124. Ya.T.Eidus and B.K.Nefedov, Dokl.Akad.Nauk SSSR, 154, 1139 (1964).
125. Ya.T.Eidus, B.K.Nefedov, and A.V.Lobzova, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 726 (1964).

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PHASE EQUILIBRIA BETWEEN IMMISCIBLE GASEOUS PHASES

D.S.Tsiklis and L.A.Rott

INTRODUCTION

Until very recently there were reckoned to be five types of equilibria: crystal–crystal, crystal–liquid, crystal–gas, liquid–liquid, and liquid–gas. The theory of these phase equilibria was developed by Konovalov[1], Stoletov[2], Gibbs[3], van der Waals[4], Kuenen[5], and others. There was also convincing experimental confirmation of the theoretical predictions.

It now seems astonishing to us why the possibility of the existence of yet another type of equilibrium — gas–gas equilibrium (the existence of which could have been postulated even by simple analogy) — was generally not discussed right up to the end of the XIXth century. Even at the time of Dalton, scientists were surprised[6] that gases did not behave as liquids and did not take up positions in relation to one another according to their specific gravities. The explanation for such behaviour of gases was found in the fact that at low pressures they are mechanically (energetically, in modern terminology) independent.

The concept of the energetic independence of gases, true only at moderate pressures, greatly suppressed interest in a search for equilibrium between gaseous phases. Even after van der Waals[7] and Kammerlingh-Onnes and Keesom[8] had made, in the 1890's, a theoretically based prediction of the possibility of the existence of such an equilibrium, about 50 years elapsed before the first experimental work appeared, carried out by Krichevskii[9]. The results completely confirmed the predictions of the Dutch scientists.

Such a prolonged break is explained not solely to the viability of the concept of the energetic independence of gases. van der Waals and his students correctly predicted that the phenomenon of restricted mutual solubility of gases is possible because there is a great similarity between liquids and strongly compressed gases. Hence it seemed natural to search for this phenomenon at high pressures. The absence of the technical means necessary for this was a second reason, which for long delayed the experimental confirmation of this interesting phenomenon. However, as we shall see subsequently, it can also be observed at comparatively low pressures.

But somehow or other, if the honour of the theoretical prediction of and basis for the new type of equilibrium belongs to the Dutch scientists, that of resurrecting their forgotten ideas, experimentally verifying these ideas, and developing further the theory of phase equilibria with allowance for this new equilibrium belongs wholly to Soviet scientists[10].

RESTRICTED MUTUAL SOLUBILITY OF GASES

The works of van der Waals and his coworkers contained not only an indication of the possibility of equilibrium between two gaseous phases at temperatures above the critical temperatures of the two components of a binary mixture but also predictions about the form of the critical curve.

According to these predictions two types of such equilibria are possible. *The first type* (to which belong systems containing helium) is characterised by the critical curve (in coordinates of pressure and temperature) in leaving the critical point of the less volatile component (Fig. 1) being directed towards the side of high temperatures. The curve is convex towards the temperature axis and at the point *M* turns towards lower temperatures. The reversal occurs at appreciable pressures and after it the curve is directed towards the side of the critical point of the more volatile component. Fig. 2 shows the phase diagram for this type of equilibrium.

Second type. On leaving the critical point of the less volatile component, the critical curve (Fig. 3) is at first directed towards the side of lower temperatures. The curve is convex towards the temperature axis and passes through a minimum — point *D*. Its name, according to van der Waals terminology, is the double homogeneous point. Then the curve turns towards the side of high temperatures and subsequently its form does not differ from that described for the first type†.

Fig. 4 shows a phase diagram for this type of equilibrium as we visualise it now. In the temperature region from the critical temperature of the less volatile component to the temperature of the double homogeneous point both liquid–gas and gas–gas equilibria exist. In the temperature region from the critical point of the less volatile component up to the temperature maximum *M* there is only gas–gas equilibrium.

METHOD OF INVESTIGATION

Phase equilibria between two gaseous phases have been investigated by analytical and synthetic methods. These methods (details of the apparatus and experimental technique) have been described in sufficient detail already[12]. Here it is possible only to mention that by analytical is meant those methods in which the compositions of the coexisting phases are determined by the analysis of specimens taken from each phase. In working by synthetic methods a mixture of the two components of known quantitative composition is made up and then the moment for the disappearance or appearance of one of the phases is observed, by measuring the temperature, pressure, or volume (or all three parameters) of the system.

Many of the studies carried out in our country employed analytical methods in equipment with a mercury piezometer (Fig. 5) (a Callietet tube[13]). The piezometer is a metal

† We will not deal with the form of the critical curve in the region close to the critical point of the more volatile component (see, for example, Vogel[11]).

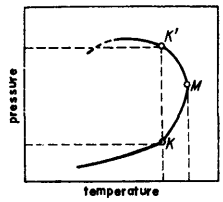


Fig. 1. Critical curve of systems giving the first type of separation. K critical point of the less volatile component; M maximal temperature of existence of gas–gas equilibrium; K' upper critical point of the gas–gas equilibrium.

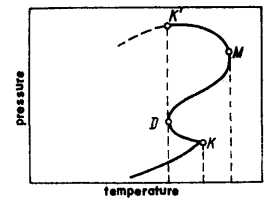


Fig. 3. Critical curve of systems giving the second type of separation. K critical point of the less volatile component; D double homogeneous point; M maximal temperature of existence of gas–gas equilibria; K' upper critical point for the gas–gas equilibrium.

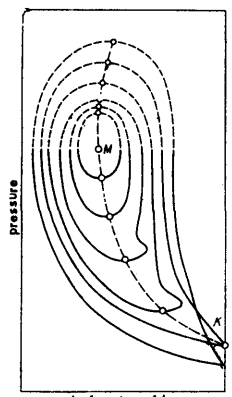


Fig. 2. Phase diagram of the gas–gas equilibrium of the first type.

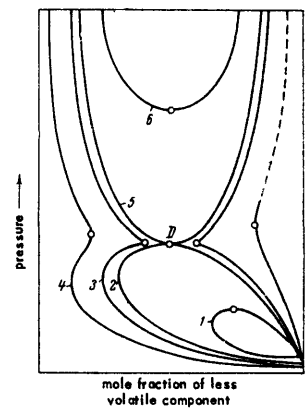


Fig. 4. Phase diagram of the gas–gas equilibrium of the second type. 1)–4) liquid–gas equilibrium curves; 5), 6) gas–gas equilibrium curves.

separating funnel filled with mercury. A mixture of known composition which is being studied is prepared outside the apparatus, run into the piezometer [14], and the temperature and pressure for the experiment created in the apparatus. Layering takes place. The upper phase is forced out by the mercury through the upper valve and is analysed. After all the upper phase has left the lower phase is forced out. The operations of forcing out the phases are carried out at constant pressure produced by pumping mercury from beneath into the piezometer under the pressure of a working fluid, which is supplied by a multiplier (Fig. 6).

The use of mercury at temperatures above 200°C is undesirable, both from the standpoint of accident prevention and also because it is soluble in compressed gases. Therefore, mercury-free equipment is used [15–18]. In this, the mixture is created in a high pressure vessel fitted with an electromagnetic stirrer and the compositions of the phases are determined by withdrawing specimens of the phases from above and below the vessel (Fig. 7).

Arons and Dipen [19] used the synthetic method for investigating gas–gas equilibria in the helium–xenon system. They prepared a mixture of xenon and helium of known concentration and filled a glass piezometer with it. The piezometer was put in a high pressure vessel with a sight glass (Fig. 8). The mixture in the piezometer was compressed by mercury. The phase diagram of the system could be constructed from observations of the appearance and disappearance of a meniscus and by noting the pressures corresponding to the appearance and disappearance of a bubble of the upper or lower phase. The volumes of the coexisting phases could also be measured with this apparatus.

Gas–gas equilibrium of the first type starts at the critical point of the less volatile component, which is usually found at moderate temperature and pressure. Making use of this, Krichevskii proposed, and Khodeeva [20] put into practice, a method in which the less volatile component is introduced into a glass ampoule of known capacity in such a quantity that it is at its critical volume. The critical temperature of the substance is measured and then a small quantity of the second component is added and the critical temperature of the mixture again measured. If the critical temperature is higher — that is, the meniscus between the phases disappears at a higher temperature — than the critical temperature of the pure component (less volatile), then a region of gas–gas equilibrium of the first type must exist in the system.

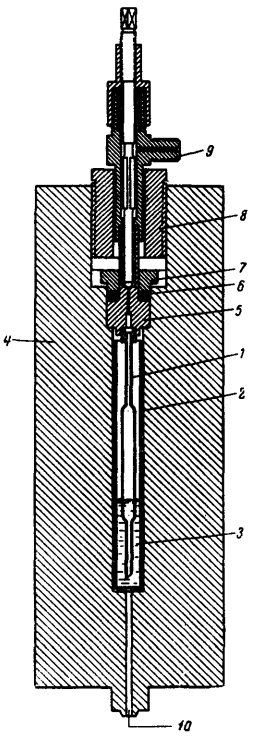


Fig. 5. Drawing of the high-pressure vessel with piezometer:
1) metal piezometer (Callietet tube); 2) beaker; 3) mercury; 4) high-pressure vessel; 5) head seal; 6) packing; 7) gland nut; 8) female screw; 9) valve for withdrawing specimens; 10) working liquid for multiplier.

REVIEW OF THE EXPERIMENTAL DATA

After Krichevskii and his coworkers[21-23] had observed the phenomenon of restricted mutual solubility of gases, another 25 systems with a region of phase equilibria between two gaseous phases were found. Table 1 lists all the systems‡.

Table 1 shows that all the systems with helium give layering of the first type. Layering of the second type is usually observed in systems containing a polar component. An exception is water: layering of the first and of the second type is observed in systems with water.

We will discuss two systems in greater detail: helium–carbon dioxide, as a representative of systems giving the first type of layering, and ammonia–nitrogen, a system with the second type of layering.

The $He-CO_2$ system[24] was studied at temperatures from 25° to 100°C and pressures up to 10 000 at. Figs. 9 and 10 give the phase diagram and critical curve and repeat the picture represented in Figs. 1 and 2, with the difference that the critical curve of the real system does not return towards lower temperatures as the pressure is raised.

‡ It is evident from the table that the great majority of investigations of this phenomenon have been made in the Soviet Union.

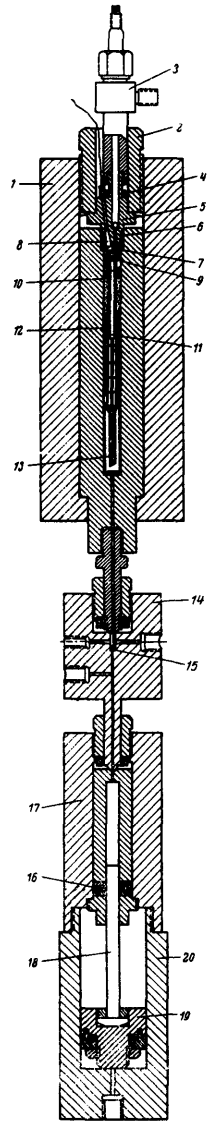


Fig. 6. Drawing of apparatus for investigating the equilibrium between two gas phases at pressures of up to 20 000 at:
1) double-walled high-pressure vessel; 2) female screw; 3) valve; 4) isolating ring; 5) head seal; 6) packing; 7) exhaust ring; 8) electrical entry; 9) head piezometer; 10) solenoid; 11) stirrer armature; 12) beaker with mercury; 13) spring; 14) valve box; 15) reversing valve; 16) packing for piston of multiplier; 17) cylinder of high-pressure multiplier; 18) high-pressure piston; 19) low-pressure piston; 20) low-pressure cylinder.

At temperatures less than the critical temperature of CO_2 liquid–gas equilibrium is observed. The curves of this equilibrium (the curve for the solubility of helium in liquid carbon dioxide and that of the latter in compressed helium) start at a point corresponding to the saturation vapour pressure of CO_2 at the given temperature. At temperatures

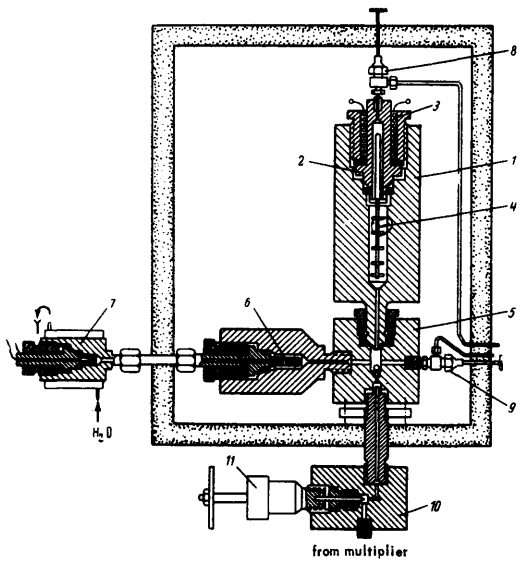


Fig. 7. Drawing of mercury-free apparatus for investigating gas–gas equilibria at high pressures and temperatures:
1) high-pressure vessel (EI437B steel); 2) seal; 3) solenoid; 4) stirrer; 5) valve box; 6) bellows for protection of the manganin manometer; 7) manganin manometer; 8) valve for removing upper phase; 9) valve for removing lower phase; 10) valve box; 11) press valve.

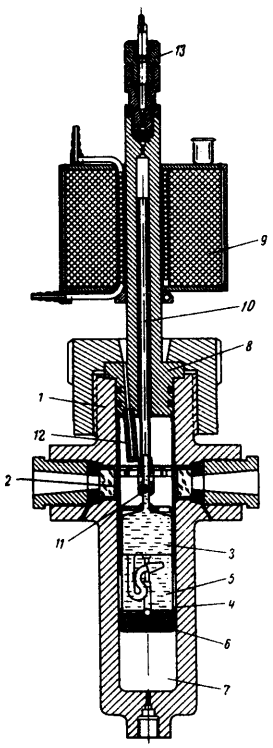


Fig. 8. Drawing of apparatus for investigating gas–gas equilibrium by a synthetic method:
1) high-pressure vessel; 2) sight window; 3) piezometer with gas mixture; 4) inner part of telescope tube; 5) mercury; 6) piston; 7) water; 8) seal; 9) solenoid; 10) armature of electromagnetic stirrer; 11) permanent magnet; 12) thermocouple pocket; 13) valve.

TABLE 1. Systems in which gas–gas equilibrium has been observed.

System	Intervals of investigation		Reference	Type of gas–gas equilibrium
	temperature, °C	pressure, at		
Ammonia–nitrogen	90—175	16 000	21—23,25	second
Ammonia–methane	45—100	10 000	23	second
Ammonia–nitrogen–hydrogen, three compositions with 22, 50, and 75 % hydrogen in the mixture without ammonia	90—120	5 500	23	second
Ammonia–nitrogen–methane with 20 and 80 % methane	55—110	5 500	26	second
Ammonia–argon	70—140	10 000	27	second
Nitrogen–sulphur dioxide	35—40	9 000	28	second
Helium–ammonia	125—175	10 000	24	first
Helium–carbon dioxide	25—100	10 000	24	first
Helium–ethylene	25—150	10 000	29	first
Helium–propane	100—150	7 000	30	first
Helium–benzene	300	1 000	31	first
Helium–methanol	245	3 000	31	first
Helium–hexane	245	3 000	31	first
Helium–sulphur dioxide	175—200	7 000	31	first
Helium–xenon	5—65	2 000	19	first
Helium–acetylene	36	64	20	first
Helium–ethane	32	51	20	first
Water–butane	200—430	6 000	15	first
Water–nitrogen	300—350	6 000	32	second
Water–carbon dioxide	250—350	3 500	16,17	second
Water–argon	350—400	4 000	33	second
Helium–dinitrogen monoxide	37	74	34	first
Helium–Freon-12	25—122	330	35	first
Helium–Freon-22	100	330	36	first
Helium–Freon-114B2	216—223	330	36	first
Helium–butane	—	—	37	—
Water–benzene	265—300	700	38	second
Water–n-heptane	295—355	700	38	second
Water–n-pentane	300—352	700	38	second
Water–2-methylpentane	300—355	700	38	second
Water–toluene	280—310	700	38	second

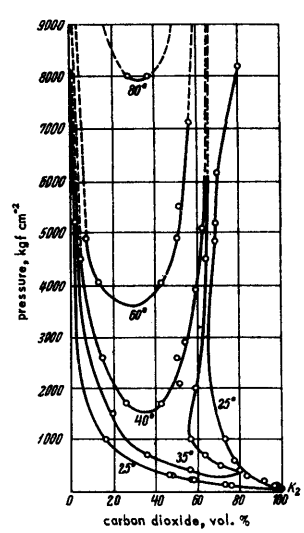


Fig. 9. Gas–gas and liquid–gas equilibria in the helium–carbon dioxide system.

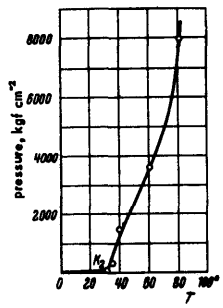


Fig. 10. Critical curve in the helium–carbon dioxide system.

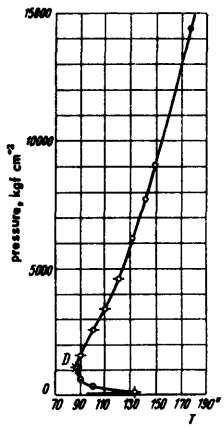


Fig. 12. Critical curve in the ammonia–nitrogen system. The symbols are the same as in Fig. 11.

greater than the critical temperature of CO_2 the curves leave the ordinate axis and form a characteristic horn. As the temperature is raised the horn is gradually obliterated.

The NH_3-N_2 system. This system was studied at temperatures from 90° to 175°C and pressures up to 16 000 at. Figs. 11 and 12 give the phase diagram and critical curve, which are similar to Figs. 3 and 4, except for the form of the curve at higher temperatures and pressures.

We will consider in greater detail the phase diagram of such a system represented three-dimensionally (Fig. 13) in the coordinates pressure–composition–temperature. Two regions of phase equilibria are clearly evident here: liquid–gas equilibrium and gas–gas equilibrium. The loops of the liquid–gas equilibrium start on the vapour pressure curve of the less volatile component (here, ammonia). The composition region occupied by these branches decreases with rise in temperature and shrinks to a point at the critical

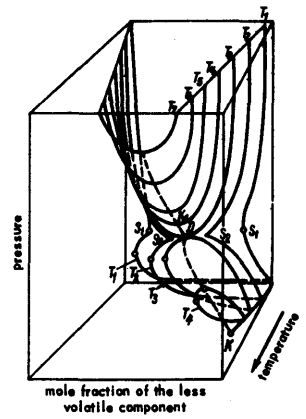


Fig. 13. Space diagram for systems which give the second type of layering.

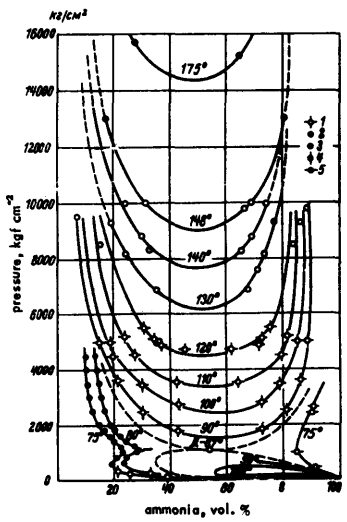


Fig. 11. Liquid–gas and gas–gas equilibria in the ammonia–nitrogen system. Data from: 1) Ref. 21; 2) Ref. 23; 3) Ref. 25; 4) Ref. 39; 5) Ref. 40.

point of the less volatile component. The gas–gas equilibrium curves are situated in the same composition interval but at other pressures. The region of this equilibrium also extends to the side of temperatures higher than the critical temperature of the less volatile component.

The point corresponding to the temperature minimum on the critical curve is clearly evident on the diagram. This is point D, at which the gas–gas and liquid–gas equilibrium curves touch. In van der Waals terminology it is called the binary homogeneous point§. The binary homogeneous point is a singular point. On raising the temperature above the temperature of this point the equilibrium loop breaks into two parts — the curves of the gas–gas and liquid–gas equilibria. On reducing the temperature below the temperature of the binary homogeneous point breaking of the loops also takes place, but now it is along the pressure axis. As a result fantastic forms of the solubility curves

§ This terminology is derived from the theory of folds[41] on the basis of which the existence of the types of gas–gas equilibria was also predicted.

for gas in liquid (right branches) and liquid in gas (left branches) are produced. It can be noted from this that at the moment of the break (longitudinal) points of return (S_2) appear on the curves; these points then degenerate into the points of the solubility maxima for gas in liquid and liquid in gas (S_1).

Fig. 13 shows that the solubility curves for gas in liquid and liquid in gas have a very complex form, especially close to the binary homogeneous point. The solubility of gas in liquid under pressure first increases with the pressure, passes through a maximum, decreases, and then (if the possibility of the existence of an upper critical point of gas–gas equilibrium is considered) should start to rise again.

The solubility of liquid in gas at first decreases with rise in pressure, passes through a minimum, starts to rise, reaches a maximum, falls again, subsequently hardly changes with the pressure, and finally (if the upper critical point is considered) can start to rise again.

This complex form for the curves has a theoretical explanation[10]. The fact is that both the minimum and the maxima on the solubility curves for liquid in gas and gas in liquid are points at which the partial molar volume of the substance and its molar volume become equal¶.

At low pressure the partial molar volume of a substance in its infinitely dilute solution ($\overline{v}_2'$) is much greater than the molar volume of the substance in the condensed phase v_2^0. But with increase in pressure the value $\overline{v}_2'$ rapidly approaches v_2^0 and becomes equal to it since the compressibility for $\overline{v}_2'$ is greater than the compressibility for v_2^0. In this a liquid in gas solubility minimum is observed. At still higher pressures $\overline{v}_2'$ becomes less than v_2^0 and the solubility starts to rise. However, this decrease cannot be continued indefinitely. With rise in pressure the intermolecular interaction starts to increase. Therefore the partial molar volume of the substance in the gas phase begins to increase. It again becomes equal to the molar volume and a solubility maximum appears on the curve.

Similar arguments show that the gas-in-liquid solubility maximum occurs at a pressure when the molar volume of the gas being dissolved equals the partial molar volume of this gas dissolved in the liquid.

Fig. 13 shows clearly that the presence of gas–gas equilibrium curves allows all the known facts about phase equilibria in binary systems to be explained. For example, it becomes quite clear that the gas–gas equilibrium curves do not start and do not end on the vapour pressure curves of the less volatile component and have nothing in common with the liquid–gas equilibrium curves. It is also understandable that the points of the maxima and minima on the curves are degenerate points of reversal formed from the double homogeneous point. Hence it can be concluded that if a solubility maximum is found in investigating the solubility of a gas in a liquid, a region of gas–gas equilibrium should occur in that system.

We will return briefly to the question of the reversal of the critical curve. On considering solutions of helium as intrusion solutions, Tsiklis and Zhukhovitskii[42] showed that here there is generally no reason to expect reversal. This, however, does not signify that it cannot happen in other instances. But if such a reversal is possible in principle, then it should occur at rather high pressures, when the solubility of the gas again starts to increase with pressure owing to a further change in the partial molar and molar volumes. But at such high pressures crystallisation of the gases can begin. In this instance the critical curve generally will not be continuous. The gas–gas equilibrium changes into a new form of equilibrium — crystal–gas equilibrium (Fig. 14).

On considering the experimental data on gas–gas equilibrium in the systems investigated it is noticeable that for each of the types (first and second) the experimental results repeat Figs. 2 and 4 well. They differ, of course, in the parameters of the curves and especially in the coordinates of the double homogeneous point and the temperature interval between it and the critical point of the less volatile component. In this respect the water–nitrogen system is especially characteristic. In it the binary homogeneous point is at 364°C, that is, 10 deg below the critical temperature of water. For the ammonia–nitrogen system it is at 87°C, that is, 46 deg below the critical temperature of ammonia; and in the CO_2–H_2O system it is at 260°C, that is, 108 deg below the critical temperature of water.

To conclude the discussion of the existing experimental data it is necessary to add the following. Visual observations have been made of the helium–ethylene system[29]; the layering process takes place instantaneously. Initially during the compression of a homogeneous mixture strong eddy currents, similar to convection currents, are observed. On reaching the pressure at which layering occurs a sharp visible meniscus appears (Fig. 15). Its appearance is rapid and is accompanied by a fall of "rain" from the drop of heavier phase. The presence of a meniscus contradicts the conclusion that gas–gas equilibrium is a phase transformation of the second order[43].

The surface tension at the boundary of separation in the helium–ethylene and helium–carbon dioxide systems was measured in an analogous apparatus with sight glasses by the capillary method[44]. It was found that, for example, in the helium–ethylene system at 600 at and 18°C the surface tension is ~ 0.5 erg cm^{-2}.

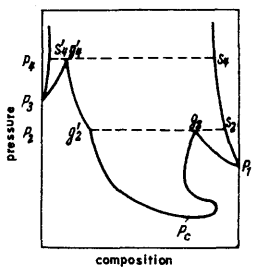


Fig. 14. Gas–gas and crystal–gas equilibria in systems of the first type. P_1 pressure of crystallisation of the pure less-volatile component; P_2 pressure at which the gas phases g_2' and g_2 and the solid phase s_2 are in equilibrium; P_4 pressure at which the two solid phases s_4' and s_4 and one gas phase g_4' are in equilibrium.

¶ Here it is necessary to consider the solvent to be a pure substance.

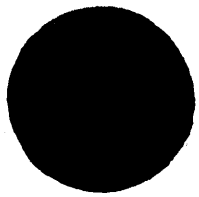


Fig. 15. Meniscus in the helium-ethylene system.

The surface tension in these systems increases with pressure and decreases with rise in temperature. The dependence of σ on P can be represented by the equation:

$$\sigma = \alpha(P - P_c)^2,$$

where α is a constant and P_c the critical pressure. Fig. 16 shows that this condition is obeyed over a wide range of pressures.

Finally, mention must be made of another interesting phenomenon, which is observed in systems with a restricted solubility of gases. We refer to the barotropic phenomenon. This is that with increase in pressure the upper phase becomes heavier and sinks in the lower. Close to the critical point (any equilibrium) the curve in coordinates v (specific volume of the phase on the curve of coexistence) and N_2 (composition) is to the first approximation a parabola with its axis perpendicular to the tangent through the critical point. The gas–gas equilibrium curve (for the second type) in coordinates of pressure against composition is symmetrical with respect to the axis passing through mole fraction 0.5. Therefore an analogous picture will be observed for curves plotted in coordinates of v and N_2.

Fig. 17 shows the liquid–gas and gas–gas equilibrium curves in coordinates v and N_2. A liquid phase of composition A_1 will be in equilibrium with gas phase A_2. At higher pressure the phase of composition B_1 is in equilibrium with a gas phase of composition and volume B_2. On approaching the binary homogeneous point tne difference in volumes decreases and close to the critical point of the gas–gas equilibrium the specific volumes of the coexisting phases become equal (D_1 and D_2). Then the phase in which there is more of the component with higher molecular weight also has the highest specific gravity. Subsequently the volumes of the phases again become unequal but now the volume of the phase containing the component with higher molecular weight diminishes more rapidly and the barotropic phenomenon intensifies.

Hence, the barotropic phenomenon can occur when the molecular weight of the liquid is less than the molecular

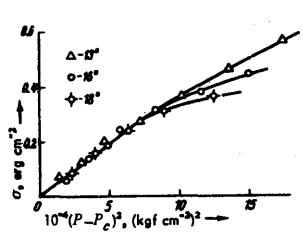


Fig. 16. Variation of σ with $(P - P_c)^2$.

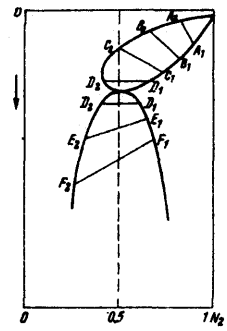


Fig. 17. The barotropic phenomenon.

weight of the gas and the form of the gas–gas equilibrium curve is such that the chords joining the coexisting phases can become parallel to the composition axis.

The barotropic phenomenon was first observed by Kammerlingh-Onnes [45] in investigating liquid–gas equilibrium in the hydrogen–helium system at 20.1°K. In investigations of gas–gas equilibria the barotropic phenomenon has been observed in the ammonia–nitrogen, ammonia–nitrogen–hydrogen (with 22% hydrogen), and ammonia–nitrogen–methane (with 17% methane) systems and also in the argon–ammonia [27,46], water–carbon dioxide [16,17], and water–argon [33] systems.

Despite the fact that the molecular weight of water is less than that of butane, the barotropic phenomenon is not observed in this system†. Evidently it is very important that the form of the phase curve should permit the condition of lines parallel to the composition axis to be fulfilled.

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An isotropic substance at temperatures greater than critical is usually called a gas. Therefore the equilibrium state of the two gaseous phases in the above systems can unreservedly be considered to be gas–gas equilibrium. The credit for the theoretical basis for the equilibrium existence of two gaseous phases at supercritical temperatures is due to Dutch physicists, as mentioned above. However, the possibility of such a state in a system was discussed independently of them, but subsequently. Thus Randall and Sosnik [47] considered gaseous solutions of argon in ethylene at supercritical temperatures. On plotting the activity γ of a component against its mole fraction they concluded that an increase in the constant a in the Hildebrand equation could lead to the mathematical conditions necessary for the separation of the mixture into two phases. However, for this the value of $\log\gamma$ should rise to the same value, which they considered improbable. In the final analysis these authors were convinced of the impossibility of phase separation.

Shottky [49], starting from general ideas about the reasons for the breakdown of a homogeneous mixture into two phases, admitted the possibility of the existence of gas–gas equilibrium at high pressures. Evidently, neither Shottky

† This confirms the correctness of the experimental data according to which a gas–gas equilibrium of the first type is observed in the system (concerning which Schneider [48] has doubts, in relation to Connoly's work [38]).

nor Randall and Sosnik knew of van der Waals' work and expressed their views before the appearance of experimental works in this field.

Even after these works had been published, Dodge[50] wrote, in 1944, ".... systems consisting of gases and vapours are always homogeneous. No one has ever observed more than one gaseous phase". However, Lindros and Dodge[18] subsequently repeated the investigation of the ammonia–nitrogen system, and on finding layering, were convinced of Dodge's error.

Hildebrand[51] wrote, in the third edition of his book: "gases are infinitely miscible and hence raise no problems of miscibility...."‡.

Nobody can now dispute that at temperatures above the critical temperatures of both components a region where the system is heterogeneous can exist. But some authors consider that the phenomena observed should be called equilibrium between two liquid phases[52,53], since the density of the phases at high pressures hardly differs from the liquid density. Others[54,55] assume that this is equilibrium between gas and liquid. Schneider[48] says: "the so-called gas–gas equilibrium" and cannot imagine why the critical curve for liquid–gas equilibrium changes smoothly (for the first type) into the gas–gas equilibrium curve. Discussion on this has been published (see Krichevskii and Tsiklis[56]) but cannot be given in this article.

Here it is proper to state the following. It becomes clear from Fig. 13 that gas–gas equilibrium has no relation to liquid–gas equilibrium. The fact that in a single region of temperature but at different pressures there are two phase equilibrium curves does not signify at all that both phase equilibria are of the same type. It is known, for example, that in the temperature region through which passes a liquid–vapour equilibrium curve there may also pass the liquid–liquid equilibrium curve. But no one ascribes these equilibria to the same type on this basis. Incidentally, Schneider[48] admits that the critical curve for liquid–gas equilibrium can be curved and change continuously into the critical curve of liquid–liquid equilibrium. But if this is possible, then why should change to gas–gas equilibrium be impossible?

van der Waals and Kohnstamm[57] wrote: ".... Hence it follows that (as Kammerlingh-Onnes and Keesom noted) in this instance with strict observance of terminology it is necessary to speak of the equilibrium of two gaseous phases. Actually, there is no basis for calling one of the two phases liquid in a completely closed fold and therefore here one must speak of gas–gas equilibrium at all temperatures exceeding the critical temperature of the second component".

It must be stated once again that liquid–gas equilibrium is the most incorrect name: the equilibrium investigated does not begin and does not end on the liquid–gas equilibrium curve of a pure component. To this it can be added that this question has been discussed repeatedly[58]. Quite recently Rowlinson[59] produced weighty evidence in support of the name gas–gas.

‡ It is interesting in this connection to note that recently Mal'nev and Pekar[68], who considered theoretically a gas in which a high percentage of the molecules are excited to the same electronic energy level (for example, in a laser regime), showed that owing to the anomalously large intermolecular forces the layering of such a gas into two phases of different (in the number of excited molecules) composition is possible. This separation can occur even at atmospheric or even lower pressures.

SOME QUESTIONS OF THEORY

As experimental results accumulate it becomes more and more necessary to give a theoretical explanation for the observed experimental facts.

The problem of the prediction of the possibility of layering of gas mixtures and even pre-calculating the parameters of the critical points of the layering would be solved relatively simply if there was an equation of state giving the behaviour of the binary systems being considered. Then by using the known thermodynamic relations (1) and (2):

$$(\partial \ln f_2/\partial N_2)_{P,T,K} = 0, \quad (1)$$

$$(\partial^2 \ln f_2/\partial N_2^2)_{P,T,K} = 0, \quad (2)$$

where f_2 is the volatility of a component, N_2 its mole fraction, and K the critical phase, the pressure and composition of the critical point can be calculated. However, such an equation does not exist and, as Rakovskii noted[60], "the enormous power of the apparatus of thermodynamics stumbles about our ignorance of the actual equations of state"§.

Such a calculation could also be carried out if we had experimental data about the variation of the volume of the gaseous solution and of the components of the mixture with pressure and composition at different temperatures. Then, by calculating the volatility of a component of the solution a graph can be constructed in coordinates of $\ln f_2$ against N_2. The existence on such a graph of a point of inflection with a horizontal tangent (see, for example, Tsiklis and coworkers[61]) signifies that there is a region of layering in the system.

Usually such data are not available in the literature, and it is more difficult experimentally to obtain them than to make a direct investigation of the phase equilibria in the system.

The literature shows that attempts have been made to judge the possibility of the appearance in a given system of a region of gas–gas layering by comparing the properties of the components of the system. Mixtures should show layering when their components have not so much strong intermolecular interaction, as different.

Thus, Kreglewski[62] used the Hildebrand solubility parameter (Δ) and showed that the greater the difference between the value of Δ^2 of the components of the mixture the more probable the layering of the mixture. The solubility parameter is determined by the expression

$$\Delta = -(E/v)^{1/2} \quad (3)$$

where E is the energy of the component and v the molar volume. According to van Dranen's hypothesis[64], at the critical point the negative potential energy of a substance is $E = \frac{3}{2}RT_c$. Consequently, relation (4) holds for the critical point:

$$\Delta^2 = {}^3/_2 \frac{RT_c}{v_c}. \quad (4)$$

Table 2 gives values of Δ^2 for the components of the mixtures investigated and shows that in reality in all the mixtures which show layering the difference in the values

§ Schäfer[63] attempted to use for this purpose an equation of state with virial coefficients. By finding the values of these coefficients, Schäfer calculated by a very complex path the conditions of layering in the N_2–NH_3 system and obtained good agreement with experiment.

TABLE 2. Values of Δ^2 of the components of the mixtures investigated.

Component	T_c, °K	v_c, cm³ mole⁻¹	$(\Delta)^2$, at	Component	T_c, °K	v_c, cm³ mole⁻¹	$(\Delta)^2$, at
He	5.23	57.7	11.2	C_2H_6	526.1	260.0	266.4
H_2	33.25	65.7	63.2	C_2H_4	283.1	124.0	381.0
N_2	126.0	90.3	172.0	CO_2	304.1	93.3	399.0
C_4H_{10}	425.8	58.0	204.0	SO_2	430.4	123.7	228.0
C_5H_{12}	507.8	283.0	221.0	CH_3OH	513.0	129.0	490.0
C_3H_8	370.6	200.0	227.0	NH_3	406.1	72.9	685.0
CH_4	190.7	99.0	237.0	H_2O	647.0	54.7	1460.0
Ar	150.7	75.5	246.7				

of Δ^2 of the components is significant. Nevertheless, Kreglevskii's criterion is approximate. It does not allow a quantitative estimation of the parameters of layering to be given. Moreover, in a series of instances the calculation leads to erroneous results. For example, for the ammonia–hydrogen system the difference in the values of Δ^2 for ammonia and hydrogen is greater than in the ammonia–nitrogen system, but layering does not occur in the ammonia–hydrogen system.

Temkin[65] proposed a strict criterion of layering. By using the van der Waals equation of state for a binary mixture and the Helmholtz equation for free energy, he found the conditions for the development of the so-called longitudinal fold on the surface in the coordinates free energy–volume–composition, which, in accordance with the theory of folds[41], is also the condition for the layering of the mixture.

For calculation according to this criterion it is necessary to find the value of the coefficients a_1 and a_2 of the equation of state for the pure components and a_{12} for the binary system. Layering in the system is possible if Eqn. (5) is fulfilled for a mixture of non-polar components¶ and Eqn. (6) for mixtures containing polar components:

$$a_1 < 0.053\, a_2 \tag{5}$$

$$^1/_2(a_1 + a_2) - a_{12} > {}^8/_{27}\, a_2. \tag{6}$$

From Eqns. (5) and (6) it is evident that layering is possible when for mixtures of non-polar components the quantity a_1 is significantly less than a_2 and for a mixture with polar components a_{12} is less than the half-sum of the values of a_1 and a_2. Calculation shows that all systems with helium should show layering. Experiment confirms the calculation. It appears that even mixtures of helium and xenon — two noble gases — show layering. The results for layering in systems which contain water also agree with calculation.

However, this criterion is also approximate, since it is based on the van der Waals equation of state and this, as is known, is only qualitative, since it does not describe fully the behaviour of a substance at high pressures.

The layering of a homogeneous system, including also a phase transformation of the gas–gas type, indeed serves as a touchstone for any statistical theory of the condensed state of a substance.

In the theory based on the use of a method of correlating functions, phase transformations are connected with the singularities of the integral equations for these functions. Attempts to connect the crystal–liquid phase transformation with the presence of branching points in the integral equation for a single-index unary distribution function appeared quite fruitful.

In Rott's works[66] the phase transformation of interest to us here is considered from the standpoint of the statistical theory of the conditions for distribution. In it the phase transformation is connected with the singularity of the configuration integral. The latter is directly extended also to the distribution function itself (in the present instance the so-called two-index correlation functions). This can be traced also to the reverse dependence. If the state of the homogeneous system cannot be realised, then the distribution functions corresponding to it, say the most minor E_{11}, should transform to zero, which transforms the configuration integral into infinity. Therefore a knowledge of even the minor distribution functions (for the binary system there are two such functions) allows the approximate condition for the phase transformation to be found without resort to calculation of the configuration integral itself.

Thus for dilute binary solutions a final evaluation is obtained which allows us to find whether the occurrence of layering of the gas–gas type is possible or impossible; the parameters of the molecular interaction are calculated during this.

The criterion for layering in the given instance is the parameter β, given by

$$\beta = \frac{3.31\,\frac{\epsilon}{k}\,\sigma^4}{Tr_0^4}, \tag{7}$$

where r_0 is the radius of the molecular volume ($v = \frac{4}{3}\pi r_0^3$), ϵ and σ are the parameters of the Lennard–Jones potential, k is Boltzmann's constant, and T the temperature.

It appears that the nature of the change in β is approximately the same for many substances. At the critical temperature $\beta \simeq 4$–5, at the triple point $\beta \simeq 28$ for the liquid phase and 34 for the solid.

In calculating the parameter β for a two-component system values of T and r_0 for the less volatile component (subsequently, for water, as an example) must be inserted in the denominator of Eqn. (7) and values of ϵ and σ for the more volatile (non-polar component) in the numerator. In this the value of β for the case when gas–gas layering of the first type is possible in the neighbourhood of the critical point of the less volatile component should be greater than its value at the critical point (that is, 4–5).

From the experimental results it is evident that features of the phase equilibrium known previously as features of helium solutions (the presence of a characteristic horn on the pressure–mole fraction curves near the critical point of the less volatile component) are present also in other binary systems the components of which do not differ greatly in energetic respects. Such are also all the systems with water considered below. Table 3 gives the values of β for a series of binary systems (aqueous solutions) in the vicinity of the critical point of water (for all the systems shown the critical density of water is greater than the density of the dissolved component at its critical point).

Experiment confirms the calculations. The layering in the water–butane systems is of the first type. In the water–nitrogen and water–carbon dioxide systems gas–gas equilibria of the first type are not observed. Gas–gas equilibria of the second type are observed.

¶ In essence Eqn. (5) is the particular case of Eqn. (6) when it is assumed that $a_{12} = \sqrt{a_1 a_2}$.

TABLE 3. Values of β for systems containing water.

System	β	Layering of the first type	System	β	Layering of the first type
Butane–water	~21	possible	Methane–water	2.4	impossible
Benzene–water	~28	»	Ethane–water	7.3	»
Propane–water	~42	»	Nitrogen–water	2.0	»
Octane–water	~82	»	Carbon dioxide–water	4.0	»

Attempts to use the methods of the statistical theory of "free volume" for the calculation of layering have been made recently [19].

New results obtained comparatively recently which relate to systems consisting of helium and fluorine compounds do not fit into the framework of any of the theories mentioned.

According to the criteria of Kreglewski, of Temkin, and of Rott, these systems (He–$CClF_3$, He–CHF_3, He–$CH_2{=}CF_2$, and He–SF_6) ought to have a region of gas–gas equilibrium of the first type. Experiment showed that they did not possess such a region [20,34].

In addition to that, mixtures of helium with other fluorine compounds, for example, He–$C_2Br_2F_4$ (Freon-114B2), He–$CHClF_2$ (Freon-22), and He–CCl_2F_2 (Freon-12) behave normally [35,36].

Evidently there is something new and interesting here in the unusual behaviour of the gaseous solutions of fluorine compounds. It is known [51,59,67] that liquid solutions which contain hydrocarbons and their fluoro-derivatives are also distinguished by unusual behaviour.

From the experiments described it is clear that the existence or absence of a region of gas–gas equilibrium of the first type in mixtures of helium and fluorine compounds is connected with features of the structure of these compounds. Evidently a negative part in the existence of layering is played by the polarity of the C–F bond and the small size of the fluorine atom. The latter assumes the approach of helium and fluorine, which can lead to polarisation of the helium and the production of additional interaction, which is unfavourable for layering†.

With a decrease in the number of fluorine atoms in the molecule, owing to the introduction of chlorine, bromine, or hydrogen, layering is produced.

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The comparatively recently observed phenomenon of restricted mutual solubility of gases was for a long time regarded as exotic. It can be hoped that the material presented in this review will disperse these doubts.

Gas–gas equilibrium is a widespread phenomenon. It has its place in the series of phase equilibria. Not only investigators occupied with the study of phase equilibria, but also technologists should take this phenomenon into account. This must be done both now (since this equilibrium starts at pressures and temperatures which are usual for many technological processes of the chemical and petroleum industries) and especially in the future, when high pressures will come into chemistry on a full scale.

This phenomenon will undoubtedly be used to explain many facts by geochemists, who are concerned with the problems of the formation and migration of petroleum, and also by scientists dealing with hydrothermal syntheses within laboratories and with the observation of these processes in nature.

It cannot be doubted that the number of experimental studies concerned with gas–gas equilibrium will grow and accordingly will extend our knowledge of this new and interesting phenomenon.

† Ya.K. Syrkin brought this to our attention.

1. D.P. Konovalov, Zhur. Russ. Fiz.-Khim. Obshch., Chast' Khim., 16, 1 (1884); "Ob Uprugosti Para Rastvorov" (Concerning the Vapour Pressure of Solutions), 3rd Edn., Izd. Akad. Nauk SSSR, Leningrad, 1928.
2. A.G. Stoletov, "Sobranie Sochinenii" (Collected Works), Gostekhizdat, Moscow–Leningrad, Vols. I and II, 1941.
3. J.W. Gibbs, "Collected Works" (Translated into Russian), Gosteoretizdat, Moscow–Leningrad, 1950.
4. J.D. van der Waals, "Die Kontinuitet des gasformigen und flussigen Zustandes", Leipzig, 1900.
5. I.P. Kuenen, "Theorie der Verdampfung und Verflussigung von Gemischen", Leipzig, 1907.
6. J. Dalton, "Collection of Works on Atomistics" (Translated into Russian) (Edited by B.M. Kedrov), GONTI, Leningrad, 1940).
7. J.D. van der Waals, Zittungsversl. k. ned. Akad. Wetenschap., Amsterdam, 133 (1894).
8. H. Kammeringh-Onnes and W.H. Keesom, Proc Sect. Sci. Roy. Acad., Amsterdam, 9, 786 (1907).
9. I.R. Krichevskii, Acta Physicochim. URSS, 12, 480 (1940).
10. I.R. Krichevskii, "Fazovye Ravnovesiya v Rastvorakh pri Vysokikh Davleniyakh" (Phase Equilibria in Solutions at High Pressures), Goskhimizdat, Moscow, 1946 and 1952.
11. R. Vogel, "Die Heterogenen Gleichgewichte", Leipzig, 1937.
12. D.S. Tsiklis, "Tekhnika Fiziko-Khimicheskikh Issledovanii pri Vysokikh i Sverkhvysokikh Davleniyakh" (Technique of Physicochemical Investigations at High and Superhigh Pressures), Izd. Khimiya, Moscow, 3rd Edn., 1965.
13. L. P. Callietet, Compt. rend., 85, 851, 1213, 1270 (1877).
14. I.R. Krichevskii and D.S. Tsiklis, Zhur. Fiz. Khim., 17, 115 (1943).
15. D.S. Tsiklis and V. Ya. Maslennikova, Dokl. Akad. Nauk SSSR, 157, 427 (1964).
16. K. Tödheide and E.M. Frank, Z. phys. Chem. (Frankfurt), 37, 387 (1963); Ber. deut. keram. Ges., 41, 60 (1964).
17. S. Takenouchi and G.C. Kennedy, Amer. J. Sci., 262, 1055 (1964).
18. A.E. Lindros and B.F. Dodge, Chem. Eng. Progr. Symp. Ser., No. 3, 48 (1953).
19. I. de Swaan Arons, "Ontmenging in de Gasfase", author's abstract of dissertation, Delft, 1963.
20. S.M. Khodeeva, Zhur. Fiz. Khim., 40, 1973 (1966) [Russ. J. Phys. Chem., 1061 (1966)].
21. I.R. Krichevskii and P.E. Bol'shakov, Zhur. Fiz. Khim., 15, 184 (1941).
22. I.R. Krichevskii and D.S. Tsiklis, Zhur. Fiz. Khim., 15, 1059 (1941).
23. I.R. Krichevskii and D.S. Tsiklis, Zhur. Fiz. Khim., 17, 126 (1943).
24. D.S. Tsiklis, Dokl. Akad. Nauk SSSR, 86, 1159 (1952).
25. D.S. Tsiklis, Dokl. Akad. Nauk SSSR, 86, 993 (1952).
26. D.S. Tsiklis, Dokl. Akad. Nauk SSSR, 76, 97 (1951).
27. D.S. Tsiklis and Yu.N. Vasil'ev, Zhur. Fiz. Khim., 29, 1530 (1955).
28. D.S. Tsiklis, Zhur. Fiz. Khim., 21, 349 (1947).
29. D.S. Tsiklis, Dokl. Akad. Nauk SSSR, 91, 1361 (1953).

30. D.S.Tsiklis, Dokl.Akad.Nauk SSSR, 101, 129 (1955).
31. D.S.Tsiklis and S.M.Khodeeva, Inzh.-Fiz.Zhur., 1, 62 (1958).
32. D.S.Tsiklis and V.Ya.Maslennikova, Dokl.Akad.Nauk SSSR, 161, 645 (1965).
33. D.S.Tsiklis and V.M.Prokhorov, Zhur.Fiz.Khim., 40, 2335 (1966) [Russ.J.Phys.Chem., 1257 (1966)].
34. D.S.Tsiklis and V.M.Prokhorov, Dokl.Akad.Nauk SSSR, in the press.
35. D.S.Tsiklis, V.Ya.Maslennikova, and N.P.Goryunova, Zhur.Fiz.Khim., in the press.
36. V.Ya.Maslennikova, N.P.Goryunova, and D.S.Tsiklis, Dokl.Akad.Nauk SSSR, in the press.
37. A.E.Jones, Thesis, Ohio State University, 1964.
38. I.F.Connoly, J.Chem.Eng.Data, 11, 13 (1966).
39. I.R.Krichevskii and N.E.Khazanova, Zhur.Fiz.Khim., 13, 1690 (1939).
40. R.Wiebe and V.Gaddy, J.Amer.Chem.Soc., 59, 1984 (1937).
41. D.J.Korteweg, Wiener Ber., 98, 1154 (1889); Arch.Neerl., 24, 295 (1891).
42. D.S.Tsiklis and A.A.Zhukhovitskii, Trudy Gos.Nauch.--Issled.i Proekt.Inst.Azoitnoi Prom., No. 8, 7 (1957).
43. V.K.Semenchenko, Zhur.Fiz.Khim., 26, 1337 (1952).
44. D.S.Tsiklis and Yu.N.Vasil'ev, Zhur.Fiz.Khim., 37, 1355 (1963) [Russ.J.Phys.Chem., 720 (1963)].
45. H.Kamerlingh-Onnes, Proc.Sect.Sci.Roy.Acad., Amsterdam, 9, 459 (1906).
46. A.Michels, E.Dumoulin, and J.J.Dijk, Physica, 27, 866 (1961).
47. M.Randall and B.Sosnik, J.Amer.Chem.Soc., 50, 967 (1928).
48. G.Schneider, Ber.Bunsenges.phys.Chem., 70, 497 (1966).
49. W.Shottky, U.Ulich, and C.Wagner, "Thermodynamik", Berlin, 1929.
50. B.F.Dodge, "Chemical Engineering Thermodynamics", McGraw-Hill (Translated into Russian), Inostr.Lit., Moscow, 1950.
51. J.H.Hildebrand and P.L.Scott, "The Solubility of Non-electrolytes", 3rd Edn., New York, 1950.
52. I.Zernike, "Chemical Phase Theory", Antwerp, 1955.
53. P.W.Bridgman, "Recent Work in the Field of High Pressures", Rev.Mod.Phys., 18, 1 (1946) (Translated and supplemented by L.F.Vereshchagina), Inostr.Lit., Moscow, 1948.
54. V.Yu.Urbakh, Zhur.Fiz.Khim., 32, 1163 (1958).
55. I.N.Ostrovskii, Zhur.Fiz.Khim., 37, 942 (1963) [Russ.J.Phys.Chem., 501 (1963)].
56. I.R.Krichevskii and D.S.Tsiklis, Zhur.Fiz.Khim., 32, 1407 (1958); 37, 945 (1963) [Russ.J.Phys.Chem., 503 (1963)]:
57. J.D.van der Waals and P.Kohnstamm, "Lehbuch der Thermostatik" (Translated into Russian), ONTI, Moscow, 1936.
58. S.D.Haman, "Physico-Chemical Effects of Pressure", Butterworth, London, 1957.
59. J.S.Rowlinson, "Liquids and Liquid Mixtures", Butterworth, London, 1959.
60. A.V.Rakovskii, foreword to Ref.57.
61. D.S.Tsiklis, A.I.Kulikova, and A.N.Kofman, Zhur.Fiz.Khim., 37, 1613 (1963) [Russ.J.Phys.Chem., 867 (1963)].
62. A.Kreglewski, Bull.Acad.polon.Sci., Classe III, 5, 662 (1957).
63. K.Schäfer, "Statistische Theorie der Materie", Gottingen, 1960, Vol. I.
64. J.van Dranen, J.Chem.Phys., 20, 1175 (1952).
65. M.I.Temkin, Zhur.Fiz.Khim., 33, 2040 (1959) [Russ.J.Phys.Chem., 275 (1959)].
66. L.A.Rott, Zhur.Fiz.Khim., 36, 2235 (1962); 38, 528 (1964); [Russ.J.Phys.Chem., 1205 (1962); 286 (1964)]; Dokl.Akad.Nauk SSSR, 160, 1140 (1965).
67. R.D.Dunlap and J.H.Simons, J.Chem.Phys., 18, 335 (1950).
68. V.N.Mal'nev and S.I.Pekar, Zhur.Eksper.Teor.Fiz., 51, 1811 (1966).

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NEWTONIAN VISCOSITY OF CONCENTRATED SOLUTIONS OF POLYMERS

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The factors which influence the irreversible flow of high-molecular compounds and of their concentrated solutions have attracted increasing attention in recent years because of their relevance to current problems in the technology of polymer fabrication. However, the study of viscoelastic properties in polymers is important not only as a route to formulating the scientific foundations of technology: it can also provide valuable information on the nature and on the rates of conformational changes in macromolecules and also on their mutual arrangement (i.e. on the structure of the polymer and of its solution[1]).

Studies of the rheological properties of concentrated solutions of polymers began in the 1930's, when it was shown[2-4] that the anomalous flow of polymer solutions (and of the polymers themselves) arises from the interplay of elastic (reversible) deformations and viscous (irreversible) flow. It was subsequently shown[5] that relaxation phenomena are associated with the elastic deformations. Thus, concentrated polymer solutions give rise to a viscoelastic system: to investigate these solutions we must separate reversible from irreversible deformations, and also examine the rate of shear as a function of stress over a wide range of these parameters.

For polymer solutions of intermediate concentration this function gives, when plotted on logarithmic coordinates, a characteristic S-shaped curve with linear lower and upper sections at 45° to the horizontal axis[6] (Fig. 1).

Over these sections of the plot (i.e. in the regions of small or large shear rates or stresses) the viscosity coefficient is constant and the flow is Newtonian. The viscosities corresponding to the two linear sections are usually termed the maximum and the minimum Newtonian viscosity. It should be noted that with very concentrated solutions of high polymers, and with melts, the upper linear section (Fig. 1) is not observed: hence, most of the published values for the maximum Newtonian viscosity have been measured at insufficiently high stresses and shear rates. However, in many systems the viscosity depends on the applied shear stress even under these conditions, as can most clearly be seen by plotting the logarithm of the viscosity against the logarithm of the stress[7]. In this case the Newtonian viscosity is obtained by extrapolation to zero stress or to zero shear rate.

Low stresses cannot break down the structures present in melts or in solutions: hence, the Newtonian viscosity at low shear rates describes the flow of the solution without any disturbance of its structure. In this sense, studies of the Newtonian viscosity of polymer solutions are a very