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# Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1965

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## Abstract

## Full Text

Reports of the Academy of Sciences of the USSR  
1965, Volume 161, No. 5

*PHYSICAL CHEMISTRY*

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# ON THE CHOICE OF A REFERENCE POINT IN THE STUDY OF THE THERMODYNAMIC SIMILARITY OF GASES

*(Presented by Academician V. A. Kirillin on 24 X 1964)*

By definition, thermodynamically similar gases are gases which, in some system of dimensionless coordinates  $\pi = P/P_0$ ,  $\tau = T/T_0$ ,  $\omega = \rho/\rho_0$ , are described by one and the same equation of state:

$$\pi = f(\omega, \tau). \quad (1)$$

The point with coordinates  $P_0, V_0, T_0$ , by means of which the system of dimensionless coordinates is constructed, will be called the reference point of similarity, and the states of gases for which the dimensionless parameters  $\omega$  and  $\tau$  are equal by name will be called corresponding states. For any one gas the reference point of similarity may be chosen arbitrarily, but with a value of  $\rho_0$  appreciably different from zero. In order then to determine the coordinates of this point for any other gas, one must make use of the fact that in corresponding states of thermodynamically similar gases any dimensionless function of the coordinates  $P, V, T$  has identical values, which is readily verified directly with the aid of equation (1). To confirm this for the dimensionless quantity  $Z = PV/RT$ , it is first necessary to prove that its particular value  $Z_0 = P_0V_0/RT_0$ , taken for the reference point, will be identical for similar gases.

For this purpose, dividing both parts of equation (1) by  $\omega\tau$ , we obtain:

$$\frac{\pi}{\omega_1\tau} = \frac{1}{\omega\tau} f(\omega, \tau) = \varphi(\omega, \tau), \quad (1a)$$

where, according to the definition,  $\varphi(\omega, \tau)$  is one and the same function for thermodynamically similar gases.

Substituting into the left-hand side of equation (1a), instead of the dimensionless parameters  $\pi, \omega, \tau$ , the coordinates themselves through which they are defined, we obtain:

$$\frac{PV}{RT} : \frac{P_0V_0}{RT_0} = Z : Z_0 = \varphi(\omega, \tau). \quad (2)$$

For  $\omega \rightarrow 0$ , when  $Z = 1$ , we obtain:

$$1/Z_0 = \varphi(0, \tau).$$

According to (1a),  $\varphi(0, \tau)$  must be identical for similar gases, which is possible only under the condition:

$$Z_0 = P_0V_0/RT_0 = \text{idem}. \quad (3)$$

In accordance with equation (2), the latter simultaneously means coincidence of the values of  $Z$  in any corresponding states of thermodynamically similar gases.

From what has been said it is clear that at the reference point of similarity, as well as in any corresponding states of gases, the proposition is valid concerning the coincidence of the values of dimensionless quantities of the same denomination, whereby the

the problem is solved of determining the coordinates of the reference point of similarity. Since the state of a gas is determined by two independent parameters, the coordinates of the reference point of similarity will be determined if one requires that the values of two dimensionless quantities of different names be respectively the same for different gases.

If one takes the quantity  $Z$  as one of these quantities, then the coordinates of the reference point are most simply determined by requiring that the other dimensionless quantity

$$\rho \left( \frac{\partial Z}{\partial \rho} \right)_T = \text{idem} = 0, \quad (4)$$

i.e., the reference point of similarity should expediently be chosen from conditions (3) and (4), which are satisfied by any point on Boyle's curve for the gas.

The choice of the critical point as the reference point is also based on the fact that at this point two dimensionless quantities have, respectively, the same values (zero) for different gases; this is easily verified by writing the critical conditions in the form:

$$\frac{V}{P} \left( \frac{\partial P}{\partial V} \right)_T = \text{idem} = 0,$$

$$\frac{V^2}{P} \left( \frac{\partial^2 P}{\partial V^2} \right)_T = \text{idem} = 0. \quad (5)$$

Of course, conditions (5) are not very convenient for determining the coordinates of the critical point. The latter are determined otherwise—on the basis of the fact that critical points characterize the limiting case of coexistence of the gaseous and liquid phases, when their properties coincide; and this also indicates that the critical states of substances must be corresponding, since for different substances they are physically identical. Geometrically this is expressed in the fact that the critical points occupy one and the same relative geometrical position on the surfaces of state of gases, being at the maximum of the curves of orthobaric densities.

At the same time, condition (3) is not satisfied for the critical point as the reference point of similarity, since the critical numbers of different gases do not coincide. Nor is the dimensionless quantity  $T/P(\partial P/\partial T)_v$  the same at the critical point for different gases. This indicates that the choice of the critical point as the reference point is not very successful. On the other hand, it also indicates that real gases do not fully satisfy the requirements of thermodynamic similarity, which is well known from experiment. Therefore it is clear that the choice of a new reference point instead of the critical one cannot appreciably change the situation connected with the similarity of real gases. However, some improvement—in the sense of better satisfaction of similarity—may to some extent be expected in going over from the critical point to a new reference point of similarity, owing to the fact that the critical point does not satisfy condition (3).

Indeed: if, from experimental data for two gases with different critical numbers, one constructs the surfaces of state with the aid of the parameters  $\pi^*, \omega^*, \tau^*$ , reduced with respect to the critical point, we obtain the following.

When constructing the complex  $\pi^*/\omega^*\tau^*$  as a function of  $\omega^*$  and  $\tau^*$ , the critical points for these gases will coincide, but the regions where  $\omega \rightarrow 0$  will not coincide, since as  $\omega$  approaches zero the complex  $\pi^*/\omega^*\tau^*$  tends to the reciprocal value of the critical number  $Z_k$ , which is not the same for these gases.

When constructing the quantity  $Z$  as a function of  $\omega^*$  and  $\tau^*$ , the surfaces of state of the gases will not coincide at the critical point, since the gases have different  $Z_k$ , but they will coincide in the region of small values of  $\omega$ , since in both cases  $Z$  will then tend to unity.

If, however, one uses the reduced coordinates determined with the aid of the new reference point from conditions (3) and (4), then the surfaces of state of the gases in both cases will coincide both at the reference point and in the region

$\omega \rightarrow 0$ . This gives some grounds for expecting a smaller discrepancy between the surfaces, i.e., better satisfaction of similarity.

Similarly, because of the coincidence of the critical numbers of gases, it is impossible to construct a universal equation of state in critical reduced parameters that would simultaneously satisfy the critical states (the reference points of similarity) of real gases and the region close to zero values. This is easily illustrated by the example of the van der Waals equation, which we shall present in two forms:

$$\frac{\pi^*}{\omega^* \tau^*} = \frac{Z}{Z_k} = \frac{8}{3 - \omega^*} - \frac{3\omega^*}{\tau^*}, \quad (6)$$

$$Z = \frac{3}{3 - \omega^*} - \frac{9}{8} \frac{\omega^*}{\tau^*}. \quad (6a)$$

Equation (6) satisfies the critical point as the reference point of similarity for all gases and does not satisfy their region  $\omega \rightarrow 0$ , while equation (6a) behaves in the opposite way. If, however, the constants of the van der Waals equation are determined not from the critical conditions (5), but from conditions (3) and (4), we arrive at the equation

$$Z = \frac{1}{1 - c\omega} - \frac{c}{(1 - c)^2} \frac{\omega}{\tau}. \quad (7)$$

Here the coordinates of the reference point  $V_0, T_0$ , hidden in the reduced parameters  $\omega, \tau$ , depend on the adopted value of  $Z_0$ , as does also the constant  $c$ , which is given by the expression

$$c = \frac{\sqrt{1 - Z_0} + Z_0 - 1}{Z_0}. \quad (8)$$

We give the values of the constant  $c$  for several values of  $Z_0$ :

$Z_0$	0.75	0.64	0.51	0.36
$c$	1/3	3/8	7/17	4/9

It is not difficult, with the aid of (7) and (8), to verify that the van der Waals equation in the new reduced coordinates satisfies both the reference point of similarity for all gases and the region of small values of  $\omega$ . The same is true for any equation of state in the new reduced coordinates.

However, the significance of the new method of choosing the coordinates of the reference point in the study of thermodynamic similarity is not determined by this alone. The importance of the new method lies in the fact that it makes

it possible to carry out investigations of thermodynamic similarity not only for individual, chemically pure substances, but also for gas mixtures, which was completely impossible to do on the old basis.

Indeed, it is well known that gas mixtures of constant composition in the homogeneous region behave qualitatively like individual substances, and this is expressed in the fact that the sections of the surfaces of state of nonreacting gas mixtures do not differ qualitatively from the corresponding sections of the surfaces of state of individual substances. This provides grounds for subjecting gas mixtures to investigation with respect to their similarity to the components of which they are formed, and also for checking the similarity of different gas mixtures to one another. But such an investigation cannot be carried out if the critical point is taken as the reference point of similarity,

the critical point, since gas mixtures do not have a state corresponding to the critical state of pure substances.

At the same time, taking into account the complexity of experimentally studying the properties of gas mixtures because of the large amount of experiment required, which increases very sharply with an increase in the number of components of the mixture, the study of gas mixtures by the method of thermodynamic similarity becomes much more important than the study of pure substances. A preliminary check of this question on a number of binary mixtures gives very encouraging results, since it has been found that, over a wide interval of density variation, where the components are approximately similar to one another, the mixture itself is similar to the components.

Taking into account certain features discovered in the study of binary mixtures by the method of thermodynamic similarity with the aid of a new reference point, as well as the lower accuracy requirements imposed on mixtures in comparison with pure substances, one may suppose that a detailed study, by the new method, of experimental data on binary mixtures can provide the key to an analytical description of mixtures with any number of components on the basis solely of data on the components themselves and on their binary mixtures.

Received  
22 X 1964

*Note: Figure translations are in progress. See original paper for figures.*

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