

THE USE OF THERMODYNAMIC SIMILARITY FOR INVESTIGATION  
OF THE PROPERTIES OF GAS MIXTURES

Ya. Z. Kazavchinskii

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A presentation is made of new ideas in the theory of thermodynamic similarity which indicate that, instead of the critical point as a reference point for similarity, we may take any other point on the Boyle curve that is far enough from the ideal gas state.

Gases are called thermodynamically similar which, in some system of dimensionless coordinates  $\pi = p/\rho_0$ ,  $\tau = T/T_0$ ,  $\omega = \rho/\rho_0$  satisfy the single equation of state

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

We call the point with coordinates  $p_0$ ,  $\rho_0$ ,  $T_0$ , used in forming the dimensionless coordinates  $\pi$ ,  $\tau$ ,  $\omega$ , the reference point. For any one gas this point may be chosen arbitrarily, but it must have density  $\rho$  appreciably different from zero. We may determine the coordinates of this point by making use of a theorem which is valid for corresponding states of similar gases, in which any two of the coordinates are equal to one another. Assuming that  $f$  in (1) is a one-to-one function, it may be shown immediately that the dimensionless quantities of the type  $\frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_\rho$ ,  $\left[ \frac{\rho}{p} \int \frac{dp}{\rho} \right]_\tau$  have identical values in corresponding states of similar gases. In order to establish the validity of this theorem for the dimensionless quantity  $Z = p/R\rho T$ , we must first prove that its particular value  $Z_0 = p_0/R\rho_0 T_0$ , formed from the coordinates of the reference point, must be identical in thermodynamically similar gases. With this aim, by dividing both sides of (1) by  $\omega\tau$ , we obtain

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

where, according to the definition,  $\varphi(\omega, \tau)$  is the same function for gases satisfying the similarity.

Replacing the dimensionless parameters  $\pi$ ,  $\omega$ ,  $\tau$  on the left of (1a) by the coordinates in terms of which they were defined, we obtain

$$\frac{p}{\rho T} : \frac{p_0}{\rho_0 T_0} = Z : Z_0 = \varphi(\omega, \tau). \quad (2)$$

When  $\omega \rightarrow 0$ , with  $Z = 1$ , we have

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

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

$$Z = p_0/R\rho_0 T_0 = \text{idem}. \quad (3)$$

Then from (2) it follows, in general, that in corresponding states of similar gases the quantities  $Z$ , as well as any other dimensionless quantities of one designation, coincide.

It is clear from what has been said, that at the similarity reference point, and in any corresponding states of the gases, the statement about the coincidence of values of dimensionless quantities of one designation is valid, which also solves the problem of determining the reference point. Since the states of gases and of gas mixtures of constant composition are determined by two independent parameters, the coordinates of the reference point may be determined, if required, so that the values of any two dimensionless quantities of different designations will be respectively identical in the different gases.

If we take  $Z$  as one such dimensionless quantity, the coordinates of the reference point will be determined most simply by taking the quantity  $\rho \left( \frac{\partial Z}{\partial \rho} \right)_T$  as the second, since there is a temperature region in the gas where this quantity goes to zero. Therefore the second equation for determining the coordinates of the reference point will be

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

i. e., the similarity reference points should be chosen on the Boyle curves of the gases at a fixed value of  $Z$ .

It is easy to show that the choice of the critical point as a reference point is also based on the fact that at this point two dimensionless quantities have respectively the same (zero) values for different gases; this may easily be verified by writing the critical conditions in the form

$$\begin{aligned} \frac{v}{p} \left( \frac{\partial p}{\partial v} \right)_T &= \text{idem} = 0, \\ \frac{v^2}{p} \left( \frac{\partial^2 p}{\partial v^2} \right)_T &= \text{idem} = 0. \end{aligned} \quad (5)$$

However, there are real differences between the new conditions (3) and (4) and the critical conditions. Conditions (3) and (4) serve immediately to determine the coordinates of the reference point from experimental data, while condition (5) is unsuitable and is not used in practice for the determination of the critical point on the basis of experimental data. The latter are determined in another way, based on the fact that the critical point describes a limiting case of co-existence of the gaseous and liquid phases, when their additive properties coincide. This means that the critical points of gases are congruent according to purely physical considerations, since they describe identical thermodynamic states, satisfying the limiting case of co-existence of phases. Moreover, condition (3) is not satisfied as a similarity reference point at the critical point, since the critical values of the gases do not agree among themselves. The dimensionless quantity  $\frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_c$  is also not the same at the critical point of different gases. This is more evidence of the fact that real gases do not fully satisfy the requirements of similarity.

Evidently, the choice of a new reference point in place of the critical point cannot change the theorem relating to the similarity of real gases in any appreciable way. However, some deterioration may occur in the degree to which similarity is satisfied, in going from the critical point to the new similarity reference point, because the critical point does not satisfy one of the real requirements of similarity, that expressed by condition (3).

In fact, if we construct surfaces of state from experimental data on two gases with different critical values, with the help of the parameters  $\pi^*$ ,  $\omega^*$ ,  $\tau^*$ , referred to the critical point, we obtain the following:

a) in constructing the group  $\pi^*/\omega^*\tau^*$  as a function of  $\omega^*$  and  $\tau^*$  for these gases, the critical points will coincide, but the regions of ideal gas state will not coincide, since as  $\omega$  approaches zero the group  $\pi^*/\omega^*\tau^*$  tends to the inverse of the critical value  $Z_c$ , which is not the same in these gases;

b) if we construct the group  $Z$  as a function of  $\omega^*$  and  $\tau^*$ , the surfaces of state of the gases do not coincide at the critical point, since the  $Z_c$  are different for the gases, but they will coincide in the region of small  $\omega$ , since  $Z$  will then tend to unity for both gases.

If we use reduced coordinates, as determined from conditions (3) and (4) with the aid of the new reference point, the surfaces of state of the gases in the two cases a) and b) will coincide, both at the reference point, and in the region of ideal gas states. This gives reason to believe that in the new reduced coordinates the similarity of the gases will be more in evidence.

In a similar way, because of the lack of coincidence of the critical values of the gases, it is impossible to create a universal equation of state in the critical reduced parameters, to simultaneously satisfy the critical conditions of real gases (the reference similarity point), as well as the region of  $\omega$  values close to zero. This is easily illustrated by the example of the Van-der Waals equation, which we can write in the two forms

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

and

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

Equation (6) satisfies the critical point as a similarity reference point for all the gases, and does not satisfy the ideal gas states, while (6a) does the opposite. If we determine the constants of the Van-der Waals equation, not from the critical conditions (5), but from (3) and (4), we obtain

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

The coordinates here of the reference point,  $\rho_0$ ,  $T_0$ , which are concealed in the reduced parameters  $\omega^*$ ,  $\tau^*$ , depend on the assumed value of  $Z$  on the Boyle curve, as well as on the constant  $C$ , which is given by the expression

$$C = (\sqrt{1 - Z_0} + Z_0 - 1)/Z_0. \quad (8)$$

For  $Z_0 = 0.75$ ,  $0.64$ ,  $0.51$ , and  $0.36$ , the constant  $C$  is equal, respectively, to  $1/3$ ,  $3/8$ ,  $7/17$ , and  $4/9$ . It is not difficult to verify, with the help of (7) and (8), that the Van-der Waals equation in the new reduced coordinates satisfies both the reference point of all gases, and also their regions of ideal gas states. The same thing is true for any equation of state in the new reduced coordinates.

This does not define the significance, however, of the new method of choosing the coordinates of the reference point in investigations of thermodynamic similarity. The importance of the new method lies in the fact that it allows us to investigate, by the method of thermodynamic similarity, not only individual, chemically pure substances, but also mixtures of gases, which was completely impossible on the old basis.

In fact, it is well known that mixtures of gases of constant composition behave qualitatively in the homogeneous region like individual substances, and this is expressed in the fact that the sections of surfaces of constant state of non-reacting gas mixtures do not differ qualitatively from the similar section of the surfaces of state of the individual substances. This offers a basis for investigation of gas mixtures from the viewpoint of similarity of their components, as well as for checking the similarity of unlike gas mixtures. However, this kind of investigation cannot be conducted if the critical point is taken as a similarity reference point, since there is no state for the mixtures of gases which corresponds to the critical state of the pure substances. In addition, taking into account the complexity of experimental investigation of properties of gas mixtures, due to the large volume of experiment required—increasing very rapidly with increase of the number of components of the mixture—the investigation of gas mixtures by the method of thermodynamic similarity acquires considerably greater importance than the investigation of pure substances.

In order to conduct an actual verification of a question connected with the similarity of a mixture of gases and its components, we shall examine the specific example of a binary mixture, and shall illustrate, at the same time, the technique of investigation, based on the new ideas about the similarity reference point. A methane-butane mixture was taken as the case under examination, there being experimental data for three compositions [1, 2]. From the available data for this mixture it was found that the Boyle curves for the different compositions start with  $Z$  values of the order of  $0.58$ , and so the reference point was chosen with the somewhat larger value of  $Z_0 = 0.634$ , to which correspond the reference point coordinates:

$$\begin{aligned} \text{for methane } T_{01} &= 1.3, & T_C &= 247.7^\circ \text{ K}, & \rho_{01} &= 10.643 \text{ kmole/m}^3, \\ \text{for n-butane } T_{02} &= 573.7^\circ \text{ K}, & \rho_{02} &= 4.080 \text{ kmole/m}^3. \end{aligned}$$

For a methane-butane mixture with molar composition of  $x = 0.396$  of butane, the reference point coordinates proved to be  $T_0 = 439.6$ ,  $\rho_0 = 5.41 \text{ kmole/m}^3$ . From the reference point coordinates found for methane and n-butane, their equations of state, as constructed in [6], were transformed to the dimensionless form  $Z = f(\tau, \bar{\omega})$ .

The experimental data for the methane-butane mixture have been represented, by graphical processing, in terms of their isotherms for spherical values of  $\omega = \rho/\rho_0 = \rho/5.41$  (Table 1). At the temperature  $T = 477.5^\circ \text{ K}$ , corresponding to the reduced temperature,  $\tau = 1.086$ . For this same reduced temperature, and for these  $\omega$ , we calculated the values of  $Z_1$  and  $Z_2$  from the equations of state for methane and n-butane. It may be seen from the table that the similarity observed between the mixture and the components is not less than that between the components themselves. With  $\omega = 1.3$  (the reduced density according to the new reference point does not differ much from that at the critical point) noticeable deviations from similarity are observed between the components, and the mixture also gives large deviations from similarity. An analogous picture is observed at the isotherms  $410.9$ ,  $444.2^\circ \text{ K}$  of this mixture with the same mole composition  $x = 0.396$ , as well as for the two other compositions of methane-butane mixture, at all the temperatures for which experimental data exist.

In Table 2 the same comparison is made for one isotherm of a methane-ethane mixture, according to the experimental data of [3, 4, 5].

The coordinates of the reference point of ethane were found to be  $T_{02} = 392.1$ ,  $\rho_{02} = 7.31 \text{ kmole/m}^3$ , while the coordinates for the mixture with  $x = 0.507$  of methane proved to be  $T_0 = 325^\circ \text{ K}$ ,  $\rho_0 = 8.68 \text{ kmole/m}^3$ .

A comparison is made in Table 2 for the isotherm  $T = 310.94^\circ \text{ K}$ , which corresponds to the value  $\tau = 0.957$ . It is seen from Table 2 that even better similarity between the mixture and methane is observed than in the first case above, in spite of the fact that the components themselves do not satisfy similarity well. Investigations were also made for other binary mixtures, and in general the picture obtained is similar to that represented in Tables 1 and 2.

This is evidence of the fact that the investigation of gas mixtures by the method of thermodynamic similarity holds out promise. If we restrict ourselves to binary mixtures, it may be assumed that the description of the behavior of binary mixtures, over a considerable range of change of densities, on the basis of only the single equations of the components, reduces in the main to the problem of determining, in general form, the dependence of the reference point temperature of the mixture,  $T_0$ , on the temperatures  $T_{01}$  and  $T_{02}$  of the components and on the molar composition, and the similar dependence for the reference point density  $\rho$  of the mixture.

Table 1

Comparison of the values of  $Z$  in the corresponding states, for methane, n-butane, and the mixture ( $x = 0.396$  of methane,  $\tau = 1.086$ ).

$\omega$	methane $Z_1$	butane $Z_2$	mixture $Z$
0.1	0.9336	0.9316	0.931
0.2	0.8743	0.8710	0.870
0.3	0.8157	0.8182	0.816
0.4	0.7762	0.7730	0.772
0.5	0.7374	0.7352	0.733
0.6	0.7052	0.7043	0.702
0.7	0.6798	0.6800	0.678
0.8	0.6614	0.6624	0.661
0.9	0.6505	0.6517	0.651
1.0	0.6476	0.6486	0.647
1.1	0.6537	0.6543	0.652
1.2	0.6704	0.6707	0.667
1.3	0.6993	0.7007	0.690

Table 2

Comparison of values of  $Z$  in corresponding states of methane, ethane, and their mixture ( $x = 0.507$  of methane,  $\tau = 0.957$ ).

$\omega$	methane $Z_1$	ethane $Z_2$	mixture $Z$
0.1	0.9411	0.9350	0.942
0.2	0.8866	0.8753	0.884
0.3	0.8367	0.8204	0.834
0.4	0.7913	0.7713	0.788
0.5	0.7503	0.7271	0.746
0.6	0.7137	0.6880	0.710
0.7	0.6819	0.6536	0.680
0.8	0.6534	0.6249	0.652
0.9	0.6296	0.6130	0.629
1.0	0.6101	0.5676	0.612
1.1	0.5938	0.5654	0.595
1.2	0.5829	0.5556	0.584
1.3	0.5788	0.5531	0.576

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Institute of Naval Engineering, Odessa