[CONTRIBUTION FROM THE THERMODYNAMICS RESEARCH LABORATORY AND THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Interaction Coefficients of Gas Mixtures[1]

BY ROBERT A. GORSKI AND JOHN G. MILLER

RECEIVED JULY 3, 1952

The method of Edwards and Roseveare has been used to study the interaction coefficients of the following gaseous mixtures at 30°: CO_2–N_2, O_2–N_2, CO_2–O_2. An apparatus of improved design is described for making the measurements. The results give proof that the method is satisfactory for evaluation of the quantity $[2B_{12} - (B_{11} + B_{22})]$, where B_{12} is the interaction coefficient and B_{11} and B_{22} are the individual second virial coefficients of the constituents of the mixture. Values of the interaction coefficients determined in this way for the CO_2–N_2 and O_2–N_2 systems agree satisfactorily with theoretical values based on simple combination rules for the force constants involved. The CO_2–O_2 results show a disagreement with the theoretical values which may be due to these combination rules.

Introduction

The second virial coefficient $B(T)$ of a gas or gas mixture is defined by the equation of state

$$pV = RT + B(T)p + C(T)p^2 + \ldots \qquad (1)$$

which is known to be valid at reasonably high temperature or low pressure. From sufficiently accurate and extensive information regarding $B(T)$ can be drawn important conclusions regarding the average (over all possible mutual orientations of molecules considered in pairs) force potential $\epsilon(r,T)$ appearing in the statistical mechanical expression

$$B(T) = 2\pi N \int_0^\infty r^2\,[1 - \exp(-\epsilon/kT)]\,dr \qquad (2)$$

where r denotes the distance of separation between members of a pair. From information regarding $\epsilon(r,T)$ can in turn be inferred reliable values of viscosity and, to some extent, of other transport properties.[2]

For a gas mixture, the second virial coefficient is given in terms of those of its constituent gases, $B_{ii}(T)$, and of certain associated *interaction coefficients*, $B_{ij}(T) = B_{ji}(T)$, where $i \neq j$, by the expression[3]

$$B = \sum_{ij} x_i x_j B_{ij} \qquad (3)$$

where the x_i and x_j are the mole fractions of the various constituents in the mixture. Despite the fact that in most practical applications a knowledge of the thermodynamic and other properties of gas mixtures rather than pure gases is required as a basis for making reliable predictions, relatively little effort has so far been directed toward the determination of the above interaction coefficients.

Edwards and Roseveare[4] have published a novel method for determining the interaction coefficients of gas mixtures. In this method, two pure gases are mixed at constant temperature, the total volume being altered by just the right amount to keep the pressure constant also. Let ΔV denote the change in total volume *per mole of mixture;* then, according to the theory of the method, which assumes the second virial coefficients of the individual constituents known and neglects possible contributions from virial and interaction coefficients of higher order than the second, the interaction coefficient B_{12} can be computed from

$$2B_{12} = (\Delta V/x_1x_2) + B_{11} + B_{22} \qquad (4)$$

According to equation (4) a relative error σ in the measurement of ΔV contributes a relative error $\sigma[1 - (B_{11} + B_{22})/2B_{12}]$ to the determination of B_{12}. Except at temperatures where $2B_{12}$ is small compared with $(B_{11} + B_{22})$, the two errors are of the same order of magnitude. In general, therefore, the Edwards–Roseveare method avoids the requirements of high precision in density measurements inherent in other methods for the determination of interaction coefficients. This appears to be its most important practical advantage.

Recently, Lunbeck and Boerboom[5] have made the first report of data obtained by this method since the original work of Edwards and Roseveare. They reported the results of an unpublished investigation by A. Michels and A. J. H. Boerboom for several gas mixtures. Those results are in fair agreement with theoretical values obtained from reasonable values of the force constants of the gases mixed.

The present paper describes an improved apparatus for use with this method and gives the results obtained by it for three different mixtures.

Experimental

The plan of the main body of the apparatus is shown in Fig. 1. Flasks A and B were approximately five liters each, and flasks C and D, the reference pressure flasks, were approximately one liter each. The principal valves, G and H, separating the large flasks, were magnetically-operated, constant-volume, mercury-in-glass valves and were equipped with capillary side arms to facilitate cleaning and to permit use of a fixed amount of mercury in them.

Stopcocks S_1, S_2, S_3 and S_4 were mercury-seal Corning 9307 stopcocks, lubricated by Apiezon N grease. The seating bulbs were kept at 15 to 20 mm. below the pressure in the flasks. Capillary tubing was used wherever needed to minimize dead-space.

In addition to the increased volume of the flasks, another important improvement over the original design of Edwards and Roseveare was the use of a capacitance gage to judge the pressure balance between flask A and the reference chamber D. A thin Dural diaphragm separated these containers and acted as one plate of a condenser K, the fixed plate being held above it by the stretching frame which held the diaphragm taut. Any slight displacement of the diaphragm due to a slight unbalance of pressure caused a change in the capacitance of this condenser. This capacitance change was detected by tapping the condenser into

---

[1] Based on a dissertation submitted in August, 1951, by R. A. Gorski in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania.

[2] J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *Trans. Am. Soc. Mech. Engrs.*, **71**, 921 (1949).

[3] J. E. Lennard-Jones and W. R. Cook, *Proc. Roy. Soc.* (*London*), **115A**, 334 (1927).

[4] A. E. Edwards and W. E. Roseveare, THIS JOURNAL, **64**, 2816 (1942).

[5] R. J. Lunbeck and A. J. H. Boerboom, *Physica*, **17**, 76 (1951).

the electron-coupled oscillator of a Philco Type BC-221-N frequency meter. The meter was thermostated to ensure constant frequency of its crystal oscillator and was provided with a constant power source. The beat note caused by a capacitance change in K was detected by either earphones or an oscilloscope. By this means, pressure differences as small as 0.0001 mm. of mercury were detected but due to the limitations set by the temperature control of the gas volumes and the stability of the capacitance measuring circuit the reproducibility of the pressure balance over the time required for the measurements of ΔV was limited to ±0.001 mm.

A second improvement was the compact mixing pump below flask B. This was a nickel cylinder carrying vanes at top and bottom and running in jewel bearings which were mounted in plates held by spring wire rings so that they remained firmly in place on the glass seats shown in the diagram. The field piece J used to energize the pump was housed in a metal box which carried a manifold jet to blow cooling gas on the piece and which was fitted with a light and mirror system to view the pump while the apparatus was submerged in the bath. This pump mixed the gases completely in two hours.

The apparatus was supported in a light-weight metal carriage to facilitate raising and lowering in the bath. The bath was controlled to 30.000 ± 0.002°. The microburet attached at F to measure the volume changes by the amount of mercury withdrawn from the bulb E had its own thermostating system which kept it at 30.00 ± 0.01°.

The procedure followed was similar to that used by Edwards and Roseveare. The apparatus was first evacuated completely with valves G and H closed. The flasks were next flushed twice, each with the gas to be used for its separate filling. The flasks were then filled simultaneously to the desired pressure which was indicated by a mercury manometer attached to flask C through cock S_3. This manometer could be read to 0.1 mm. After cocks S_1, S_2 and S_3 were then closed, precise pressure balance to within ±0.001 mm. was obtained by varying the volume of the system by the mercury microburet. Cock S_4 was then closed, valves G and H opened and the pump set to mixing the gases. After mixing was complete, the original pressure was restored in flasks A and B by withdrawing a measured volume of mercury (ΔV) into the microburet.

For each mixture studied check runs were carried out with the initial placements of the gases reversed. This was an improvement over the procedure of Edwards and Roseveare and gave a means of detecting possible effects of adsorption and desorption of the gases on the glass and metal surfaces during mixing. No such effects were detected by this interchange of the fillings.

The nitrogen contained approximately 0.3% oxygen as its principal impurity. The carbon dioxide was 99.5% pure, the impurities being air and moisture. The oxygen was 99.7% pure, the contamination being due principally to nitrogen and argon.

Results and Discussion

The experimental results for the three gas mixtures are shown in Table I. The ΔV values are the measured volume changes used to compute the values of $\Delta V/x_1x_2$ per mole of mixture as listed in the last column. The numbers of moles were calculated from the pressures and the volumes of the flasks by use of equation (1) and the appropriate values of the second virial coefficients.

Principally because of the lack of data for interaction coefficients in the literature, the following scheme was used to test the method in the form of equation (4) for the computation of interaction coefficients. The 30° values of B_{11} and B_{22} were calculated according to equation (2) by use of the ϵ_m/k, r_0 and $F(\epsilon_m/kT)$ values of Hirschfelder, Bird and Spotz.[2] The values of B_{12} detd. listed in Table II were then determined by equation (4) from the average values of $\Delta V/x_1x_2$ and these calculated second virial coefficients for the pure components.

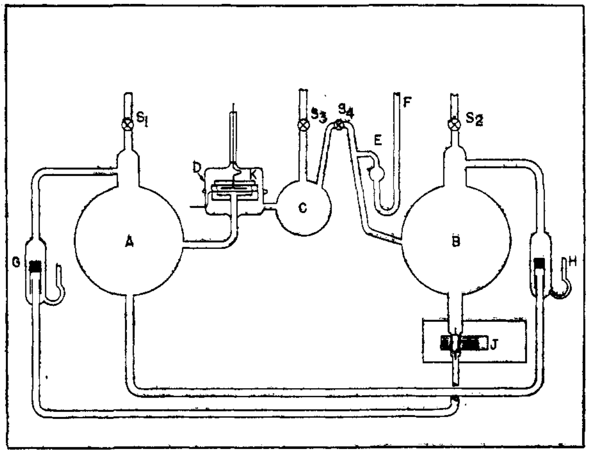

Fig. 1.—The plan of the improved Edwards and Roseveare apparatus.

The success of the method was then judged by comparison of these results with the values of B_{12} calculated by equation (2) from the same ϵ_m and r_0 values as used for the pure gases by averaging the first of these constants geometrically and the second arithmetically for the mixtures. These B_{12} values are shown in Table II as B_{12} calcd. The virial and interaction coefficients are all given in cc. per mole. The errors shown for the values of B_{12} detd. are the errors contributed only by the deviations of the individual measurements of $\Delta V/x_1x_2$ from their mean.

TABLE I

THE VOLUME INCREASE IN THE MIXING OF THE GASES AT CONSTANT PRESSURE AND TEMPERATURE (30°)

Moles[a] Gas 1	Moles[a] Gas 2	Pressure, atm.	ΔV, cc.	$\Delta V/x_1x_2$, cc. mole^{-1}
		$CO_2(1)-N_2(2)$		
0.2198	0.2221	0.9953	4.930	44.63
.2198	.2221	.9949	4.826	43.69
.2198	.2221	.9952	4.852	43.92
.2234	.2188	.9959	4.871	44.07
.1611	.1581	.7193	3.470	43.49
.1734	.1754	.7861	3.771	43.25
		$CO_2(1)-O_2(2)$		
0.2233	0.2190	0.9957	6.043	54.65
.2230	.2187	.9945	5.829	52.79
.2230	.2187	.9943	5.959	53.97
.2197	.2221	.9946	5.976	54.11
.1727	.1748	.7830	4.671	53.77
.1621	.1641	.7347	4.344	53.27
		$N_2(1)-O_2(2)$		
0.2222	0.2189	0.9955	0.000	0.00
.2222	.2189	.9955	.129	1.17
.2188	.2223	.9955	.043	0.39
.2187	.2223	.9953	.153	1.39
.2187	.2223	.9953	.128	1.16

[a] Flask A, 5467 cc., flask B, 5551.5 cc.

The agreement between the B_{12} detd. and B_{12} calcd. values for both the CO_2–N_2 and O_2–N_2 mixtures appears to be satisfactory in view of the uncertainty of the ϵ_m and r_0 values and of the combination rules used in obtaining B_{12} calcd. The ΔV values are all positive and the results for the

TABLE II

THE INTERACTION COEFFICIENTS OF THE GAS MIXTURES AT 30°

Mixture	ϵ_0/k, °K.	r_0, Å.	B_{11}	B_{22}	B_{12} Calcd.	B_{12} Detd.
CO_2–N_2	185, 95.9	4.57, 3.72	−120.7	− 4.34	−39.1	−40.6 ± 0.2
CO_2–O_2	185, 117.5	4.57, 3.58	−120.7	−15.96	−49.9	−41.5 ± .2
O_2–N_2	117.5, 95.9	3.58, 3.72	−15.96	− 4.34	−10.1	− 9.7 ± .3

N_2–O_2 system show definitely that the interaction coefficient even for this pair is not the arithmetic mean of the virial coefficients for the separate constituents.

The Table I values for the CO_2–O_2 mixtures are in good agreement among themselves, showing no large effects of interchange of the placements of the gases in the apparatus. The large discrepancy between the two B_{12} values shown in Table II for this mixture is difficult to explain. It does not appear to be caused by experimental error or by error in the theory of Edwards and Roseveare.[6] The molar value of $\Delta V/x_1x_2$ corresponding to B_{12} calcd. would be only 36.61 cc.

Efforts to get better agreement between B_{12} calcd. and B_{12} detd. for the CO_2–O_2 system by a different choice of the force constants failed. Values chosen from viscosity data[2] and use of the 0–200° values given by MacCormack and Schneider[7] for carbon dioxide gave no improvement. It is possible that the cause of the difficulty is the set of combination rules used to obtain the parameters for the computation of B_{12} calcd.

Edwards and Roseveare are the only other workers who have determined B_{12} for the CO_2–O_2 system. Using their $\Delta V/x_1x_2$ value measured at 25° and the force constants of Table II, we obtain a B_{12} detd. value of −58.3 cc. mole^{-1}, while B_{12} calcd. comes to −52.1 cc. mole^{-1} at this temperature. Their high value of B_{12} detd. may be due to experimental error. The comparisons made by Lunbeck and Boerboom[5] indicate that the ΔV values obtained by Edwards and Roseveare in their pioneering work are generally too low.

Acknowledgment.—It is a pleasure to acknowledge the aid of the Bureau of Ships and the Office of Naval Research, both of the Navy Department, who have sponsored this work. The assistance of Dr. J. A. Goff, C. Nocka, S. Voltz and V. Folen in the preliminary stages of this study is also gratefully acknowledged.

---

[6] A novel test of the method was made for the CO_2–O_2 system by mixing one of the pure gases with a prepared mixture of both. This was done by flushing the whole apparatus with one of the gases and filling with this gas to a pressure of one-half atmosphere. The second of the two gases was then added to flask A while at the same time the first gas was used to complete the filling of flask B until the pressure balance was obtained at one atmosphere. The approximately equimolecular mixture of the two gases in flask A was then mixed with the pure gas in flask B, the resultant volume change, ΔV, being measured in the usual manner. For this case it can be shown, with the same assumptions as made in the derivation of equation (4), for the mixing of pure gases, that

$$\Delta V = (n_1 + n_2' + n_2)^{-1}\,[n_1^2B_{11} + 2n_1(n_2' + n_2)B_{12} + (n_2' + n_2)^2B_{22}] - n_2B_{22} - (n_1 + n'_2)^{-1}[n_1^2B_{11} + 2n_1n_2'B_{12} + n_2'^2B_{22}]$$

where n_1 is the number of moles of gas 1 in flask A, while n_2' and n_2 are the numbers of moles of gas 2 in flask A and flask B, respectively, before the mixing which produces the measured volume change at constant temperature and pressure. Two experiments of this type were carried out at 30°. In the one, pure oxygen was mixed with a mixture of oxygen and carbon dioxide; in the other, pure carbon dioxide was mixed with the mixture. The values of B_{12} determined for the CO_2–O_2 system in this way, using the same B_{11} values as given in Table II, were −41.9 and −41.6 cc. per mole, respectively.

[7] K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.*, **19**, 849 (1951).

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Solutions of Halogens in Highly Acidic, Polar Solvents[1]

BY ROBERT E. BUCKLES AND JACK F. MILLS

RECEIVED AUGUST 4, 1952

A study of the absorption spectra of iodine, iodine chloride and bromine in various solvents showed that in the highly acidic, polar solvents, trifluoroacetic acid and sulfuric acid, the halogens behaved spectrophotometrically very much as they did in relatively non-polar solvents, *e.g.*, carbon tetrachloride or ethylene chloride, where little if any complexing is expected to take place. On the other hand a comparison of the halogens in these very acidic solvents with solutions in anhydrous acetic acid, a typical complexing solvent for halogens, showed much wider spectrophotometric differences. Estimation of equilibrium constants for the complexing of iodine and iodine chloride with acetic acid and with trifluoroacetic acid also showed that the latter highly acidic solvent has considerably less tendency to complex than does the former less acidic solvent.

Recent studies[2] of the 1:1 complexes formed between halogens and aromatic compounds or compounds containing oxygen, nitrogen or iodine have led to the opinion that the halogen molecule acts as a generalized acid or acceptor of the available electrons of the generalized base with which it complexes. This view of the colors observed in such solvents as compared with those observed in relatively non-complexing solvents has been preferred to alternative explanations[3] involving polarization of the halogen molecules by the solvent mole-

---

[1] Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1952. Abstracted from the Ph.D. thesis of Jack F. Mills.

[2] (a) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948); (b) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949); (c) R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952); (d) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677, 5170 (1950); **73**, 462 (1951); **74**, 458, 1891 (1952); (e) T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950).

[3] (a) S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952); (b) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).