THERMODYNAMIC EFFECTS OF MIXING IN GASES AT MODERATE DENSITIES

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A parameter is found that governs the magnitude of thermodynamic mixing effects in gases. Values are calculated for the excess second virial coefficient and its derivatives for a number of binary gas systems at 298.15°K.

As is known [1, 2], deviations from the Amag and Dalton laws that are valid for ideal gases hold for real gas mixtures. The imperfection of a gas mixture is determined by the magnitudes of the bulk and thermal mixing effects at constant temperature and pressure:

$$\Delta v^E = \left\{v_{\text{mix}} - \sum_k x_k v_k\right\}_{T,p}, \tag{1}$$

$$\Delta H^E = \left\{H_{\text{mix}} - \sum_k x_k H_k\right\}_{T,p} \tag{2}$$

and the baric mixing effect at constant temperature and volume:

$$\Delta p = \left\{p_{\text{mix}} - \sum_k x_k p_k\right\}_{T,v}, \tag{3}$$

where v_k and H_k are the molar volume and enthalpy of the individual components, and x_k and p_k are their molar concentrations and partial pressures.

The thermodynamic mixing effects can be computed if the equation of state of the gas mixture is known. At moderate densities when the virial equation of state is valid, in a first approximation we have for binary gas systems [2]

$$\Delta v^E = 2x_1x_2E, \tag{4}$$

$$\Delta H^E = 2x_1x_2p\left(E - T\frac{dE}{dT}\right), \tag{5}$$

$$\frac{\Delta p}{p} = 2x_1x_2E\,\frac{p}{RT + 2x_1x_2Ep}, \tag{6}$$

where

$$E = B_{12} - \frac{1}{2}(B_{11} + B_{22}) \tag{7}$$

is the excess second virial coefficient.

Therefore, the thermodynamic mixing effects in gases are determined in a first approximation by the magnitude of the excess second virial coefficient and its derivatives.

Experimental data on the excess second virial coefficient are not numerous and do not possess sufficient accuracy even in those cases when the properties of the individual components have been studied well. Consequently, utilization of the results of the molecular theory of gases here is of special value.

The possibility is investigated below of utilizing a model pair potential (12-7, δ) [3, 4] and modified combination Kong relationships [5] to compute thermodynamic mixing effects in gases at moderate densities.

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TABLE 1. Comparison between Computed Values of the Excess Second Virial Coefficient and Experimental Data [7],* E in cm^3/mole

T, K	Ne—Ar		Ne—Kr		Ne—Xe		Ar—N_2	
	exp.	comp.	exp.	comp.	exp.	comp.	exp.	comp.
213	18,5	20,3	45,4	50,1	120,5	125,4	—4,7	0†
223	18,5	19,1	43,1	46,7	113,2	116,4	—4,8	0
242	17,1	17,2	38,5	41,7	99,7	102,7	—3,5	0
262	16,5	15,5	34,8	37,3	87,6	91,3	—1,6	0
276	14,9	14,4	33,9	34,7	81,0	84,6	—1,1	0
295	13,1	13,5	31,2	31,9	74,1	77,0	—0,5	0
330	11,3	11,6	25,9	27,6	62,4	65,9	+0,1	0
365	9,6	10,2	23,0	24,2	54,0	57,4	+2,7	0
400	7,9	9,1	19,3	21,5	47,1	50,9	+2,1	0
425	6,9	8,4	18,0	20,0	43,0	46,9	+1,3	0
450	5,9	7,8	17,0	18,6	39,0	43,7	+0,6	0
475	4.3	7.4	14.4	17.4	35.0	40,9	—0,8	0

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*Absolute error of the data in [7] is ±5 cm^3/mole.

†Computed values less than 0.05 are rounded off to zero.

Values of the excess second virial coefficient and its first derivative were calculated for binary systems of nonpolar gases. Comparison of the computations with available experimental data [6-9] showed that the results are in agreement within the limits of measurement error. Presented as an illustration in Table 1 is a comparison between calculated values for a number of binary systems and experimental data in [7]. It can be seen that the magnitude of the excess second virial coefficient diminishes as the temperature rises and can vary strongly with the replacement of one of the system components. For a given reduced temperature the magnitude of the excess second virial coefficient is greater for those systems for which the "mixed" force constants a_{12} and ε_{12} differ most radically from the geometric mean values.

According to the modified Kong combination relationships [5], for a model pair potential (12-7, δ) the constants a_{12} and ε_{12} are written in the form

$$a_{12} = \sqrt{a_{11}a_{22}}\, f, \tag{8}$$

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}\, f^{-7}, \tag{9}$$

where

$$f = \left[\frac{(K)^{\frac{1}{26}} + (K)^{-\frac{1}{26}}}{2}\right]^{\frac{13}{5}}, \tag{10}$$

where by definition

$$a_{ij}^2 = \sigma_{ij}^2 - r_{eij}^2, \quad K = \frac{\varepsilon_{22}}{\varepsilon_{11}}\left(\frac{a_{22}}{a_{11}}\right)^{12}. \tag{11}$$

The function f can be represented as a series in powers of the parameter $\alpha = (\log K)^2$:

$$f = 1 + 1.019 \cdot 10^{-2}\alpha + 4.00 \cdot 10^{-5}\alpha^2 + \ldots \tag{12}$$

It follows from expressions (8) and (9) that the "mixed" force constants a_{12} and ε_{12} will differ the more radically from the geometric mean values, the greater the magnitude of the parameter α. For a system with low values of the parameter α (argon—nitrogen, neon—hydrogen) the function f is quite close to one and the excess second virial coefficient and its derivatives are close to zero. In such systems the thermodynamic mixing effects are small, while the thermodynamic functions can be computed from the additivity rule (as is verified in test [10]).

In systems whose components differ noticeably in the magnitude of the force constants of the intermolecular interaction, the parameter α has the order of magnitude of 10 (helium—heavy gases). In such systems the thermodynamic mixing effects are substantial, especially

TABLE 2. Values of the Excess Second Virial Coefficient and Its Derivatives for a Number of Binary Systems, T = 298.15°K

System	α	E, cm³/mole	$-E_1$, cm³/mole	E_2, cm³/mole	System	α	E, cm³/mole	$-E_1$, cm³/mole	E_2, cm³/mole
He—Ne	1,013	1,7	1,9	4,0	Ne—N_2	2,220	11,1	14,5	33,3
He—Ar	6,502	22,7	27,4	62,5	Ar—Kr	0,217	4,4	6,5	18,3
He—Kr	9,091	44,3	55,9	135,8	Ar—Xe	1,163	29,8	46,7	137,1
He—Xe	13,163	92,5	125,4	327,3	Ar—H_2	2,110	12,0	15,2	35,9
He—H_2	1,204	2,1	2,4	4,7	Ar—N_2	0,003	0*	0,1	0,2
He—N_2	6,233	20,2	25,0	55,5	H_2—Kr	3,679	29,8	39,4	100,4
Ne—Ar	2,381	13,1	16,6	38,9	H_2—Xe	5,950	73,7	103,9	281,4
Ne—Kr	4,034	31,4	41,3	104,4	H_2—N_2	1,958	10,2	13,4	30,7
Ne—Xe	6,872	75,8	106,6	287,3	N_2—Kr	0,269	5,5	8,1	22,7
Ne—H_2	0,008	0*	0*	0,1	N_2—Xe	1,280	32,7	50,5	147,9

*Values less than 0.05 are rounded off to zero.

at low temperatures. Noticeable deviations from the additivity rule for such systems are well known from experiments [11, 12].

The connection between the parameter α and the magnitude of the thermodynamic mixing effects in gases is seen in Table 2. It becomes more graphic if the results are represented in the reduced quantities

$$E^* = \frac{E}{\frac{2}{3}\pi N\sigma_{12}^3}, \quad T^* = \frac{kT}{\varepsilon_{12}},$$

as is ordinarily done for the second virial coefficient.

Also presented in Table 2 are values of the functions $E_1 = T(dE/dT)$ and $E_2 = T^2(d^2E/dT^2)$. The function E_2 describes the excess isobaric specific heat for mixing gases at constant temperature and pressure:

$$\Delta c_p^E = \left(\frac{\partial \Delta H^E}{\partial T}\right)_p = -2x_1x_2\frac{p}{T}E_2. \tag{13}$$

The excess isobaric specific heat of binary gas systems is negative in magnitude.

Unfortunately, there are no experimental data on the excess specific heat of binary gas systems at moderate densities. Only results of measurements for a nitrogen—carbon dioxide mixture at high densities are known [13]. They indicate that the isobaric specific heat of gas mixtures can be several times lower than the corresponding quantity computed by the additivity rule.

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CALCULATION OF THE TRANSPORT COEFFICIENTS IN MULTICOMPONENT GAS MIXTURES

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An approximate method is discussed for calculating the transport coefficients in multicomponent gas mixtures.

It is well known that the numerical integration of the equations of gasdynamics for multicomponent mixture with transport coefficients calculated rigorously using kinetic theory is beset with serious difficulties. This is because 1) the mass diffusion flux of the i-th component and the heat flux depend on the fluxes of all the other components and their gradients; 2) for an N-component mixture it is necessary to compute the set of Ω_{ij} integrals, where i, j = 1, ..., N; 3) in order to calculate the transport coefficients ratios of determinants of orders N and N + 1 are required. Hence with increase in the number of components, the number of computational operations and the memory required progressively increase.

These difficulties have stimulated the development of various approximate methods of calculating transport coefficients. A widely used approximate relation for the thermal conductivity and viscosity is based on the fact that the nondiagonal elements in the determinants are much smaller than the diagonal elements, and thus perturbation theory can be used. It should be noted that satisfactory results from first- and second-order perturbation theory can be achieved only by introducing an additional empirical parameter fitted to experimental data [1].

In the simplest method of calculating the mass-exchange coefficients, the diffusion coefficients are set equal to each other and the coefficient of thermal diffusion is ignored even where this leads to serious error.

The bifurcation method [2, 3] is used widely in engineering calculations. The use of different diffusion coefficients for the different components leads to only a slight complication of the algebra and a somewhat increased execution time for the calculations. The main advantage of this method is that the resulting expression for the mass diffusion flux of the i-th component involves only variables and their gradients characterizing the system as a whole and the i-th component, but not any of the other components. In addition, in the calculation of the mass diffusion flux, it is sufficient to use only N quantities dependent on the molecular properties of the components. The error in the coefficients can be as large as 10% for the systems studied in [2].

In the approximation method used in [4], the mass diffusion flux of the i-th component is directly proportional to the concentration gradient of the i-th component only. In [4], approximate expressions were given for the constants of proportionality between these quantities (the effective diffusion coefficients) and it was shown that in several cases involv-

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