A METHOD OF CORRELATING THE LAW OF CORRESPONDING STATES IN CALCULATING THE THERMODYNAMIC PROPERTIES OF REAL GASES AND THEIR MIXTURES

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A method of correlating the law of corresponding states is described, aimed at enhancing the accuracy of calculation of the thermodynamic properties of gases and mixtures of gases.

In spite of the law of corresponding states being an approximation, thermodynamic similarity has engaged the interest of investigators as a method of studying the properties of substances which have received little attention. Possibilities of using thermodynamic similarity to investigate the properties of pure substances and mixtures have recently been widened considerably, thanks to Kazavchinskii [1], who showed that any point on the Boyle curve with a fixed value of Z for different gases may be chosen as the similarity reference point. Moreover, the method of choosing the reference point has itself created good premises for developing a new method of correlating the law of corresponding states.

States on the Boyle curve with identical values of Z for different gases are corresponding states [1]. Therefore when similarity exists, the following relations between like parameters of substances on the Boyle curves will be valid:

$$\frac{\rho_i}{\rho_{o.i}} = \frac{\rho_b}{\rho_{o.b}}; \quad \frac{T_i}{T_{o.i}} = \frac{T_b}{T_{o.b}}; \quad \frac{P_i}{P_{o.i}} = \frac{P_b}{P_{o.b}},$$

where the subscripts "i" and "b" refer, respectively, to the i-th and to the base substances with the parameters of the reference points T_o, ρ_o, P_o. For thermodynamically similar substances the graphs of the relations between like parameters of the Boyle curves at identical Z are straight lines passing through the origin of coordinates, with slopes equal to the ratio of the corresponding reference parameters. Because the similarity of real gases is approximate, the above graphs are lines of small curvature, described by the expressions:

$$T_i = aT_b + bT_b^2, \tag{1}$$

$$\rho_i = c\rho_b + d\rho_b^2. \tag{2}$$

To reduce (1) to dimensionless form, we shall choose points with fixed Z_o on the Boyle curves of the various substances. With the aid of the coordinates of these points, (1) transforms to the form

$$T_i/T_{o.i} = aT_b/T_{o.i} + bT_b^2/T_{o.i}.$$

Here T_i and T_b are the temperatures on the Boyle curves of the substance under examination and the reference substance; $T_{o.i}$ is the temperature of the point with fixed Z_o. Introducing the notation $\tau_i = T_i/T_{o.i}$ and $\tau_b = T_b/T_{o.b}$, we obtain

$$\tau_i = (aT_{o.b}/T_{o.i})\tau_b + (bT_{o.b}^2/T_{o.i})\tau_b^2.$$

We shall designate by a' and b', respectively, the constant groups in the brackets for the given substances; then the last expression may be written in the form

$$\tau_i = a'\tau_b + b'\tau_b^2. \tag{3}$$

Equation (3) relates the reduced temperatures on the Boyle curves for different Z values. It is easy to see that the Boyle curves represented in $Z-\tau$ coordinates do not coincide, generally speaking, with the exception of the reference point, where $\tau_i = \tau_b = 1$. Obviously, then

$$a' + b' = 1. \tag{4}$$

For thermodynamically similar gases the quantity a' would be equal to unity, and b' to zero.

Because real gases are only approximately similar, $b' \neq 0$, and in the general case, $\tau_i \neq \tau_b$. Denoting $(\tau_i - \tau_b)$ at identical Z by λ, and taking account of (3) and (4), we find

$$\lambda = b'(\tau_b^2 - \tau_b). \tag{5}$$

In other words, the values of Z on the Boyle curves coincide, not at equal values of reduced temperatures $(\tau_i - \tau_b)$, as predicted by the law of corresponding states, but for $\tau_i = \tau_b + \lambda$.

Thus the surfaces of state of different gases, represented in the coordinates $Z-\omega-(\tau + \lambda)$, are characterized by the fact that the Boyle curves coincide at them, because of which the surfaces will be close one to another even at other points.

It should be noted that congruence of the surfaces along the Boyle curves may be achieved, by introducing an analogous correlation for the reduced densities ω on the Boyle curve. However, such a correlation may introduce a large error, because the accuracy of density values assigned on the Boyle curve is below that of the law of corresponding states.

Thus, calculation of the thermodynamic properties of a gas or gas mixture being studied is predicated on the availability of reliable detailed data on the base substance, on the parameters of the reference points,

Table 1

Comparison of Compressibility Coefficients Z of the Test Substance and the Base Substance (Nitrogen) at Identical Values of Reduced Density

iC_4H_{10}

ω	$T_{iC_4H_{10}}$=423.15°K			$T_{iC_4H_{10}}$=498.15° K		
	Z_{N_2}	$Z_{iC_4H_{10}}$	δZ, %	Z_{N_2}	$Z_{iC_4H_{10}}$	δZ, %
0.1	0.873	0.874	0.11	0.913	0.915	0.22
0.3	0.666	0.667	0.15	0.775	0.777	0.26
0.5	0.507	0.504	—0.60	0.678	0.679	0.15
0.7	0.397	0.395	—0.51	0.611	0.608	—0.49
0.9	0.324	0.322	—0.62	0.584	0.582	—0.34
1.1	0.288	0.287	—0.35	0.600	0.599	—0.17
1.3*)	0.299	0.298	—0.34	0.684	0.684	0.50

CH_4

ω	T_{CH_4}=273.15° K			T_{CH_4}=373.15° K		
	Z_{N_2}	Z_{CH_4}	δZ, %	Z_{N_2}	Z_{CH_4}	δZ, %
0.1	0.882	0.885	0.34	0.959	0.962	0.31
0.3	0.686	0.689	0.44	0.902	0.904	0.22
0.5	0.538	0.539	0.19	0.876	0.878	0.23
0.7	0.435	0.435	0.00	0.877	0.879	0.23
0.9	0.369	0.370	0.27	0.915	0.919	0.44
1.1	0.341	0.341	0.00	1.006	1.008	0.20
1.3	0.361	0.363	0.55	1.172	1.173	0.09

CO_2

ω	T_{CO_2}=398.15° K			T_{CO_2}=473.15° K		
	Z_{N_2}	Z_{CO_2}	δZ, %	Z_{N_2}	Z_{CO_2}	δZ, %
0.1	0.924	0.928	0.43	0.954	0.958	0.42
0.3	0.812	0.813	0.12	0.893	0.893	0.00
0.5	0.736	0.734	—0.27	0.863	0.861	—0.23
0.7	0.690	0.690	0.00	0.860	0.861	0.12
0.9	0.678	0.681	0.44	0.893	0.891	—0.22
1.1	0.717	0.720	0.42	0.986	0.979	—0.71
1.3	0.819	0.825	0.73	1.140	1.147	0.10

C_2H_4

ω	$T_{C_2H_4}$=373.15° K			$T_{C_2H_4}$ = 423.15° K		
	Z_{N_2}	$Z_{C_2H_4}$	δZ, %	Z_{N_2}	$Z_{C_2H_4}$	δZ, %
0.1	0.922	0.927	0.64	0.942	0.947	0.53
0.3	0.807	0.810	0.37	0.862	0.866	0.46
0.5	0.727	0.726	—0.14	0.818	0.815	—0.37
0.7	0.679	0.677	—0.30	0.796	0.797	0.13
0.9	0.667	0.667	0.00	0.812	0.815	0.37
1.1	0.700	0.705	0.71	0.880	0.888	0.90
1.3	0.800	0.809	1.21	1.021	1.034	1.26

C_3H_6

ω	$T_{C_3H_6}$=373.15° K			$T_{C_3H_6}$=423.15° K		
	Z_{N_2}	$Z_{C_3H_6}$	δZ, %	Z_{N_2}	$Z_{C_3H_6}$	δZ, %
0.1	0.869	0.869	0.00	0.915	—0.911	0.44
0.3	0.653	0.656	0.46	0.777	—0.772	0.65
0.5	0.494	0.494	0.00	0.678	0.678	0.00
0.7	0.380	0.379	0.26	0.613	0.612	0.16
0.9	0.304	0.302	0.66	0.584	—0.582	0.34
1.1	0.264	0.262	0.76	0.595	0.600	0.83
1.3	0.264	0.264	0.00	0.628	0.637	1.41

*Our value of reduced density, equal to 1.3, corresponds to a value ω = 1.7 with respect to the critical point.

Table 2

Comparison of Compressibility Coefficients for the Test Mixtures and the Base Substance (Nitrogen) at Identical Values of Reduced Density

Propane — CO_2, T=477.57° K

ω	$X_{C_3H_8}$ = 0.4116			$X_{C_3H_8}$ = 0.5983			$X_{C_3H_8}$ = 0.8038		
	Z_{N_2}	Z_{CM}	δZ, %	Z_{N_2}	Z_{CM}	δZ, %	Z_{N_2}	Z_{CM}	δZ, %
0.1	0.925	0.927	0.21	0.913	0.914	0.11	0.900	0.900	0.00
0.3	0.805	0.807	0.25	0.778	0.778	0.00	0.744	0.742	—0.27
0.5	0.725	0.721	—0.55	0.687	0.686	—0.14	0.634	0.636	0.31
0.7	0.676	0.675	—0.15	0.624	0.626	0.32	0.556	0.560	0.71
0.9	0.661	0.663	0.30	0.598	0.601	0.49	0.515	0.517	0.39
1.1	0.702	0.708	0.84	0.618	0.622	0.64	0.519	0.520	0.19
1.3	0.745	0.754	1.19	0.705	0.708	0.42	0.574	0.566	—1.20

Ethane–propylene T=410.92° K

ω	$X_{C_2H_6}$ = 0.1821			$X_{C_2H_6}$ = 0.4958			$X_{C_2H_6}$ = 0.8249		
	Z_{N_2}	Z_{CM}	δZ, %	Z_{N_2}	Z_{CM}	δZ, %	Z_{N_2}	Z_{CM}	δZ, %
0.1	0.922	0.925	0.32	0.911	0.912	0.11	0.898	0.901	0 33
0.3	0.803	0.805	0.25	0.769	0.772	0.39	0.736	0.737	0.14
0.5	0.718	0.718	0.00	0.670	0.670	0.00	0.619	0.619	—0.16
0.7	0.668	0.667	—0.15	0.602	0.601	—0.17	0.540	0.540	0.00
0.9	0.650	0.653	0.46	0.511	0.573	0.35	0.492	0.496	0.81
1.1	0.683	0.685	0.29	0.588	0.592	0.67	0.495	0.497	0.40
1.3	0.782	0.787	0.64	0.667	0.675	1.18	0.554	0.561	1.25

Methane–isobutane T=477.57° K

ω	X_{CH_4}=0.2771			X_{CH_4}=0.4681			X_{CH_4}=0.7101		
	Z_{N_2}	Z_{CM}	δZ, %	Z_{N_2}	Z_{CM}	δZ, %	Z_{N_2}	Z_{CM}	δZ, %
0.1	0.927	0.929	0.22	0.944	0 944	0.00	0.970	0.970	0.90
0.3	0.821	0.822	0.12	0.868	0.867	—0.12	0.933	0.932	—0.11
0.5	0.750	0.747	—0.40	0.823	0.821	—0.24	0.921	0.922	0.11
0.7	0.708	0.705	—0.43	0.808	0.808	0.00	0.941	0.943	0.21
0.9	0.702	0.703	0.14	0.826	0.826	0.00	0.996	1.001	0.50
1.1	0.744	0.747	0.40	0.898	0.897	—0.11	1.041	1.046	0.48
1.3	0.851	0.861	1.16	1.040	1.032	—0.77			

Table 3

Comparison of Compressibility Coefficients Z for CO_2 and N_2 at Identical Values of Reduced Density and Temperature

ω	T_{CO_2}=398.15° K			T_{CO_2}=473.15° K		
	Z_{N_2}	Z_{CO_2}	δZ, %	Z_{N_2}	Z_{CO_2}	δZ, %
0.1	0.922	0.924	0.12	0.949	0.958	0.95
0.3	0.805	0.813	0.86	0.879	0.893	1.57
0.5	0.727	0.734	0.95	0.844	0.861	1.97
0.7	0.676	0.690	2.03	0.834	0.861	3.14
0.9	0.661	0.681	2.94	0.859	0.891	3.59
1.1	0.695	0.720	3.47	0.938	0.979	4.19
1.3	0.791	0.825	4.12	1.087	1.147	6.10

and on the value of coefficient b′, which is determined from the Boyle curve of the gas examined.

Verification of the method has been based directly an experimental data. To this end the data for nitrogen [3] as base* and for CO_2 [4], CH_4 [5], C_2H_4 [6], iC_4H_{10} [7], C_3H_6 [8] as test substances were processed and represented in $Z-\omega-\tau$ coordinates. As similarity reference points we chose points on the Boyle curves with a value $Z_0 = 0.5$. The parameters of the reference points and of the quantity b′ were calculated from (1) and (3). The comparison was made at various values of reduced density $\omega_i = \omega_{N_2}$ and with $\tau_i = \tau_{N_2} + b'(\tau_{N_2}^2 - \tau_{N_2})$. the results being shown in Table 1.

It is well known that a mixture of gases of constant composition in a uniform region behaves, in principle, as a single substance. This is due to the fact that different sections of the surfaces of state for mixtures and for pure substances do not differ qualitatively. For this reason the relative construction of the Boyle curve of a mixture from the Boyle curve of the base substance also gives curves of small curvature described by Eqs. (1) and (2), thus permitting the proposed correlation to be extended to mixtures. From the experimental data for the mixtures CH_4—C_4H_{10} [9], C_3H_8—CO_2 [10], C_2H_6—C_3H_6 [11] we extracted Boyle curves, determined the coefficients of (1) and (2), found the parameters of the reference points with $Z_0 = 0.5$, and calculated values of b′. The comparison was made for various values of reduced density $\omega_i = \omega_{N_2}$ and with $\tau_i = \tau_{N_2} + b'(\tau_{N_2}^2 - \tau_{N_2})$, the results being shown in Table 2.

To evaluate the effectiveness of the correlation method described, we compared values of compressibility of gases at various reduced densities and temperatures $\omega_i = \omega_{N_2}$ and $\tau_i = \tau_{N_2}$. Table 3 shows the comparison for CO_2.

*For nitrogen we used a reference grid compiled from all the experimental data available in [3].

It may be seen from the comparison (Tables 1 and 2) that the method described may be used to calculate the thermodynamic properties of gases and their mixtures. The accuracy achieved by the method is close to that of methods based on construction of an equation of state for each mixture separately [2].

$Z = PV/RT$—compressibility factor; a, b, c, and d—coefficients of Eqs. (1) and (2); T_i, ρ_i—current parameters of the Boyle curve of the test substance; T_b, ρ_b—current parameters of the Boyle curve of the base substance; $T_{o.i}$. $\rho_{o.i}$—parameters of reference point on the Boyle curve of the test substance; $T_{o.b}$, $\rho_{o.b}$—parameters of reference point on the Boyle curve of the base substance; $\omega = \rho/\rho_0$; $\tau = T/T_0$. The subscript i refers to the test substance, and b to the base.

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