid.

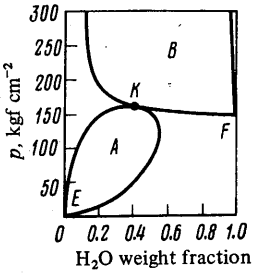


Figure 4. The pressure–composition diagram for a water–non-polar substance system at the temperature of the critical end point (*K* is the critical end point); for the significance of the remaining symbols, see Fig.3.

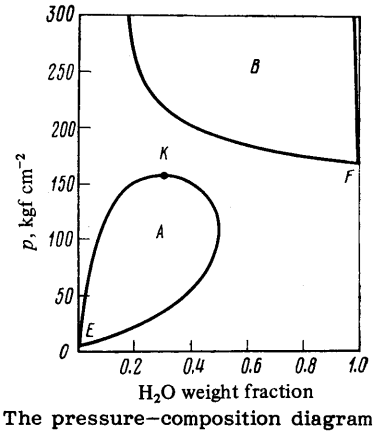


Figure 5. The pressure–composition diagram for a water–non-polar substance system at a temperature above that of the critical end point; for the significance of the symbols, see Figs.3 and 4.

Starting with the temperature of the critical end point and over a certain temperature range above it, region *B* extends up to high pressures without the establishment of the critical state. The establishment of the critical state in region *B* is observed only after the attainment of an extremely high temperature. This is evident from the location of the branch of the critical curve beginning at the critical point of water (Fig.1). For all the water–non-polar substance systems, this branch is bounded by temperatures which are comparatively close to the critical temperature of water. In terms of its nature, the critical curves are of two types in the given case (Figs.1*a* and 1*b*). The commonest type of the critical curve is illustrated in Fig.1*a*. In this case the critical curve is directed from the critical point of water towards low temperatures, reaches a minimum critical temperature, and then rises sharply towards high pressures as the temperature increases. The curve of the second type (Fig.1*b*) is directed from the critical point of water towards high temperatures with a sharp increase of pressure.

Below the minimum critical temperature on the curve illustrated in Fig. 1*a*, critical phenomena are not observed between the gas and the aqueous liquid. At higher temperatures (but not above the critical temperature of water) the constant temperature straight line intersects twice the critical curve and two critical points, characterised by different pressures and compositions, correspond to each temperature T_1 and T_2. The phase diagram in Fig. 6 illustrates precisely this case. The critical points at lower pressures belong to the region of the aqueous liquid–gas phase equilibrium, while those at high pressures belong to the special region of phase equilibria observed when mixtures split up into two layers[4,5] and referred to sometimes as the gas–gas equilibrium. The $p-T$ diagram for systems whose $p-N$ diagrams are illustrated in Figs. 3–6 is presented in Fig. 7. For the system whose critical curve is shown in Fig. 1*b*, the pressure–composition phase diagram has the form illustrated in Fig. 8.

A considerable number of binary systems showing the above type of phase behaviour have now been investigated at high temperatures. Table 1 presents certain characteristics of such systems. Almost all the systems investigated are binary. The phase equilibria in the nitrogen–hexadecane–water ternary systems have been studied[28,29]. The naphthalene–water[21], tetrahydronaphthalene–water[30], and decahydronaphthalene–water[30] systems exhibit the second type of phase behaviour of hydrocarbon–water systems.

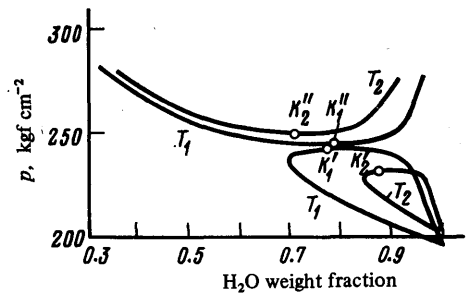


Figure 6. The pressure–composition diagram for a water–non-polar substance system in the vicinity of the critical point of water; K'_1 and K'_2—critical points for the liquid–gas equilibrium; K''_1 and K''_2—critical points for the gas–gas equilibrium.

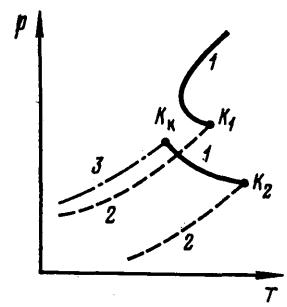


Figure 7. The pressure–temperature diagram for a water–non-polar substance system; K_1 and K_2—critical points of water and the non-polar substance: 1) critical curve; 2) vapour pressure of pure substance; 3) three-phase curve; K_t—critical end point.

Table 1. Characteristics of binary water–non-polar substance systems.

Non-polar component	Critical end point			Refs.	Minimum critical temperature			Refs.
	t, °C	p_k, kgf cm^{-2}	H_2O, mole fraction		°C	p, kgf cm^{-2}	H_2O, mole fraction	
Methane	*	—	—	—	351.9	965	0.825	6,7
Ethane	*	—	—	—	350	716	0.78	8
Propane	96.5	43.3	0.0099	9	—	—	—	—
Propane	96.7	42.7	—	10	—	—	—	—
n-Butane	152.0	43.4	0.0483	11	351.0	374	0.89	8
n-Butane	150.0	41.6	—	10	**			12
n-Pentane	190.6	44.8	—	10	351.0	340	0.595	13
n-Hexane	222.0	52.1	0.322	14	349.5	312	0.881	15
n-Hexane	225.0	52.3	—	10	—	—	—	—
n-Hexane	225.1	54.4	0.260	16, 17	—	—	—	—
n-Heptane	245.4	67.9	0.370	16, 17	353	290	0.651	13
n-Heptane	246.1	64.4	—	10	—	—	—	—
n-Octane	267.2	73.1	—	10	351.5	281	0.906	15
n-Octane	267.2	76.7	0.490	16, 17	—	—	—	—
n-Nonane	280.0	90.0	0.575	16, 17	—	—	—	—
n-Nonane	282.2	87.2	—	10	—	—	—	—
n-Decane	296.1	98.1	—	10	353.0	258	0.923	15
n-Decane	296.0	99.7	0.680	16, 17	—	—	—	—
n-Dodecane	314.0	133	0.770	16, 17	342.0	205	0.948	15
n-Hexadecane	338.0	160	0.900	18	362.0	244	0.976	18
n-Eicosane	352.0	185	0.923	16, 17	—	—	—	—
Benzene	287.8	95.7	—	19	294.0	216	0.777	20
Benzene	288.3	92.8	0.602	20	294.0	216	0.780	21
Benzene	289.4	96.5	—	10	—	—	—	—
Toluene	285.0	102.9	—	10	—	—	—	—
Ethylbenzene	301.1	114.2	—	10	—	—	—	—
Cyclohexane	255.6	81.8	0.493	22	341	300	0.8	15
	256.7	82.0	—	10	—	—	—	—
Methylcyclohexane	271.1	84.9	—	10	—	—	—	—
Propene	—	—	—	—	**	—	—	23
Argon	—	—	—	—	350	—	—	25
Argon	—	—	—	—		—	—	24
Xenon	—	—	—	—	344	700	0.640	26
Nitrogen	—	—	—	—	364	760	0.820	27

*Does not exist.
**Gas–gas equilibrium of the first type.

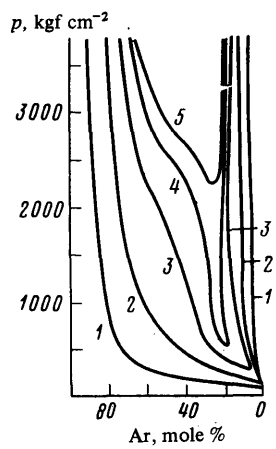


Figure 8. The pressure–composition diagram for a water–non-polar substance system (for a system with the critical curve illustrated in Fig. 1*b*) in the vicinity of the critical point of water at different temperatures (°C): 1) 300; 2) 350; 3) 375; 4) 385; 5) 390.

III. GASEOUS MIXTURES OF WATER AND NON-POLAR SUBSTANCES

The fugacities, partial volumes, and partial enthalpies of the components of the gaseous mixture can be found from the relation between the volume, pressure, temperature, and mixture composition ($p-V-T-N$ data). Such data are available for a number of binary gaseous mixtures of water vapour and non-polar substances. Table 2 lists the mixtures investigated and gives the temperatures and pressure ranges where the relevant experimental determinations were made over a wide range of compositions.

Table 2. The temperature and pressure ranges in which the volumes of gaseous mixtures of water and non-polar substances were investigated.

t, °C	p, kgf cm^{-2}	t, °C	p, kgf cm^{-2}
Methane (Refs.31,32)		Nitrogen (Refs.31,32)	
250	65	250	50
300	85	300	80
350	150	390	600
380	600	Xenon (Ref.26)	
n-Hexane (Ref.33)		375	3000
250	42	400	3000
300	85	450	3000
350	150	500	3000
n-Octane (Ref.33)		Argon (Ref.24)	
350	100	450	3000
n-Decane (Ref.34)			
275	60		

The volumes of the gaseous mixtures of water vapour with hydrocarbons and nitrogen below the critical temperature of water and at pressures which do not exceed greatly the water vapour pressure are reproduced satisfactorily with the aid of the Redlich–Kwong equation of state modified by Prausnitz and coworkers[35] for mixtures of water and non-polar components. This equation is apparently suitable for the description of the volumes of gaseous mixtures of non-polar components with water vapour also above the critical temperature of water, provided that the pressure does not exceed 200–250 kgf cm^{-2}.

The Redlich–Kwong equation is

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)\,T^{0,5}}. \qquad (1)$$

The coefficient of Eqn.(1) for a mixture is usually expressed in terms of the coefficients of the mixture components and their mole fractions with the aid of the equations

$$b = \sum_i b_i N_i,\ a = \sum_i \sum_j a_{ij} N_i N_j, \qquad (2)$$

$$b_i = 0{,}0867 RT_{K_i}/P_{K_i},\ a_{ii} = 0.4278\ R^2 T_{K_i}^{2,5}/P_{K_i}, \qquad (3)$$

$$a_{ij} = a_{ii}^{0,5} a_{jj}^{0,5},$$

where p is the pressure, v the molar volume, N the mole fraction, R the gas constant, and T the absolute temperature.

Eqns.(2) and (3) are relatively unsuitable for both water and for water–non-polar substance mixtures. Two modifications have been introduced[35] into Eqns.(3). Firstly, account was taken of the fact that the coefficient a for water is not constant but decreases appreciably with temperature. This is because the interaction between water molecules is to a large extent determined by hydrogen bonds and dipole–dipole interactions. The above interactions are extremely sensitive to the mutual orientation of water molecules and therefore diminish sharply with increased temperature. The coefficients a_{11} for water (henceforth water will be designated by subscript 1 and the non-polar substance by 2) at different temperatures have been determined from data for the dependence of the volume of water vapour on pressure; the corresponding values of a_{11} have been tabulated as a function of temperature[35].

The necessity for the second modification in Eqn.(3) arises from the fact that, when water molecules interact with non-polar molecules, neither hydrogen bonds nor dipole–dipole interactions, which play the main role in the interaction of water molecules with one another, occur. The coefficient a_{11} was divided into two parts:

$$a_{11}(T) = a_{11}' + a_{11}''(T). \qquad (4)$$

The quantity a_{11}' is independent of temperature and is determined by dispersion interaction forces, while a_{11}'' is determined by hydrogen bonds and dipole–dipole interactions. In the calculation of the mixed coefficient a_{1j} for water and the non-polar substance from the last Eqn.(3), account is not taken of the entire coefficient a_{11} but only of that part of it which contributes to the water–non-polar substance interaction (a_{11}')†:

$$a_{1j} = (a_{11}'\, a_{jj})^{0,5}. \qquad (5)$$

According to Prausnitz and coworkers[35], $a_{11}' = 35$ kg K$^{1/2}$ litre^2 mol^{-2}.

The unsuitability of the method of Prausnitz and coworkers[35] for the description of $p-V-T-N$ data for mixtures in which water vapour predominates at temperatures above the critical temperature of water and at pressures in excess of 200 kg cm^{-2} is due to the fact that the coefficient a_{11} of the Redlich–Kwong equation for pure water vapour begins to depend appreciably on pressure when the latter is above 200–300 kg cm^{-2}.

The Redlich–Kwong equation with the modifications described has been tested not only for the volumes of gaseous mixtures but also in relation to the phase equilibria. The equation

$$\ln f_i = \ln \frac{N_i RT}{v-b} + \frac{b_i}{V-b} - \frac{2\sum_j N_j a_{ij}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_i}{RT^{3/2} b^2}\left[\ln \frac{v+b}{v} - \frac{b}{v+b}\right] \qquad (6)$$

with the aid of which the chemical potential (fugacity) of the mixture component f_i is determined, corresponds to the equation of state (1). Eqn.(6) was tested with the aid of data for phase equilibria between water and gas. Since the solubility of non-polar substances in water is as a rule very low, the fugacity of water in the aqueous liquid can be set equal to the tabulated fugacity of pure water multiplied by the mole fraction of water in the liquid, which is close to unity, and by Poynting's correction, which takes into account the amount by which the pressure exceeds the water vapour pressure. Having substituted this value in Eqn.(6), we find from Eqns.(6) and (1) the concentration of water vapour in the gas saturated with water at the given pressure.

†An analogous approach has been proposed by M.I.Temkin[36].

Table 3[37] presents systems for which calculation of the water vapour content in the gas in equilibrium with water proved to be satisfactory over a specific range of temperatures and pressures.

Table 3. Errors in the calculation of the water vapour content of the gas in equilibrium with water (average for several pressures).

t, °C	P_{max}, kgf cm^{-2}	Error, %	t, °C	P_{max}, kgf cm^{-2}	Error, %
	Methane			n-Hexane	
150	400	2.7	200	37	1.8
200	400	3.6	220	53	2.2
250	400	3.4	235	150	3.1
300	400	2.8	250	150	3.7
			275	150	4.5
	n-Butane			n-Decane	
171.1	562	2.4			
204.4	562	2.3	300	100	8.9
237.8	421	2.9	310	100	9.2

Attention should be drawn to the fact that in many instances calculation of the water vapour content in a non-polar gas by Eqns.(1) and (6) leads to satisfactory results also at those temperatures and pressures at which Eqn.(1) is unsuitable for the calculation of the volume of pure water vapour. The cause of this discrepancy lies in the fact that the region of applicability of Eqn.(1) to non-polar gases is wider than the region of its applicability to water vapour. When the content of water vapour in the gaseous mixture is low, Eqn.(1) describes the volumes of the mixture at pressures where it is unsuitable for mixtures with a high content of water vapour.

The applicability (within certain regions of the parameters of state) of the equation of state to gaseous mixtures of water vapour and non-polar components makes it possible to calculate the chemical potentials of the components of the above systems and their dependence on pressure and composition, i.e. all the data required for calculations on phase equilibria. The majority of the calculations based on the equation of state are carried out on a computer; the calculations can yield information about the behaviour of specific systems. However, general analysis of the behaviour of systems as a function of the properties of a non-polar substance with the aid of a computer is difficult. The approximate method for estimating the volume behaviour of mixtures described below is therefore of interest. The volumes of mixtures are frequently described by means of a quantity called the excess volume:

$$v_{exc} = v - v_1^0 N_1 - v_2^0 N_2, \qquad (7)$$

where v_1^0 and v_2^0 are the molar volumes of the pure components and v is the molar volume of the mixture.

Figs.9 and 10 present the excess volumes in the water–methane[31,32] and water–octane[33] systems. At low and moderate pressures the excess volume is positive in all the systems investigated; in individual instances the volume exceeds by 20–30% the additive volume of the components. With increase of pressure, the excess volume behaves in a fairly complex manner in many instances. Thus in the water–octane system (Fig.10) mixtures in which water predominates are characterised, as before, by the increase of the volume above the additive value, while mixtures in which the hydrocarbon predominates have a volume smaller than the additive value, i.e. the excess volume curve has a maximum and a minimum. On further increase of pressure, the excess volume becomes negative over the entire range of compositions.

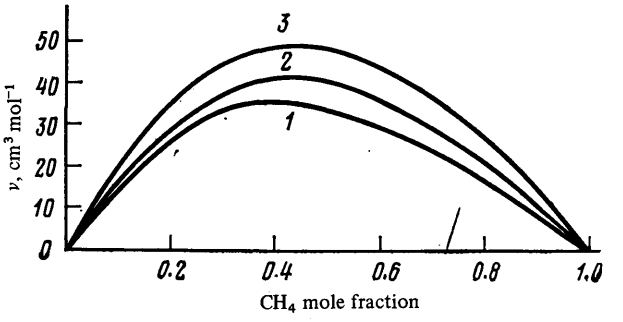


Figure 9. The excess molar volumes in the methane–water system at 350 °C and at different pressures (kgf cm^{-2}): 1) 60; 2) 100; 3) 140.

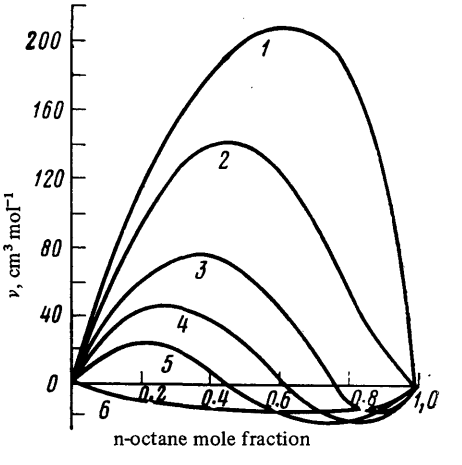


Figure 10. The excess molar volumes in the octane–water system at 350 °C and at different pressures (kgf cm^{-2}): 1) 40; 2) 60; 3) 80; 4) 100; 5) 120; 6) 140.

Calculations of the volumes by the Redlich–Kwong equation with Prausnitz's modifications reproduce the different forms of dependence on the excess volume and composition presented in Fig.10. On the assumption that this equation is applicable to the description of excess volumes in gaseous

solutions, it is possible to carry out a general analysis of the volume behaviour of the test systems as a function of the nature of the non-polar substance, which is determined by the coefficients a_{22} and b_2.

Since the equation of state (1) has been solved for pressure, analysis is greatly simplified when the excess pressure is used instead of the excess volume. The excess pressure is the difference between the true pressure of the mixture and the pressure calculated from Dalton's law, i.e. obtained by adding together the pressures of the pure components (p_1^0 and p_2^0) of the mixture occupying the same volume as the mixture:

$$p_{exc} = p - p_1^0 N_1 - p_2^0 N_2. \quad (8)$$

Since the behaviour of the excess pressure and excess volume is qualitatively similar, for an approximate estimate of the behaviour of the excess volume one can employ data for the behaviour of the excess pressure.

The form of the dependence of the excess pressure on composition is determined primarily by the sign of the derivatives $\partial p_{exc}/\partial N_1$ at the ends of the composition axis, i.e. at $N_1 = 0$ and $N_1 = 1$. For the excess pressure maximum, it is necessary that

$$(\partial p_{exc}/\partial N_1)_{v,T,N_1=0} > 0 \text{ and } (\partial p_{exc}/\partial N_1)_{v,T,N_1=1} < 0. \quad (9)$$

For the simultaneous presence of an excess pressure minimum in mixtures with a high content of the non-polar substance and an excess pressure maximum in mixtures with a high water vapour content, it is necessary that

$$(\partial p_{exc}/\partial N_1)_{v,T,N_1=0} < 0 \text{ and } (\partial p_{exc}/\partial N_1)_{v,T,N_1=1} < 0. \quad (10)$$

Finally, for an excess pressure minimum, it is necessary that

$$(\partial p_{exc}/\partial N_1)_{v,T,N_1=0} < 0 \text{ and } (\partial p_{exc}/\partial N_1)_{v,T,N_1} > 0. \quad (11)$$

The van der Waals equation

$$p = RT/(v-b) - a/v^2 \quad (12)$$

can be used for the approximate analysis of the above problem instead of the Redlich–Kwong equation (1). Eqn.(12) differs little from Eqn.(1) at constant temperature and at not unduly high pressures. It is noteworthy that, despite the identical designation of the coefficients of Eqns.(1) and (12), their numerical values are different. Using Eqns.(12), (2), and (5), it is possible to obtain the expressions

$$(\partial P_{exc}/\partial N_1)_{v,T,N_1=0} = \frac{RT(b_1-b_2)}{(v-b_2)^2} - \frac{RT}{v-b_1} + \frac{RT}{v-b_2} + \frac{a_{11}+a_{22}-2a_{12}}{v^2}, \quad (13)$$

$$(\partial P_{exc}/\partial N_1)_{v,T,N_1=1} = \frac{RT(b_1-b_2)}{(v-b_1)^2} - \frac{RT}{v-b_1} + \frac{RT}{v-b_2} + \frac{2a_{12}-a_{11}-a_{22}}{v^2}. \quad (14)$$

For higher values of v (i.e. at low pressures), the sum of the first three terms of Eqns.(13) and (14) can be neglected compared with the fourth term. Since $a_{12} < (a_{11}+a_{22})/2$ conditions (9) hold at low pressures. With increase of v, the first terms of Eqns.(13) and (14) begin to increase in absolute magnitude; their sign is negative for $b_2 > b_1$. The first term of Eqn.(13) then increases faster than the first term of Eqn.(14), so that, on passing to small volumes (i.e. high pressures), the derivative $(\partial p_{exc}/\partial N_1)_{v,T,N_1=0}$ can change sign before $(\partial p_{exc}/\partial N_1)_{v,T,N_1=1}$ and two extrema are observed [condition (10)]; finally, on further increase of pressure, the derivative $(\partial p_{exc}/\partial N_1)_{v,T,N_1=1}$ also changes sign and an excess pressure minimum is observed [condition (11)].

Thus, subject to the condition that the volume of the molecule of the non-polar substance exceeds that of the water molecule ($b_2 > b_1$), conditions (9), (10), and (11) should be established successively with increase of pressure. The greater the volume of the molecule of the non-polar substance, the higher the pressure at which the above changes in the excess volume (pressure) occur. One should recall that the behaviour described is observed only in the region of applicability of the equation of state adopted.

It is noteworthy that the principal specific feature of gaseous solutions of water and a non-polar substance is an extremely weak interaction between unlike molecules. This feature is manifested both at low and at high temperatures. The structural order characteristic of the liquid phase is not significant in gaseous solutions at low densities. The inapplicability of simple two-parameter equations of state to high-density water vapour should apparently be attributed to this factor.

IV. LIQUID SOLUTIONS OF NON-POLAR SUBSTANCES IN WATER

There are very few data for solutions of non-polar substances in water which could yield information about the thermodynamic quantities of the solutions over a wide range of temperatures and pressures. The solutions of methane in water have been most thoroughly investigated. Data for the solubility of methane in water and the volumes of the solutions at low and moderate temperatures have been available for a comparatively long time[38,39] and those for the range 200–350 °C were obtained more recently[7,40,41].

The Henry coefficient H_i can be found from solubility data. By definition[42], it is related to the difference between the chemical potential of component i at infinite dilution, extrapolated to the pure substance, and the chemical potential of the component in the ideal gas state at $p = 1$:

$$RT \ln H_i = \mu_i(p, T) - \mu_i(\text{id.gas}, T, p=1). \quad (15)$$

Here H_i is the Henry coefficient, μ_i is the chemical potential of component i, and the dot under the symbol means that the given quantity refers to the state of infinite dilution. Knowing the dependence of the Henry coefficient on temperature, it is possible to obtain by means of Eqn.(15), with the aid of a familiar thermodynamic relation, the enthalpy change for transfer of component i from the ideal gas state to an infinitely dilute solution:

$$\left(\frac{\partial \ln H_i}{\partial T}\right)_p = -\frac{(h_i - h_{i,\text{id.gas}})}{RT^2}, \quad (16)$$

where h_i is the partial molar enthalpy of component i.

The solutions of methane as well as the majority of other non-polar substances in water are characterised by two features at low temperatures: firstly, on formation of these solutions from an ideal gas and water, the enthalpy decreases (heat is evolved) and, secondly, the Henry coefficient of the non-polar substance dissolved in water is very high (and correspondingly the solubility is extremely low).

The characteristics of the solubility of non-polar substances in water at low temperatures are said to be related to the ideas concerning the structure of liquid water. It is known that at low temperatures liquid water to a large extent retains the structure of ice within the limits of short-range order. In the structure of ice water molecules are distributed relative to one another in such a way that each is involved in the maximum possible number of hydrogen bonds (four bonds). By virtue of the high energy of the hydrogen

bonds, ice is fairly stable despite the small coordination number; the small coordination number is responsible for the extremely loose packing characterised by the presence of comparatively large cavities. In liquid water at low temperatures some of the cavities are filled by water molecules[43], which are linked to the molecules surrounding the cavities by dispersion interaction forces.

Apparently at low temperatures the non-polar molecules incorporated in water disrupt the hydrogen bonds existing between water molecules to only a slight extent, but they transform the water structure around themselves in such a way that cavities arise in the latter in which the non-polar molecules can be accommodated. The evolution of heat (decrease of enthalpy) on formation of a liquid solution from a non-polar substance in the ideal gas state and water is then related to the absence of a significant energy expenditure on the dissociation of hydrogen bonds and to the gain of the dispersion interaction energy by the molecules of the non-polar substance. A certain amount of energy is also evolved because the water molecules displaced by the non-polar substance from the cavities form hydrogen bonds with one another[44-46].

The second feature of solutions of non-polar substances in water at low temperatures, namely their low solubility, has not yet received a generally accepted explanation[46,47]. Attempts to explain the low solubility of non-polar substances in water have been made in two investigations[48,49]. It has been suggested[49] that the formation of cavities in water, whose volume makes it possible to accommodate non-polar molecules larger than helium and neon atoms and hydrogen molecules#, is not accompanied by a change in enthalpy, but proceeds with a decrease of entropy. The decrease of entropy is associated with the increase of the Henry coefficient in accordance with the thermodynamic equation

$$RT \ln H_i = \Delta h_i - T\Delta S_i; \qquad (17)$$

where Δh_i and ΔS_i are the change in the enthalpy and entropy on transfer of the non-polar substance from the ideal gas state at $p = 1$ to the hypothetical state of the solute extrapolated to the pure substance.

At high temperatures (starting from ~100 °C) the solubility of methane in water increases with temperature at an increasing rate[41]. According to Eqn.(16), this corresponds to a negative heat of solution, i.e. to the absorption of heat. This finding is consistent with data showing that, under the conditions of intense thermal movement, ordered structures in water lose their importance. In the limit at a sufficiently high temperature both water and methane molecules in solutions are distributed completely at random and water–water interactions are replaced by water–methane interactions in the dissolution process. As already mentioned, this change should take place with loss of energy. The internal energy for the intermolecular interaction of the ideal gas is zero. Thus at high temperatures the change in the internal polar energy on dissolution will be greater than zero ($e_i - e_{i,\text{id.gas}} > 0$). The work associated with the decrease of the volume of the gas when the latter dissolves is also positive; consequently the entropy change is likewise positive ($h = e + pv$).

The difference in the nature of the solubility of non-polar substances in water at low and high temperatures is also indicated by the partial molar volume of the substance dissolved in water. For example, the partial molar volumes of methane dissolved in water at 0° and 50 °C [40] are much smaller than the corresponding quantities for the methane dissolved in other solvents[48].

Partial molar volumes of methane dissolved in water at 400 kgf cm^{-2} and different temperatures

t, °C	0	50	100	150	200	250	300	350
v, /cm^3	36	38	40	43	49	60	96	141

It is seen from the data presented that, starting from 250 °C and at higher temperatures (300° and 350 °C), the partial molar volume of methane dissolved in water increases sharply. This finding is consistent with the idea that at high temperatures the water–water interaction is replaced by the water–methane interaction on dissolution of methane, which should be accompanied by a considerable decrease of the forces of interaction between molecules.

A sharp difference between the mechanisms of the dissolution of methane in water is apparently observed at markedly different temperatures. For intermediate temperatures, there is probably a possibility of a mixed dissolution mechanism in which methane molecules are both incorporated in cavities and replace water molecules in the quasi-crystal lattice of the liquid (the "cavity" and "solvation" mechanisms according to Borina and Samoilov[52]).

Using data for the solubility of methane in water, the equations of state for the gas phase (the Lewis–Randall rule at low concentrations of water vapour and the Redlich–Kwong equation at high concentrations), and data for the change in the volume of water on dissolution of methane in the latter, it is possible to determine the changes in the fugacity of methane as a function of its concentration in solution. It has been established for the range 25–171 °C that a solution of methane in water at pressures up to 700 kgf cm^{-2} obeys Henry's law in terms of the thermodynamic formulation[53]:

$$f_2 = H_2(p, T)N_2, \qquad (18)$$

$$H_2(p,T) = H_2(p_1^0, T) \cdot 10^{\frac{v_2(p-p_1^0)}{2.303\,RT}}; \qquad (19)$$

here subscripts 2 and 1 correspond to methane and water respectively. When Eqn.(18) holds and v_2 is independent of pressure, there should be a linear relation between $\lg(f_2/N_2)$ and $p - p_1^0$.

Between 300° and 350 °C, the linear relation between $\lg(f_2/N_2)$ and $p - p_1^0$ does not hold, which can be attributed both to a decrease of the partial molar volume of methane with pressure at high temperatures and to the failure of the Henry law (or to both causes simultaneously). When Henry's law breaks down, an additional multiplier is introduced into Eqn.(18)—the activity coefficient γ, which determines the degree of deviation from Henry's law:

$$f_2 = H_2(p,T)N_2\gamma_2^\infty, \qquad (20)$$

where ∞ refers to infinite dilution. The activity coefficient γ_2^∞ is close to unity in the region of low methane concentrations, but apparently diminishes as the concentration increases. The hypothesis of the decrease of the activity coefficient with concentration is associated with the fact that, at temperatures exceeding the minimum critical temperature in the water–methane system (352 °C), the critical state can be reached; at the critical point of the mixture the fugacity of the component does not vary with concentration:

$$(\partial \ln f_i/\partial N_i)_{p,T} = 0. \qquad (21)$$

#Molecules whose size exceeds these dimensions cannot be accommodated within the cavities of the ice lattice[50,51].

Fig.11 illustrates the variation of the fugacity with the mole fraction when Henry's law holds (dashed line) and the variation of the fugacity in the vicinity of the critical point associated with condition (21), which is obligatory for the critical point of a binary system. It is seen from Fig.11 that, as the critical is approached, the fugacity deviates from the value which it should have when the Henry law holds. This means that the activity coefficient should become less than unity.

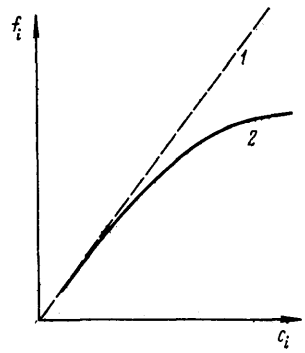


Figure 11. Variation of the fugacity of the component in solution with its concentration: 1) Henry's law; 2) real relation.

The problem of the variation of the properties of a solution of a non-polar substance in water under the influence of the addition of a salt to water is extremely interesting. Bearing in mind that the solubility of non-polar substances in water is extremely low, in most cases it is possible to assume that the chemical potential of water in the aqueous salt solution of a non-polar substance is the same as in the aqueous salt solution without the non-polar substance. The corresponding chemical potentials of water can be found from its vapour pressure over the salt solution. If necessary, a correction is introduced for the difference between the vapour pressure and fugacity and a correction for the Poynting effect when the external pressure exceeds the vapour pressure.

The influence of the salt dissolved in water on the chemical potential of the non-polar solute is much more complex. The solubility of non-polar substances in water in most cases decreases under the influence of salts. The change in solubility is usually described with the aid of Sechenov's equation

$$N_i^* = N_i \cdot 10^{-K_i n}, \qquad (22)$$

where the superscript * refers to the electrolyte solution.

Eqn.(22) holds fairly accurately only at low salt concentrations. At salt concentrations in excess of 0.5–1 M the Sechenov coefficient K_i usually decreases with increase of concentration.

An expression for the Henry coefficient of the non-polar component dissolved in a salt solution in water can be obtained from Eqn.(22) and the definition of the Henry coefficient:

$$H_i^* = H_i \cdot 10^{K_i n}.$$

It is usually assumed that the limits of the applicability of the Henry law [Eqns.(18) and (19)] to non-polar gases dissolved in aqueous salt solutions do not differ significantly from the limits of the applicability of this law to solutions of gases in water without salts.

The temperature dependence of the Sechenov coefficient has been investigated mainly in the range 0–70 °C. At high temperatures the influence of salts on the solubility of non-polar gases has been studied only for carbon dioxide[54,55] and methane[56] and it has been found that the Sechenov coefficient passes through a minimum as a function of temperature. To account for this phenomenon, one must relate the Sechenov coefficient to the thermodynamic functions of component i disssolved in water[57].

Consider the equilibrium between component i in the gas state and both pure water and a salt solution of water in the region where Henry's law holds:

$$\mu_i(\text{gas}) = \mu_i + RT \ln N_i = \mu_i^* + RT \ln N_i^*. \qquad (23)$$

It follows from Eqns.(22) and (23) that

$$\mu_i^* - \mu_i = 2.303\, RT\, n K_i. \qquad (24)$$

According to Eqn.(24), the Sechenov coefficient is related to the difference between the chemical potential of component i in pure water and in the salt solution. Differentiation of Eqn.(24) with respect to temperature yields

$$\frac{h_i - h_i^*}{RT^2} = 2.303\, n \frac{\partial K_i}{\partial T}, \qquad (25)$$

The minimum in the plot of the Sechenov coefficient against temperature is apparently associated with the different natures of solutions of non-polar substances in water at low and high temeratures. If the non-polar molecules in solution in water at low temperatures are located in cavities, then, according to Eqn.(25), the temperature variation of the Sechenov coefficient is determined by the difference between the internal energies of the non-polar substance in pure water and in the salt solution. The internal energy of the intermolecular interaction between the non-polar substance and the skeleton of the water lattice is relatively small and the change in this interaction under the influence of the salt is even smaller.

At a high temperature[57] the formation of the solution involves mainly the replacement of water molecules by those of the non-polar gas in the quasi-crystal lattice. The enthalpy of formation of the solution from the non-polar gas in the ideal gas state and from liquid water can then be regarded as consisting of two components: the main, positive part—the enthalpy of the separation of water molecules from one another on formation of a cavity for the incorporation of the non-polar molecules (e_1)—and a small negative part—the enthalpy of incorporation of non-polar molecules at a quasi-crystal lattice site of water (e_{inc}).

Neglecting the enthalpy of the incorporation of the non-polar substance compared with the enthalpy of formation of a cavity in the water lattice, we find that, for a small difference between the sizes of water molecules and the molecules of the non-polar substance,

$$\left(\frac{\partial K_i}{\partial T}\right)_p \approx \frac{h_1 - h_1^*}{2.3 n RT^2}; \qquad (26)$$

where n is the molality of the electrolyte in solution. It can be shown that

$$\frac{h_1 - h_1^*}{2.3 \cdot RT^2 n} = \left(\frac{\partial \lg (f_1^*/f_1^0)}{\partial T}\right), \qquad (27)$$

where f_1^0 and f_1^* are the fugacities of pure water and the water in the salt solution.

Calculations based on the experimental water vapour pressures over salt solutions[58] show that $h_1 - h_1^* > 0$ and increases with temperature. It follows from this finding that, in conformity with Eqn.(26), the Sechenov coefficient should increase with temperature at high temperatures. The available data for the variation of the Sechenov coefficients confirm Eqn.(26) approximately[54-56] (Fig.12).

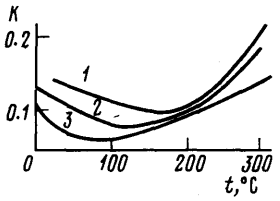


Figure 12. Temperature dependence of the Sechenov coefficients K of gases dissolved in aqueous salt solutions: 1) methane in NaCl solution; 2) carbon dioxide in $CaCl_2$ solution; 3) carbon dioxide in NaCl solution.

On the whole, one should note that the nature of solutions of non-polar substances in water at low temperatures is determined by the distribution of the molecules of the non-polar substance in the structural cavities. At high temperatures the specific features of the dissolution process involve the substitution of water molecules by solute molecules. The changes in the nature of the dissolution process with temperature lead to minima in the temperature variations of the Henry and Sechenov coefficients of non-polar substances dissolved in water.

V. LIQUID SOLUTIONS OF WATER IN NON-POLAR SUBSTANCES

It was noted above that water as a solvent for non-polar substances differs sharply from other solvents: the Henry coefficients of non-polar substances dissolved in it exceed by 2–3 orders of magnitude (and more) their values for the same substances in the majority of other solvents§. Water as a solute in non-polar solvents is not exceptional among other solutes. This is because the specific features of water are manifested in the interaction of its molecules with one another—mainly in the formation of hydrogen bonds. On the other hand, the separated molecules of the water dissolved in a non-polar solvent do not exhibit features characteristic of a collection of water molecules. If the properties of water in its dilute liquid solutions in non-electrolytes are extrapolated to the hypothetical pure substance, then the latter should have properties close to those of non-polar substances with small molecules—for example, methane or nitrogen, i.e. substances whose critical temperature is lower by hundreds of degrees than that of water.

Henry coefficients (kgf cm^2) of water and methane in different solvents (Refs.59-62)

Solvent	n-Butane	n-Decane	n-Hexadecane
t, °C	37.7	237.8	250
Water	140	150	190
Methane	190	250	200

§Certain aromatic hydrocarbons are an exception.

Evidently the Henry coefficients of water and methane in different non-polar solvents are of the same order of magnitude.

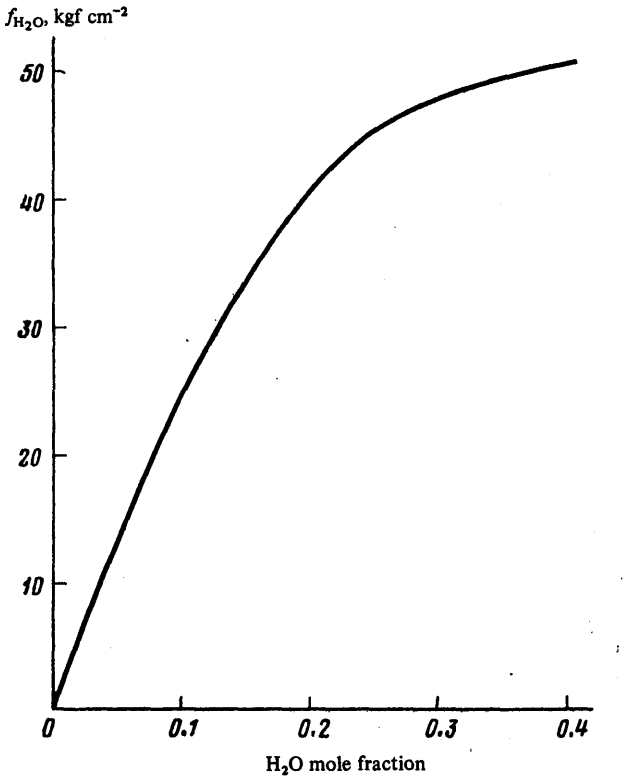


Figure 13. Dependence of the fugacity of water on its concentration in a decane–water mixture at 275 °C and a pressure of 73.2 kgf cm^{-2}.

There are at present numerous data for the phase equilibria between liquid non-polar substances and gaseous mixtures and between liquid non-polar substances and liquid aqueous solutions. Information concerning certain thermodynamic properties of solutions of water in non-polar substances can be obtained from these data. For example, in view of the possibility of calculating the fugacities of the components in gaseous solutions from the equation of state (see Section III), it is possible to find the fugacities of the components in liquid solutions in equilibrium with the gas phase along the saturation line. There are fewer data for the volumes of solutions of water in liquid non-polar substances.

Relatively detailed information is available about both phase equilibria and the volumes for solutions of water in decane at 275 °C.[34] The dependence of the fugacity of water on its mole fraction in its liquid solution at 275 °C and a pressure of 73.2 kgf cm^{-2} has been obtained from these results (Fig.13). Fig.13 shows that, at water concentrations not exceeding a mole fraction of 0.1, a linear relation holds between the fugacity and concentration (thermodynamic formulation of the Henry law) within the limits of experimental accuracy; for mole fractions in excess of 0.1, the increase of fugacity slows down. The activity coefficient γ_1^{∞} in Eqn.(20), corresponding to a mole fraction of 0.4, is appreciably smaller than unity (0.48). The decrease of the activity coefficient is apparently associated with the approach to the critical state [see Eqn.(27)].

The data of Lotter et al.[34] show that at 275 °C and 69.5 kgf cm^{-2} the molar volume of a liquid solution of water in decane varies linearly with concentration when the latter changes from a mole fraction of 0.1 to 0.35. From this it follows that the partial molar volume of water in the above concentration range is constant. Its value under these conditions is 119 cm^3 mol^{-1}, which is much greater than the molar volume of pure water under the same conditions (23.6 cm^3 mol^{-1}).

Measurements of the volumes of solutions of water in various non-polar substances at the same concentration for each hydrocarbon[63] made it possible to calculate the apparent molar volume of dissolved water as the ratio of the volume increment on dissolution of water in the non-polar substance to the number of moles of dissolved water:

$$v_1^{app} = [v - v_2^0(1 - N_1)]/N_1 . \qquad (28)$$

The results (Table 4) exceed severalfold the molar volumes of pure water, which varies from 21.4 to 28.1 cm^3 mol^{-1} under the given conditions.

Table 4. The apparent molar volumes of water v_{eff} dissolved in hydrocarbons.

Hydrocarbon	t, °C	p, kgf cm^{-2}	v_{eff}, cm^3 mol^{-1}	Mole fraction
n-Hexane	220	48	641	0.185
n-Decane	285	67	146	0.319
n-Hexadecane	275	56	86	0.338
	300	81	99	0.428
	330	125	110	0.531

The partial molar volumes of water dissolved in hydrocarbons apparently decrease markedly with increase of pressure. Using data for the phase equilibria in liquid water and decane at 275 °C and pressures up to 800 kgf cm^{-2},[34] neglecting the solubility of decane in water, and assuming (as mentioned above) that the Henry law holds for a water mole fraction in the hydrocarbon less than 0.1, the partial molar volume of water in decane can be found from the differential equation for the phase equilibrium

$$\left(\frac{\partial N_1^n}{\partial p}\right)_T = \frac{v_1^w - \bar{v}_1^n}{RT\,(\partial \ln N_1^n/\partial N_1^n)} \qquad (29)$$

where superscripts n and w refer to the non-polar liquid phase and to the aqueous phase respectively. It was found that, at a pressure of 700 kgf cm^{-2}, it is much smaller than the experimental partial volume of water at 70 kgf cm^{-2}.

VI. CHARACTERISTICS OF THE PHASE EQUILIBRIA IN THE SYSTEMS UNDER CONSIDERATION

The knowledge of the thermodynamic properties of the individual phases in a water–non-polar substance system makes it possible to explain the characteristic features of the phase equilibria in such systems. We shall consider individual types of phase equilibria.

Liquid Water–Non-polar Liquid Equilibria

For systems of the first type (see Section II), these equilibria exist in temperature and pressure ranges located on the p–T diagram (Fig.7) above the three-phase curve. For systems of the second type, the equilibria are observed in the region above the critical liquid–liquid curve or above the three-phase curve in Fig.2.

As long as the temperature is not very high and the miscibility of the liquids considered is small, the solutions are dilute and the solubility of the non-polar component in the aqueous phase N_2^w as well as the solubility of water in the non-polar liquid N_1^w obey Henry's law:

$$N_2^w = \frac{1}{H_2^w(p,T)} f_2^n, \qquad N_1^n = \frac{1}{H_1^n(p,T)} f_1^w \qquad (30)$$

The Henry coefficients of non-polar substances in water at low temperatures are anomalously high, which is responsible for the low solubility of non-polar substances in water; the Henry coefficients of water and non-polar substances do not exhibit anomalies. However, apart from the Henry coefficients of the component dissolved in a given phase, the solubility is determined by the fugacity of the component in the phase in equilibrium with the given phase [Eqn.(30)]. At equilibrium between two dilute liquid solutions this fugacity is close to that of the component in the state of the pure liquid. Both pure water and non-polar liquids have in most cases low vapour pressures at low temperatures and hence low fugacities. According to Eqn.(30), this finding is one of the causes of the low miscibilities of the phases under consideration at low temperatures. With increased temperature, the vapour pressures of the pure liquids also increase, which leads to an increase in the miscibility of the liquids. Here one should bear in mind that, as a consequence of the high Henry coefficients of substances dissolved in water, their solubilities in water are in most cases small and the solubilities of water in non-polar substances, characterised by comparatively small Henry coefficients, become considerable. This factor is responsible for some asymmetry in the miscibility of water and non-polar substances.

An increase of pressure reduces the solubility of water in a non-polar liquid. In the region of the applicability of Henry's law this decrease is defined by Eqn.(29) and can be explained by the fact that the molar volume of pure water is much smaller than the partial molar volume of water dissolved in a non-polar substance. The effect diminishes with increase of pressure owing to the diminution of the partial molar volume of water as the pressure increases. As the critical state is approached, the decrease of the solubility of water in a non-polar liquid under the influence of pressure is intensified, since the denominator of Eqn.(29) should then be replaced by $RT\,\partial \ln f_1^n/\partial N_1^n$, which tends to zero at the critical point (and $\partial N_1^n/\partial p$ tends correspondingly to infinity).

The experimental data referring to both the first and second types of water–non-polar substance systems confirm these findings. Thus Fig.14 illustrates the pressure dependence of the water content in decane in equilibrium with liquid water[64]. The closer the state of the system to the critical end point (Fig.4), the sharper the decrease of the water content in the non-polar liquid with increase of pressure. Fig.15 presents the miscibility in the tetrahydronaphthalene–water system[30] (system of the second type); in this case too the influence of pressure on the solubility of water in tetrahydronaphthalene increases sharply as the critical point is approached.

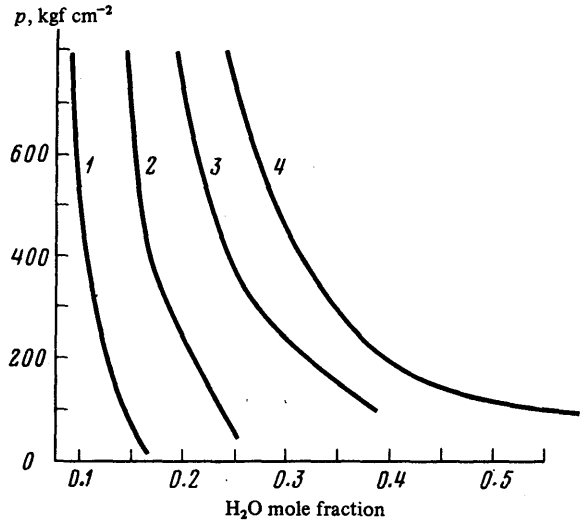


Figure 14. The influence of pressure on the water content in liquid decane in equilibrium with liquid water at different temperatures (°C): 1) 225; 2) 250; 3) 275; 4) 290.

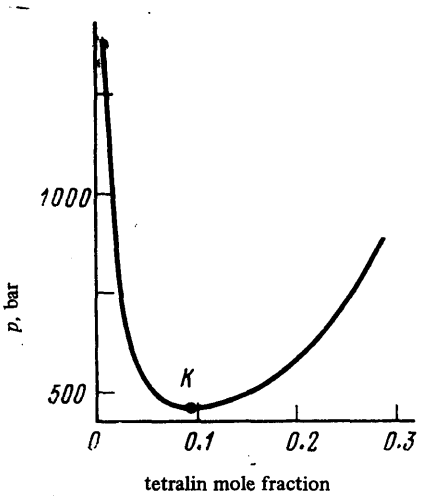


Figure 15. The influence of pressure on the compositions of the equilibrium liquid phases in the tetrahydronaphthalene–water system at 350 °C; *K*—critical point for the liquid–liquid equilibrium.

The solubility of non-polar liquids in water at low and moderate temperatures increases with pressure. This is because at low temperatures the vacancy mechanism of the dissolution[52] of non-polar substances in water plays a major role. In this dissolution mechanism the partial molar volume of the non-polar substances dissolved in water is anomalously small—smaller than the molar volume of the pure liquid non-polar substance. The dissolution of the liquid non-polar substance in water is then accompanied by a decrease of volume and, in conformity with the requirements of thermodynamics, an increase of pressure should promote an increase of solubility. As an example, one may quote data for the water–n-butane system[65]. At high temperatures the vacancy mechanism of dissolution loses its importance and the partial molar volumes of non-polar substances in water increase sharply (see Section IV) and an increase of pressure leads to a decrease of their solubility in water.

Thus at a high temperature the miscibilities of water and a non-polar substance decrease with pressure.

The Non-Polar Liquid–Aqueous Liquid–Gas Phase Three-Phase Equilibrium

If the miscibilities of the liquids are small, then the fugacity of each component in the gas phase in equilibrium with the two liquids is almost equal to the fugacity of this component in the state of the pure liquid. When Dalton's law holds, the pressure in the gas phase of the three-phase state is in this instance almost equal to the sum of the vapour pressures of both components and is therefore higher than the pressure of each component; the composition of the gas phase is intermediate between the compositions of the two liquid phases. The phase diagram then has the form illustrated in Fig.3.

With increase of temperature, the following possibilities for the evolution of the three-phase state exist.

(a) The properties of solutions of water in a non-polar liquid approach those of the gas phase and a critical end point is established (Fig.4). Since the three-phase equilibrium pressure is higher than the vapour pressure of the pure non-polar liquid, the pressure at the critical end point, which belongs to the three-phase equilibrium, is also higher than the vapour pressure of the non-polar liquid. The temperature at the critical end point must be lower than at the critical point of the non-polar substance. For this reason, the branch of the critical curve beginning at the critical point of the pure non-polar substance should be directed towards increasing pressures and decreasing temperatures on the $p-T$ diagram regardless of whether or not the critical temperature of the non-polar substance exceeds the critical temperature of water. Phase equilibria of this kind are characteristic of the first type of water–non-polar substance equilibrium.

(b) The critical end point is established as a result of the mutual approach of the properties of the solution of the non-polar substance in water and of the gas phase. Equilibria of this type are at present unknown.

(c) An azeotrope appears in the system and there is a change of the three-phase equilibrium from the type illustrated in Fig.3 to the type illustrated in Fig.16¶. A characteristic feature of this three-phase equilibrium is that the water content in the gaseous solution is greater than in the

¶If the non-polar substance passes from the solid to the liquid state at an extremely high temperature, there is a possibility of only the three-phase equilibrium of the type illustrated in Fig.16.

liquid aqueous solution. In this case there is a possiblity of the establishment of a critical end point as a result of the mutual approach of the properties of the two liquid phases. The establishment of the critical end point is possible at a temperature below the critical temperatures of both water and the non-polar substance. These features are characteristic of water–non-polar substance systems of the second type (Fig.2).

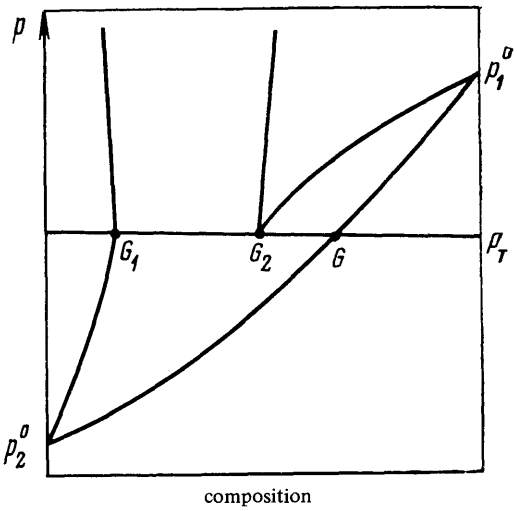


Figure 16. Three-phase equilibrium of the second type; L_1, L_2, and J—compositions of the coexisting liquid and gas phases.

For the above type of equilibria to occur, it is necessary that the content of the non-polar substance in the gas phase should be smaller than in the aqueous solution. For a rough estimate of the possibility of the realisation of this condition, we shall assume that the content of the non-polar substance in the gas phase N_2^g is determined by Dalton's law as the ratio of the partial pressure of the non-polar substance to the sum of the vapour pressures of water (p_1^0) and the non-polar substance (p_2^0):

$$N_2^g = p_2^0/(p_2^0 + p_1^0),$$

and the mole fraction of the non-polar component in the aqueous phase is determined by Henry's law: $N_2^W = p_2^0/H_2^W$. From the condition $N_2^g < N_2^W$, we obtain $H_2^W < p_1^0 + p_2^0$, which requires relatively low values of the Henry coefficient, i.e. a high solubility of the non-polar substance in water. Since a high solubility of the non-polar substance in water is possible at an extremely high temperature, the type of three-phase equilibria under discussion is apparently possible in systems incorporating a non-polar liquid with a high critical temperature and with an increased ability to dissolve in water.

The Aqueous Liquid–Gas Phase Equilibrium

The region of aqueous liquid–gas phase equilibria in systems of the first type is designated by the latter B in Fig.3, which refers to temperatures below the temperature of the critical end point. Above the temperature of the critical end point (Fig.4), the aqueous liquid–gas phase equilibrium frequently extends to extremely high pressures. Thus in the water–ethane, water–benzene, water–carbon dioxide, and water–xenon systems equilibria of the above type have been traced up to pressures of $(3–3.5) \times 10^3$ kgf cm^{-2}.

This behaviour of the equilibrium under consideration is observed in a range of temperatures between that of the critical end point and the minimum in the critical temperature. It resembles the behaviour of the aqueous liquid–non-polar liquid equilibrium discussed above, which is reasonable, because, at the terminal critical point of systems of the first type, the non-polar liquid and the gas phase become identical and the resulting phase "inherits" the properties of both phases. At high pressures and low temperatures the properties of the liquid phase are manifested to a greater extent, while at low pressures and high temperatures the properties of the gas phase predominate. As already stated, in the aqueous liquid–non-polar liquid equilibrium the pressure does not promote the mutual approach of the properties of the phases and in the equilibrium between the aqueous liquid and the gas phase at high pressures the compositions of the phases do not approach one another as the pressure is raised.

In systems of the first type, at temperatures exceeding the minimum critical temperature, a critical state arises under certain conditions between the gas and the aqueous liquid when the pressures are low. If the pressure is then increased under isothermal conditions, the system remains homogeneous over a certain range of pressures and then splits into two phases when the pressure attains a sufficiently high value; a further increase of pressure increases the degree of layer formation, as in the non-polar liquid–aqueous liquid equilibrium. Such behaviour is characteristic of the separation of gaseous mixtures of the second kind into layers (Fig.1*a*). The majority of the water–non-polar substance systems investigated belong to this kind. In systems of the kind described by Fig.1*b* there are no gas–aqueous liquid critical states at all and, starting from the critical point of water and at higher temperatures, there exist critical states referring to the so-called gas–gas equilibrium.

The gas–liquid critical phenomena beginning at the critical point of pure water in water–non-polar substance systems of the first type are in most cases possible over a short range of temperatures between the critical temperature of water and the minimum critical temperature. For paraffinic hydrocarbons, the minimum critical temperature does not fall below 350 °C, while for mixtures of water and aromatic hydrocarbonds it is lower (294 °C in the case of benzene).

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Simple two-parameter equations of state (van der Waals and Redlich–Kwong) reproduce qualitatively the characteristics of the phase equilibria in the water–non-polar substance systems[66]. The quantitative agreement between the calculations and experiment is unsatisfactory, particularly for the van der Waals equation.

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