

crystals are white with a slight tint of blue. Direct analysis of the crystals was not successful since but a small amount was available. The crystals were very small and were contaminated always with the mother liquor of highly concentrated sulfur trioxide. They are very soluble in ether-alcohol or water solutions.

In Table II a comparison of the most probable calculated value with the theoretical value of the composition is shown.

Gerland³ identified an anhydrous normal vanadyl sulfate which he prepared by boiling the soluble hydrated sulfates in concentrated sulfuric acid. His resulting gray compound is very insoluble even in boiling water. While Gerland's insoluble compound was encountered in the course of this work, as previously mentioned, our anhydrous sulfate is quite soluble in water and dilute acid as well as in alcohol.

Summary

Solubility measurements are given for the ternary system $\text{VO}_2\text{-SO}_3\text{-H}_2\text{O}$ at 30° and an isothermal ternary diagram has been constructed.

Over the total range of solubilities these five compounds only, $\text{VO}_2\cdot\text{H}_2\text{O}$, $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$, $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$, $2\text{VO}_2\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$, and VO_2SO_3 , were found to exist as stable solid phases at equilibrium with the various solutions.

For purposes of inoculation, attempts were made to prepare other compounds prepared previously by methods described in the literature in order to establish equilibrium relationships for the other reported hydrates. But no evidence was found for their existence.

A soluble form of the anhydrous normal vanadyl sulfate found in our study has not previously been reported.

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[CONTRIBUTION OF THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Second Virial Coefficients of Gaseous Mixtures¹

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Introduction.—Accurate p - V - T data at low pressures are few for pure gases and are almost non-existent for gaseous mixtures. This paper reports on the theory and experimental techniques of an indirect method of determining the second virial coefficients of gaseous mixtures. The method consists of measuring the change in volume on mixing two different gases at constant temperature and pressure and does not require determinations of absolute densities of gaseous mixtures.

Theoretical.—In this paper the virial equation of state is used in the form³

$$PV = RT + BP + CP^2 + DP^3 + \dots \quad (1)$$

where $B, C, D \dots$ are the second, third, fourth . . . virial coefficients. Pressures are expressed in mm. of mercury and volumes are expressed either in cc. or in Amagat units. The Amagat unit is considered to be 2.24×10^4 cc. for all gases used.

If two different gases are mixed at constant temperature and pressure, there is usually a change

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(3) For a discussion of the various forms of the virial equation of state, see Hirschfelder, Ewell and Roebuck, *J. Chem. Phys.*, **6**, 205 (1938).

in total volume. The magnitude of this volume change depends upon the intermolecular forces between the molecular species making up the mixture and may be interpreted in terms of the virial coefficients of the pure gases and of the gaseous mixture in the following manner.

If n_1 moles of gas 1 and n_2 moles of gas 2, occupying volumes v_1 and v_2 , respectively, are mixed at constant pressure P and constant temperature T and if we neglect the effect of virial coefficients higher than the second,⁴ we may write

$$P(v_1/n_1) = RT + B_1P \quad (2)$$

$$P(v_2/n_2) = RT + B_2P \quad (3)$$

$$P(v_m(n_1 + n_2)) = RT + B_mP \quad (4)$$

where v_m is the volume occupied by the mixture and B_m is the second virial coefficient of the mixture. By combining these equations, we have for the volume change on mixing at constant temperature and pressure

$$\Delta v = v_m - (v_1 + v_2) = (n_1 + n_2)B_m - n_1B_1 - n_2B_2 \quad (5)$$

or in terms of the mole fractions in the mixture

$$\Delta v/n = B_m - N_1B_1 - N_2B_2 \quad (6)$$

(4) The contribution of virial coefficients higher than the second is very small at low pressures. It will be shown that no significant error is introduced in this work by neglecting these terms.

where n denotes the total number of moles of gas. By combining this equation with that derived by Lennard-Jones and Cook⁵ for molecules having symmetrical fields, *i. e.*

$$B_m = N_1^2 B_1 + 2N_1 N_2 B_{12} + N_2^2 B_2 \quad (7)$$

we have

$$\Delta v/nN_1N_2 = 2B_{12} - (B_1 + B_2) \quad (8)$$

where B_{12} may be interpreted as the second virial coefficient representing only the interaction between the unlike molecules in the mixture.

Therefore, if known volumes of two gases are mixed at constant temperature and pressure and the resulting volume change measured, the value of B_{12} may be calculated providing the second virial coefficients of the pure gases are known.

Experimental.—The apparatus is shown in Fig. 1. The gases were first contained in the Pyrex bulbs A and B, each bulb having a capacity of approximately 3 liters. Bulb C, which was used to maintain gas at a constant reference pressure, had a volume of approximately one liter. Bulbs A and B were separated by magnetically operated mercury sealed glass valves V_1 and V_2 and by the diaphragm gage G. The gage consisted of a thin Pyrex diaphragm on which was mounted a small mirror M_1 . Minute movement of the diaphragm could be detected by means of the optical lever, shown in Fig. 1, used in conjunction with a reference mirror M_2 , the position of which was fixed with respect to the equilibrium position of M_1 , a straight filament lamp L and a scale. The diaphragm gage used in this work would withstand pressure differentials of 10 cm. in either direction without rupture. Since the gage was used only as a null indicator it was unnecessary to calibrate it in terms of pressure differential.

Stopcocks S_1 and S_2 were similar in design to those described by Roper⁶ and were lubricated with sirupy phosphoric acid. The consistency of the lubricant made it advantageous to maintain a pressure of 200 mm. of nitrogen in the space within the stopcock below the plug rather than to evacuate this space completely. The other stopcocks were of the ordinary type and were lubricated by stopcock grease. This made it necessary to fill bulbs B and C only with those gases which were not affected by stopcock grease and to interpose a 20-cm. length of 1-mm. capillary tubing between bulb B and stopcock S_3 in order to prevent diffusion of the gas mixture to the stopcock.

After evacuation, bulbs B and C were filled with one gas simultaneously with the filling of bulb A with the other gas. The pressures were balanced to within 0.01 mm. by means of the gage, and stopcocks S_3 and S_6 were closed, thus isolating the gas in bulb C. The valves V_1 and V_2 were opened and the contents of A and B mixed by the all glass pump P. This pump was a modification of that described by Funnell and Hoover⁷ and circulated an estimated 2 to 4 liters per hour. After thorough mixing of the two gases the pressure was returned to the original value (the pressure in bulb C

being used as a reference) by adding or removing mercury by means of the calibrated buret Bu. The volume change could then be determined from the initial and final mercury levels in the buret.

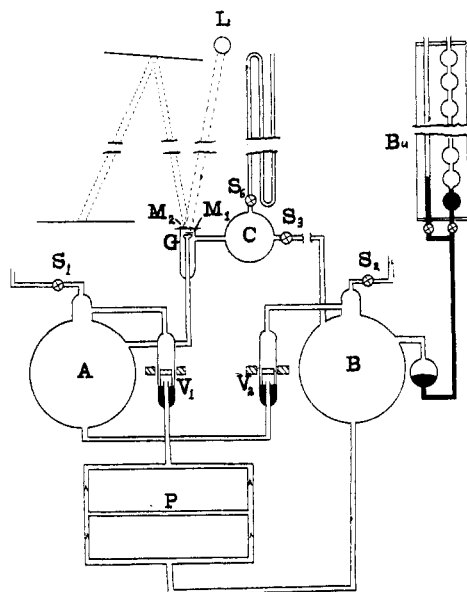


Fig. 1.

The apparatus, except for the buret and the manometer was held on a frame of brass and transite in a water thermostat which was maintained at $25 \pm 0.01^\circ$ throughout all experiments. The buret was held at $25 \pm 0.1^\circ$ by pumping thermostated water through the outer tube. The apparatus was arranged in such a manner that all stopcocks and valves could be operated from outside the thermostat.

Materials.—The hydrogen, oxygen and nitrogen used were 99.7% pure, the carbon dioxide was 99.5% pure and the helium and ethylene had a minimum purity of 99%. Further purification of the gases used in a number of runs had no observable effect upon the experimental results. Care was taken in all runs to sweep out all inlet tubes thoroughly and the bulbs were flushed several times before each run with the gases with which they were to be filled.

Experimental Results.—The data obtained for nine pairs of gases are given in Table I. Two runs were made at 760 mm. and two at 380 mm. for each pair of gases. The absolute error in the values of Δv is constant throughout the data. The percentage error in values of the function $2B_{12} - (B_1 + B_2)$, which are calculated by use of the relationship derived above, vary inversely with the magnitude of the function. It is estimated to be not more than 2% in the case of the H_2 - C_2H_4 mixture but may be as much as 12 to 15% at most, *i. e.*, for the CO_2 - C_2H_4 mixture.

It will be noted that values obtained for the function $2B_{12} - (B_1 + B_2)$ at 760 and 380 mm. are the same within the limits of the experimental error. Hence, omission of the virial coefficients

(5) Lennard-Jones and Cook, *Proc. Roy. Soc. (London)*, **115A**, 334 (1927).

(6) Roper, *J. Phys. Chem.*, **44**, 836 (1940).

(7) Funnell and Hoover, *ibid.*, **31**, 1099 (1927).

TABLE I

Temperature = $25 \pm 0.01^\circ$; mole fraction of gas A = 0.5187; mole fraction of gas B = 0.4183; total volume = 6595 cc.

Gas A	Gas B	Pressure, mm.	Volume change, cc.	$[2B_{12} - (B_1 + B_2)]10^4$	
				Exp.	Average
H ₂	N ₂	760	1.21	8.07	
		760	1.23	8.15	
		380	0.60	7.96	
		380	0.59	7.82	8.02
H ₂	CO ₂	760	2.11	13.99	
		760	2.16	14.32	
		380	1.05	13.92	
		380	1.06	14.05	14.07
N ₂	CO ₂	760	1.83	12.13	
		760	1.85	12.27	
		380	0.91	12.07	
		380	0.93	12.33	12.20
O ₂	CO ₂	760	1.69	11.20	
		760	0.82	11.34	
		380	0.82	10.87	
		380	0.87	11.54	11.12
H ₂	C ₂ H ₄	760	2.95	19.62	
		760	2.92	19.36	
		380	1.50	18.89	
		380	1.46	19.23	19.53
CO ₂	C ₂ H ₄	760	0.49	3.25	
		760	0.50	3.32	
		380	0.22	2.92	
		380	0.26	3.45	3.24
N ₂	C ₂ H ₄	760	2.40	15.91	
		760	2.37	15.71	
		380	1.14	15.12	
		380	1.20	15.91	15.66
He	N ₂	760	1.23	8.15	
		760	1.18	7.82	
		380	0.58	7.69	
		380	0.61	8.09	7.94
He	CO ₂	760	2.10	13.92	
		760	2.12	14.06	
		380	1.06	14.06	
		380	1.05	13.92	13.99

higher than the second appears to be justified in work of this accuracy at pressures near one atmosphere.

Discussion.—For a number of gases, p - V - T data have been expressed in terms of the virial equation of state, the range of pressures covered being determined by the number of virial coefficients used. Such equations, calculated by Newitt⁸ from the data of Holborn and collaborators,^{9,10,11} over a pressure range 0–200 atm. yield for the second virial coefficient of hydrogen 6.60 ×

10^{-4} ; of nitrogen -2.0×10^{-4} ; and of helium 5.26×10^{-4} . These values are considered to be the best available for these gases at the present time.

If we consider the virial equation

$$PV = RT + BP \quad (9)$$

or, rearranged

$$B = (PV - RT)/P \quad (10)$$

the value of B as expressed by this equation may be termed the *apparent* second virial coefficient and it must approach the true second virial coefficient as the pressure approaches zero. Hence if values of B apparent are plotted against pressure the intercept of the extrapolated curve and the axis $P = 0$ will be the true second virial coefficient. This procedure has been followed for carbon dioxide, oxygen and ethylene, using the data of Masson and Dolley¹² and Michels¹³ for carbon dioxide. The best curves through these data yield for the second virial coefficient of oxygen -9.2×10^{-4} ; of ethylene -62.5×10^{-4} ; and of carbon dioxide -52.5×10^{-4} . Roper's data¹⁴ give B for ethylene as -65.9×10^{-4} which agrees with the above value within Roper's maximum experimental error. Schafer's data¹⁵ give B for carbon dioxide as -56×10^{-4} by extrapolating B from data at 0 to -70° .

These values of the second virial coefficients of the pure gases and the values of B_{12} calculated by substitution of them into the function $2B_{12} - (B_1 + B_2)$ are collected in Table II.

TABLE II

SECOND VIRIAL COEFFICIENT OF GASES AND OF GASEOUS MIXTURES AT 25°

Gas	$B \times 10^4$ (Amagat units)	Gas mixture	$B_{12} \times 10^4$ (Amagat units)
H ₂	6.60	H ₂ -N ₂	6.31
N ₂	- 2.0	H ₂ -CO ₂	-14.7
He	5.26	N ₂ -CO ₂	-21.2
O ₂	- 9.2	O ₂ -CO ₂	-25.2
CO ₂	-52.5	H ₂ -C ₂ H ₄	-17.7
C ₂ H ₄	-62.5	N ₂ -C ₂ H ₄	-24.4
		CO ₂ -C ₂ H ₄	-55.9
		He-N ₂	5.60
		He-CO ₂	-16.1

The values of B_m for mixtures of various compositions have been calculated for each of the nine pairs of gases by substituting the values of B and B_{12} from Table II into the equation of Len-

(8) Newitt, "High Pressure Plant and Fluids at High Pressures," Chapter VIII, Oxford University Press, New York, N. Y., 1940.

(9) Holborn, *Ann. Physik*, **63**, 674 (1920).

(10) Holborn and Schultze, *ibid.*, **47**, 1089 (1915).

(11) Holborn and Otto, *Z. Physik*, **10**, 367 (1922).

(12) Masson and Dolley, *Proc. Roy. Soc. (London)*, **103A**, 524 (1923).

(13) Michels and Michels, *ibid.*, **153A**, 201 (1936).

(14) Roper, *J. Phys. Chem.*, **44**, 835 (1940).

(15) Schafer, *Z. physik. Chem.*, **B26**, 93 (1937).

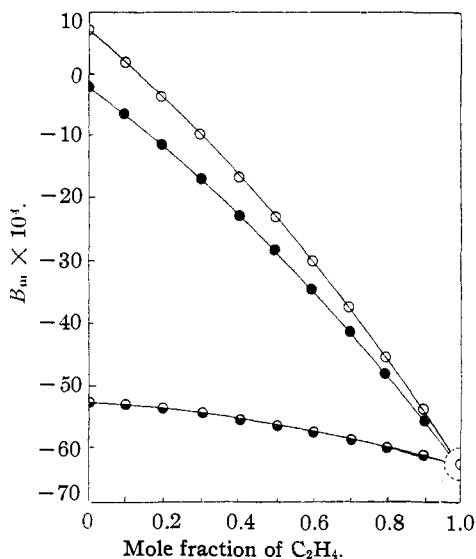


Fig. 2.—Second virial coefficients of mixtures: O, $\text{H}_2\text{-C}_2\text{H}_4$; ●, $\text{N}_2\text{-C}_2\text{H}_4$; ◐, $\text{CO}_2\text{-C}_2\text{H}_4$.

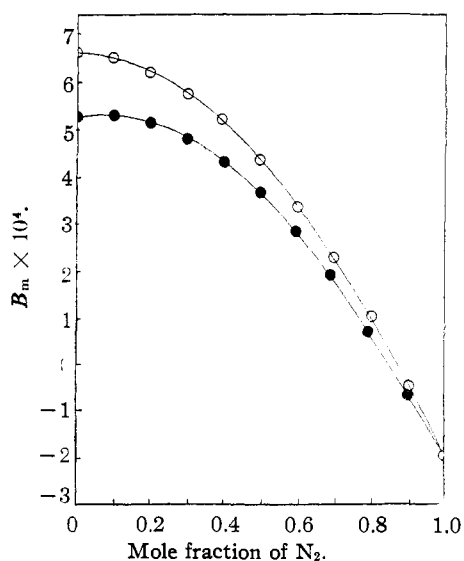


Fig. 3.—Second virial coefficient of mixtures: O, $\text{H}_2\text{-N}_2$; ●, He-N_2 .

nard-Jones and Cook. This equation, derived on

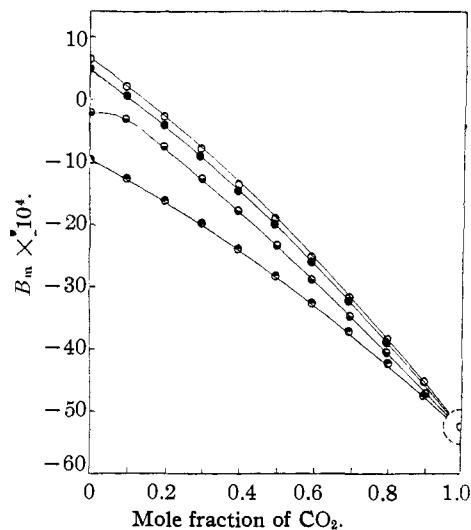


Fig. 4.—Second virial coefficients of mixtures: O, $\text{H}_2\text{-CO}_2$; ●, He-CO_2 ; ◐, $\text{N}_2\text{-CO}_2$; ◑, $\text{O}_2\text{-CO}_2$.

the assumption of symmetrical fields about the molecules, has been introduced into the derivations above and has been shown elsewhere¹⁶ to be valid in similar cases.

The values of B_m thus obtained have been plotted against mole fractions in Figs. 2, 3, and 4.

Summary

The theory and practice of a method for determining the second virial coefficients of gaseous mixtures has been described. The method gives data for mixtures corresponding in accuracy to those obtained by gas density measurements to approximately 0.002%.

Values for the second virial coefficients B_{12} for nine pairs of gases at 25° have been reported.

Values of B_m for each of the nine pairs of gases have been plotted as functions of the compositions of the mixtures.

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(16) Fowler and Guggenheim, "Statistical Thermodynamics," The Macmillan Co., New York, N. Y., 1939. p. 298.