

mixed isotherms shown in Fig. 7. There are thus no adjustable constants. These isotherms reproduce only the qualitative features of the experiments. The two sets of experimental points illustrate the degree of agreement. For a krypton coverage of 0.47 the agreement is satisfactory; disagreement increases with the krypton coverage until, at 3.76 layers the pressures are off by as much as 20%. Leaving w_{AB}/kT as an adjustable parameter merely improves the fit in one region at the expense of another. The values of w_{AB}/kT necessary for perfect fit, calculated from the experimental points and equation 12, fluctuate, but in addition show a definite increasing trend with the ratio of argon to krypton, both within a given isotherm and with the isotherms considered together. This is shown in Fig. 8 where the experimental values of w_{AB}/kT are plotted for the isotherms on 0.47 and 3.76 layers of krypton. No adjustment in the low coverage uncertainties of the function δ will remedy the lack of a constant w_{AB}/kT within the isotherm when applied to these data. In other words, the argon is too soluble in krypton-rich layers, and krypton is not soluble enough in argon-rich layers. A suitable refinement of the theory would abandon the assumption that the two components were randomly mixed. Arnold,⁸ in treating the adsorption of oxygen-nitrogen mixtures on anatase concluded that there was an enrichment of nitrogen on the stronger sites. The complications caused by such an improvement would be very great, because a local population function would have to be calculated by minimizing the free energy. Merely going on to the quasi-chemical approximation of Fowler and Guggenheim would neglect the effect

(8) J. R. Arnold, *J. Am. Chem. Soc.*, **71**, 104 (1949).

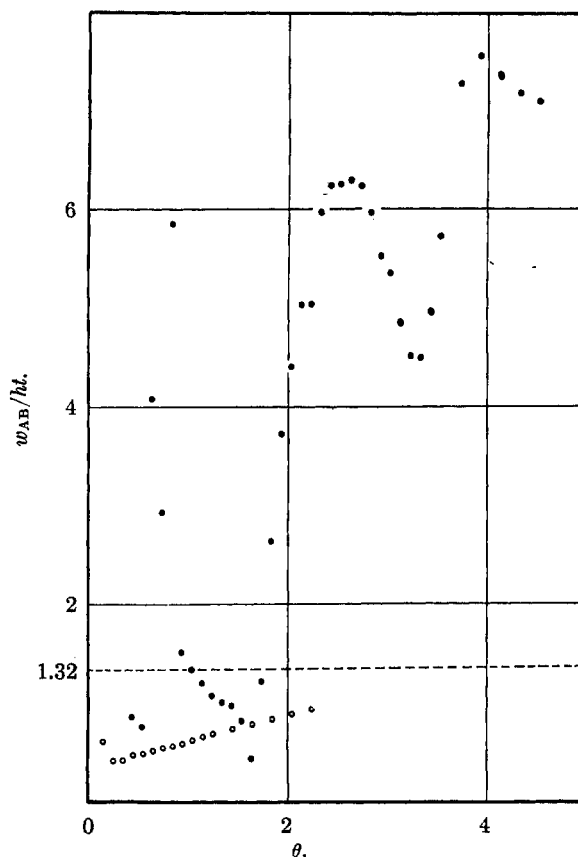


Fig. 8.—The variation of w_{AB}/kT , calculated from the isotherms in Fig. 3: ●, 0.47 layer; ○, 3.76 layers.

of the adsorption potential on local concentrations, and would therefore be of doubtful significance.

THERMODYNAMICS OF VAPOR-PHASE MIXTURES OF IODINE AND BENZENE, WITH APPLICATION TO THE RATE OF RECOMBINATION OF IODINE ATOMS*

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A study has been made of the pressure-temperature-volume relationships of vapor-phase mixtures of iodine and benzene, and the equilibrium constant for the association of iodine and benzene to form a complex $C_6H_6 \cdot I_2$ has been calculated for a range of temperatures. The magnitude of the equilibrium constant and the energy of association can be accounted for by van der Waals forces. The amount of the association is, however, sufficient to account for the high rate of dissociation of iodine molecules in the presence of benzene (as computed from the rate of association of iodine atoms and the equilibrium constant of the reaction $2I \rightleftharpoons I_2$). The entropy of association of benzene and iodine to form the complex has been explained in terms of a physical picture. Finally, the present results have been compared with those of Benesi and Hildebrand in liquid solution, and it is shown that the type of association found by them may be expected to be negligible in the vapor phase.

Studies of the recombination of iodine atoms in the presence of benzene vapor¹ indicate that the rate of this process is very rapid. This can be seen by considering the reverse process, namely, the dissociation of I_2 due to collisions with benzene, which

can be calculated from the rate of association of iodine atoms in the presence of benzene and the equilibrium constant for the reaction $I_2 \rightleftharpoons 2I$. From calculations of this sort, based on the results of Rabinowitch and Wood, one of us^{2a} estimated that the effective collision diameter σ_0 for an I_2 -

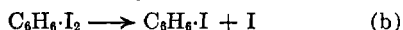
* Work supported by the Office of Naval Research.

(1) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 907 (1936); *J. Chem. Phys.*, **4**, 497 (1936); K. E. Russell and J. Simons, *Proc. Roy. Soc. (London)*, **A217**, 271 (1953).

(2) (a) O. K. Rice, *J. Chem. Phys.*, **9**, 253 (1941); (b) for effect of rotation of I_2 , see O. K. Rice, *ibid.*, **21**, 750 (1953).

benzene collision was about 28 Å. If the results of Russell and Simons were used the effective diameter would be about 20 Å. In making the calculation the effect of the rotation of the I_2 molecule on the probability of dissociation was neglected.^{2b} Correction for this would give values of σ_0 about half as great. The resulting values of 10 to 14 Å. are still high, though not far outside the range of reasonable possibilities with such large molecules. However, effective values of σ_0 for other inert gases suggest that the collision process is not too efficient, and comparison with these gases (even for CO_2 the value of σ_0 is only about half as great as for benzene) leaves little doubt that the recombination of iodine atoms in the presence of benzene is anomalously fast.

In order to explain these large rates it has been postulated that a $C_6H_6 \cdot I$ complex forms in the case of the association reaction and a $C_6H_6 \cdot I_2$ complex in the case of a dissociation reaction. As a matter of fact, if an explanation is to be obtained on this basis, it is necessary to suppose that both complexes are formed.^{2a} The dissociation reaction will proceed according to the mechanism



We let K_c be the equilibrium constant of (a), expressed in terms of concentration, and k_b be the rate constant for (b). The over-all rate of reaction will then be given by

$$-d[I_2]/dt = k_b[C_6H_6 \cdot I_2] = k_b K_c [C_6H_6][I_2] \quad (1)$$

and a large apparent collision diameter can be explained through a sufficiently large value for K_c .

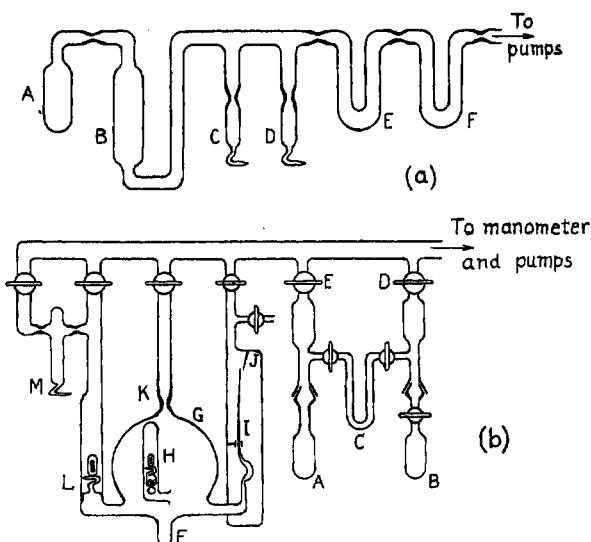


Fig. 1.—Schematic sketches of apparatus.

There are other reasons which might lead one to believe that there are some special forces which result in complexing of iodine and benzene, for example the work of Benesi and Hildebrand³ on solutions of iodine in liquid benzene, and theoretical considerations of Mulliken.⁴ It therefore appeared

(3) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **70**, 2832 (1948); **71**, 2703 (1949).

(4) R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952); *THIS JOURNAL*, **56**, 801 (1952).

desirable to investigate the pressure-volume-temperature relations of mixtures of iodine and benzene in the vapor phase. It may be said that these studies have resulted in the conclusion that there is no special type of complex, which is of importance in the vapor phase, all the complexing being adequately explained by van der Waals forces. It does turn out, however, that the effects are sufficient to account for the recombination experiments.

Experimental

Materials.—A known weight of A. R. grade iodine, which had previously been sublimed from potassium iodide, was introduced together with a small amount of potassium iodide into bulb A of the purification train shown in Fig. 1a. A was cooled in a Dry Ice-carbon tetrachloride mush and quickly sealed to the train. This train had been previously sealed to a vacuum system, and liquid air placed around trap F to prevent back diffusion of mercury to the train. The iodine was sublimed slowly from A to B, with a liquid air trap around E and a Dry Ice-acetone bath around B, pumping all the time. The iodine in B was then allowed to sublime at room temperature with continuous pumping for six hours, by which time it was thought that all bromine, occluded air and water would have been removed. The sample was sublimed into C which was pulled off to form a capsule with a breakseal. Any iodine remaining was condensed into D and the iodine content of D and E was determined by titration with sodium arsenite. Thus, the amount in the capsule could be fairly accurately estimated by difference. The total iodine content of the capsule was again determined at the end of the experiment by titration with sodium arsenite.

A. R. grade benzene, thiophene free, was fractionated at atmospheric pressure through an efficient column, rejecting the first and last fractions. About 20 ml. of the middle cut was introduced into trap A [Fig. 1b] and several trap to trap distillations were carried out, stopcock D being open when distilling into B, and stopcock E open when distilling in the reverse direction. The benzene vapor in all distillations was led through a phosphorus pentoxide trap, C, to remove moisture. The fraction of benzene used was distilled from B to F, a small appendix in the gas reservoir G, with the pump cut off by a stopcock. B was weighed before and after this final transfer. A vacuum technique was employed throughout.

Procedure.—The gas reservoir G [Fig. 1b] of approximately one liter capacity, was fitted with a side arm H. At the base of H a stout glass cross served to hold the iodine capsule and plunger. A soft glass spoon gage, I, was attached to the system through a graded seal, and the pressure inside the spoon balanced by the pressure of dry air admitted to the outer jacket, the pressure of the latter being measured in a manometer by means of a cathetometer. The spoon gage, which had been annealed together with the gas reservoir, was calibrated with pressure differences of 0–3 cm. over a total pressure range of 0–760 mm. and at temperatures up to 200°. It was always arranged that the total pressure in the spoon was greater than that in the jacket in the following determinations. Under this condition of operation the sensitivity of the gage remained sensibly unchanged, at 13.7 mm. per mm. movement of the pointer, throughout the whole pressure and temperature range to be investigated. A Pyrex reference pointer J was inserted in the jacket; both pointers could be focussed simultaneously by a traveling microscope, which was mounted so as to be free from vibration.

The thermostat, which consisted of a well insulated glass bath containing about five gallons of polyethylene glycol "600," was supported on a platform, and could be raised so that the gas reservoir and spoon gage were immersed to a level about two inches above K. Temperature control was maintained by sealed mercury regulators in conjunction with a thyatron circuit to better than $\pm 0.005^\circ$, and the temperature was measured using a platinum resistance thermometer (calibrated by the Bureau of Standards).

Before inserting the benzene, the iodine capsule and plunger were put into the side arm which was then sealed. The volume of G was measured roughly by a sharing method, using dry air from a calibrated volume of approximately one-liter capacity, the pressures being read on a constant volume

manometer. The required amount of benzene was then frozen into F and the reservoir sealed at K. After a series of measurements the contents of the reservoir G could be removed through the break-seal L and collected in the trap M.

The pressure of the known weight of benzene was measured as a function of temperature before the capsule containing the iodine was broken, and using values for the second virial coefficient, B , of benzene, calculated from an expression quoted by Guggenheim⁵

$$B = 68 - 13.2 \times 10^7 T^{-2} \text{ ml./mole} \quad (2)$$

values for the volume of the system were obtained. This equation was stated by Allen, Everett and Penney to be correct within about 40 ml./mole up to 360°K. We tested the equation by noting the consistency of the calculated volume from measurements at 10° intervals from about 350 to nearly 470°K. The values showed no trends over this range, and the probable error of the mean volume was of the order 0.01 to 0.02%. In the sharing method of measuring the volume the probable error was considerably larger, so the method based on eq. 2 was used. In every case the internal volume of the capsules was added to obtain the total volume in which the mixture of iodine and benzene was measured.

Vapor pressure values obtained for benzene were in good agreement with those of Baxendale, Enüstün and Stern⁶ and this was a good criterion of the purity of the sample.

After breaking the iodine capsule, the iodine was completely sublimed into F by heating gently with a blowtorch flame. In this manner the subsequent volatilization of the iodine and the attainment of equilibrium was enormously hastened.

At the end of each run the breakseal, L, was broken and the iodine condensed into M, which was removed, and the iodine titrated. In the first experiment quoted here two capsules were broken consecutively to give two samples (samples 1 and 2) with different amounts of iodine; the total amount of iodine was estimated by titration and compared with the sum of the original weighings; agreement was within 0.8 mg. In the last and most exhaustive run only one capsule was employed, and the estimates agreed within 0.4 mg.

Results

The pressure-temperature data for the three mixtures are given in Table I. All the pressures p of the mixture of benzene and I_2 have been corrected to mm. at 0°. At all temperatures, the benzene pressures p_1 which would obtain were no iodine present were calculated from the weight, and the volume found as indicated above, using eq. 2 for B . This effectively smooths the measurements of the benzene pressure made before the iodine capsule was broken.

An equation of state given by Gerry and Gillespie⁷ was used to calculate the iodine pressures which would exist if no benzene were present

$$p_2 = \frac{nRT}{V} + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{T^2} \right) \frac{n^2 RT}{V^2} \quad (3)$$

The following values were used (units atmospheres, liters, degrees Kelvin)

A_0	B_0	C_0	R	Mol. wt.	Ice-point
17.0	0.325	4.0×10^7	0.08206	253.864	273.13°K.

The data on which this equation was based extended to about 370°K. We made some measurements over the range 390 to 450°K. with only iodine present, and with the volume measured by the sharing method. The spread of the measurements

(5) E. A. Guggenheim, "Mixtures," Oxford Univ. Press, N. Y., 1952, p. 235. See P. W. Allen, D. H. Everett and M. F. Penney, *Proc. Roy. Soc. (London)*, **A212**, 149 (1952).

(6) J. H. Baxendale, B. V. Enüstün and J. Stern, *Phil. Trans. Roy. Soc.*, **A243**, 169 (1951).

(7) H. T. Gerry and L. J. Gillespie, *Phys. Rev.*, **40**, 269 (1932).

of the volume made in this way was about 3.5 ml. or a little over 0.3% in a volume of about 1100 ml. In addition, since the volume had to be sealed off with a capsule of iodine in it, some further corrections had to be made. However, using the iodine pressure measurements to find the volume from eq. 3, we obtained results as consistent as we did with benzene and agreeing with the volume measured by sharing to within the accuracy of the latter. It is to be further noted that the virial correction in eq. 3 is only about 0.6% of the total pressure. On the basis of all this evidence we believe that eq. 3 cannot be more than 0.1% in error.

TABLE I

CALCULATION OF K_p

Sample 1: 0.015085 mole benzene, 0.010956 mole iodine in 1161.11 ml.; sample 2: 0.015085 mole benzene, 0.016433 mole iodine in 1162.23 ml.; sample 3: 0.019918 mole benzene, 0.011653 mole iodine in 1164.19 ml.

Sample	T , °K.	No. of observations	p_1 , (C ₆ H ₆), mm.	p_2 , (I ₂), mm.	p , mm.	$-\Delta p$, mm.	$K_p \times 10^3$, atm. ⁻¹
1	427.27	2	343.31	249.84	589.36	3.79	4.00
1	427.74	2	343.70	250.12	589.99	3.83	4.02
1	435.96	2	350.43	255.01	601.71	3.73	3.80
1	445.18	2	357.97	260.51	614.90	3.58	3.54
1	466.59	1	375.47	273.24	645.45	3.26	3.02
2	437.43	2	351.26	382.27	728.01	5.52	3.74
2	445.50	2	357.86	389.52	741.86	5.52	3.62
2	466.55	2	375.04	408.38	778.56	4.86	3.01
3	429.62	6	452.94	266.15	713.82	5.27	3.94
3	439.05	4	463.12	272.11	730.15	5.08	3.68
3	439.13	4	463.20	272.16	730.17	5.19	3.74
3	439.27	4	463.35	272.25	730.48	5.12	3.70
3	445.50	4	470.08	276.18	741.09	5.17	3.63
3	446.73	4	471.41	276.96	743.19	5.18	3.62
3	447.36	4	472.09	277.35	744.30	5.14	3.58
3	465.06	8	491.21	288.52	774.83	4.90	3.21

Discussion of Errors

As may be seen from Table I, the temperature coefficient of the difference, $\Delta p = p - p_1 - p_2$ between the total measured pressure and the sum of the separate pressures of benzene and iodine, is quite small. It therefore becomes very necessary carefully to assess the errors which may arise in the individual measurements.

(1) Errors in total pressure measurement.

(a) **Manometry Errors.**—The manometer used to measure the pressure of the air surrounding the spoon gage was constructed of 26 mm. bore tubing and was viewed through a rigidly supported Gaertner cathetometer. Independent observations of a fixed line were made, and after each setting the telescope was raised through about 700 mm., lowered and reset. The maximum irreproducibility for ten such settings was ± 0.02 mm. Thus any individual pressure reading, involving two such settings, exhibits a maximum irreproducibility of ± 0.04 mm.

During the duration of a measurement the temperature of the manometer does not vary more than $\pm 0.1^\circ$ corresponding to an error of 0.02 mm. The traveling microscope used to follow the pointer of the spoon gage could be read reproducibly to 0.01

mm. and this incurred an error of ± 0.14 mm. in any single pressure measurement.

From these sources we obtain a total maximum manometry error of ± 0.20 mm.

(b) **Thermostat Fluctuations.**—The temperature control was to better than $\pm 0.005^\circ$ and the error in the pressure (sum of pressures of benzene and iodine) due to this fluctuation is 0.001% or less than 0.01 mm.

The maximum error in the total pressure will thus be 0.21 mm. However, in the last mixture several readings of the pressure were taken at each temperature, and the mean of these readings taken. It is felt that much more weight should be given to these values.

(2) **Errors in the Benzene and Iodine Pressures.**—These pressures were calculated for the stated temperature from the equations of state. Any errors in thermometry are to be referred to the total pressure. The errors in the benzene and iodine pressures arise from the other quantities which appear in the equations of state, and will be systematic for any given mixture. The errors may arise from the measured volume or the weight of the samples.

(a) **Weighing Errors.**—In the case of the iodine this error is estimated as ± 0.001 g. for the first two runs and ± 0.0004 g. for the last run, resulting in errors in the iodine pressure of about 0.11 and 0.05 mm., respectively. In the case of the benzene it is estimated as ± 0.0002 g., causing an error of 0.06 mm. in the pressure.

(b) **Volume Errors.**—Since the volume of the vessel was calculated from the equation of state of benzene using eq. 2, and since the pressure of benzene was then obtained by reversing the calculation, no inconsistencies can be introduced by the use of eq. 2 and the error in the pressure of benzene can be considered to be equal, percentagewise, to the probable error of the volume. The latter was about 0.025% for the first two mixtures and 0.010% for the last one; the resulting errors in the benzene pressure are about 0.10 mm. for the first mixture, about 0.10 mm. for the second mixture, and about 0.05 mm. for the last one.

Any error in the volume which is caused by inaccuracy in eq. 2 will be reflected in the pressure of iodine. According to Allen, Everett and Penney the error in B will be about 6%, which will cause about 0.06% error in the volume, and hence in the calculated iodine pressure, in the first two runs, and about 0.07% in the last one. Accepting 0.1% as the error in eq. 3, we believe then that the overall error in the iodine pressure will surely be less than 0.2%; which would amount to about 0.5 mm. in the first mixture, about 0.8 mm. in the second, and about 0.55 mm. in the last.

If all the errors were added (including 0.2% error in the iodine pressure) we could have a total error in Δp of about 0.98 mm. or 28% in the first mixture, of about 1.28 mm. or 25% in the second mixture and of about 0.92 mm. or 18% in the third mixture. The actual errors may, on the whole, be expected to be considerably smaller than these. Temperature coefficients may be expected to be reasonably accurate also, since the non-systematic part of these errors is small enough so that it should not too

greatly affect the results if a careful average is made.

We have made no correction for the local value of the acceleration due to gravity. This will affect all the pressures in the same way, and so the effect on Δp will be negligible.

Treatment of the Data

It was pointed out some time ago by Goodeve⁸ that, since the attractive forces between two molecules tend to make them move faster when in the neighborhood of each other, on this basis alone the attractive forces would only make the effective excluded volume larger, and so could not result in the lowering of the total pressure. Though it is not certain that Goodeve allowed sufficiently for collisions which would have been near misses were it not for the attractive forces, still the lowering of pressure by the attractive forces will occur largely because some of the pairs of molecules have less than enough mutual translational energy to escape from each other, and so form "complexes." This is true even if only the van der Waals type of force is operative. In the present case Δp is sufficiently small so that we may conjecture that only van der Waals forces are involved, but we may interpret Δp in terms of complex formation.⁹

The equation of state for n moles of gas may at sufficiently low pressures be approximated by

$$p = nRT/V + n^2RTB/V^2 \quad (4)$$

where B is the second virial coefficient. B contains contributions from pair formation and from the excluded volume. At pressures as low as one atmosphere we may take the excluded volume into account by subtracting it directly from V . We do this only in the large (first) term on the right-hand side of eq. 4, obtaining thus

$$p = nRT/(V - nb) + n^2RTB^0/V^2$$

where B^0 is that part of the virial coefficient arising from pair formation. Expanding the first term we obtain, to the second power of V^{-1}

$$p = nRT/V + n^2RT(B^0 + b)/V^2 \quad (5)$$

whence we see that

$$B^0 = B - b \quad (6)$$

In the case of a pure gas b will be given by

$$b = N(2\pi/3)\sigma^3 \quad (7)$$

where σ is the effective collision diameter (not, of course, the same as σ_0), and N is Avogadro's number. Hirschfelder, McClure and Weeks¹⁰ chose quite a large value for σ , which might be done to allow for the effect of the attractive forces noted by Goodeve, though their point of view was somewhat different. However, we do not believe that this effect will actually be very great, since the depth of the potential well with which we have to deal will, at its deepest point, be at most about double the radial mutual velocity component, and, of course, there is one point, the turning point of the collision, where this component of velocity is zero. We

(8) C. F. Goodeve, *Nature*, **140**, 424 (1937).

(9) See also A. Eucken and L. Meyer, *Z. physik. Chem.*, **53**, 452 (especially 465 f) (1929).

(10) J. O. Hirschfelder, F. T. McClure and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

shall therefore obtain b from viscosity data using the equation of Chapman¹¹

$$\sigma = 2.14 \times 10^{-10} M^{1/2} \eta_{273.1}^{-1/2} (1 + C/273.1)^{-1/2} \quad (8)$$

Here M is the molecular weight, C is Sutherland's constant, $\eta_{273.1}$ is the viscosity at 273.1°K. We then obtain from eq. 7 and 8, using data tabulated by Partington¹²

$$\sigma_{11} = 4.76 \times 10^{-8} \text{ cm. (benzene)} \quad (9a)$$

$$\sigma_{22} = 4.37 \times 10^{-8} \text{ cm. (iodine)} \quad (9b)$$

Equation 8 is based on the fairly crude model of attracting rigid spheres, but should be sufficient for our purposes.

We may apply eq. 4, 5 and 6 to mixtures of gases if we set

$$b = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad (10)$$

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \quad (11)$$

and

$$B^0 = x_1^2 B_{11}^0 + 2x_1 x_2 B_{12}^0 + x_2^2 B_{22}^0 \quad (12)$$

whence it follows that

$$B_{11}^0 = B_{11} - b_{11}; B_{12}^0 = B_{12} - b_{12}; B_{22}^0 = B_{22} - b_{22} \quad (13)$$

x_1 and x_2 are mole fractions of molecules of species 1 and species 2, respectively, while the subscripts on the b 's, B 's and B^0 's have a fairly obvious significance. We will have

$$b_{11} = N(2\pi/3)\sigma_{11}^3; b_{12} = N(2\pi/3)\sigma_{12}^3; b_{22} = N(2\pi/3)\sigma_{22}^3 \quad (14)$$

where, at least to a good approximation

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \quad (15)$$

The significance of eq. 10 can be seen from the following considerations. The total volume excluded by all other molecules for a molecule of species 1 is $2nx_1 b_{11} + 2nx_2 b_{12}$ and that for a molecule of species 2 is $2nx_2 b_{22} + 2nx_1 b_{12}$. In each case $2b$, with appropriate subscript, is the volume (per mole) of the exclusion sphere. The average excluded volume will therefore be

$$\frac{1}{2} [x_1(2nx_1 b_{11} + 2nx_2 b_{12}) + x_2(2nx_2 b_{22} + 2nx_1 b_{12})] = nx_1^2 b_{11} + 2nx_1 x_2 b_{12} + nx_2^2 b_{22}$$

the factor $1/2$ appearing as usual, because otherwise each exclusion sphere is counted twice, once for each molecule of a pair. It will be seen that this amounts to an average according to pairs, since the ratios of the numbers of pairs of different kinds are $x_1^2:2x_1 x_2:x_2^2$. The B^0 's should clearly be averaged in the same way. The usual equation,¹³ eq. 11, will then follow.

If species 2 were absent, the observed pressure of species 1 would be, from eq. 5

$$p_1 = nx_1 RT/V + n^2 x_2^2 RT(B_{11}^0 + b_{11})/V^2 \quad (16)$$

while if species 1 were absent the pressure of species 2 would be

$$p_2 = nx_2 RT/V + n^2 x_1^2 RT(B_{22}^0 + b_{22})/V^2 \quad (17)$$

Applying eq. 5 to the total pressure of the gas, using

(11) See T. S. Wheeler, *Rec. trav. chim.*, **51**, 1204 (1932).

(12) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., New York, N. Y., 1949, Vol. I, pp. 858 ff.

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

eq. 10 and 12, subtracting eq. 16 and 17 from the result, and recalling that $x_1 + x_2 = 1$, we obtain

$$\Delta p = p - p_1 - p_2 = 2x_1 x_2 n^2 RT(B_{12}^0 + b_{12})/V^2 \quad (18)$$

Δp is essentially the quantity we have measured in the case of the iodine-benzene mixtures. The change of pressure arising from pair formation, which we will call Δp^0 , is given by

$$\Delta p^0 = \Delta p - 2x_1 x_2 n^2 RT b_{12}/V^2 = 2x_1 x_2 n^2 RT B_{12}^0/V^2 \quad (19)$$

Since the gas imperfections are relatively small we may use the ideal gas law for the pressures of the unpaired molecules. Thus they are approximately $n_1 RT/V$ and $n_2 RT/V$, respectively, where $n_1 = x_1 n$ and $n_2 = x_2 n$. The equilibrium constant for the formation of pairs will be approximately

$$K_p = -V^2 \Delta p^0 / n_1 n_2 (RT)^2 \quad (20)$$

Values of K_p are included in Table I. These were calculated directly from the values of Δp given in the table, by means of eq. 20 and the first relation of eq. 19, using eq. 9a, 9b, 15 and 14 to obtain b_{12} . In Fig. 2 we have plotted $\log K_p$ against T^{-1} , and have put the best straight line through these points by least squares, weighting according to the number of observations given in Table I. The slope of the line may be used to calculate ΔH , the heat of formation of a pair. The thermodynamic functions for formation of a pair at 450°K., taking 1 atm. pressure as the standard state, are as follows

$$\Delta H = -2.44 \text{ kcal. mole}^{-1} \quad (21)$$

$$\Delta G^0 = 3.00 \text{ kcal. mole}^{-1} \quad (22)$$

$$\Delta S^0 = -12.1 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \quad (23)$$

For comparison we have included in Fig. 2 curves representing $-2B_{11}^0/RT$ (benzene) and $-2B_{22}^0/RT$ (iodine), calculated from eq. 2 and 3, respectively. (K_p for association in a pure gas actually has the form B_{ii}/RT , but the comparison should be with $2B_{ii}/RT$ to reflect the actual difference in molecular forces.) It will be seen that they are of the same order of magnitude and have the same general behavior as K_p or $-2B_{12}^0/RT$, which indicates that the forces between iodine and benzene are of the van der Waals type.

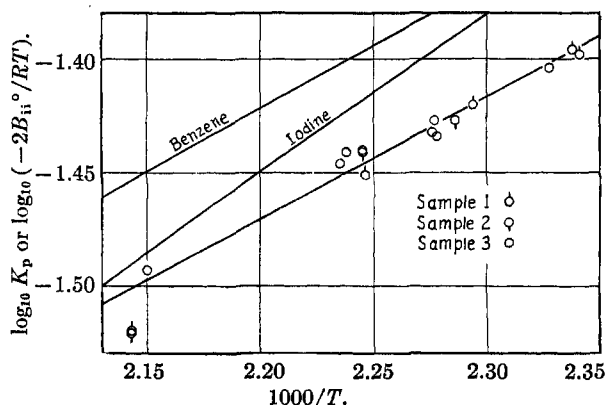


Fig. 2.—Van der Waals association constants.

Effective Cross Section for Dissociation of I_2 by Benzene

In order to see whether we can account for the apparent large collision diameter for dissociation of I_2 by benzene, it will first be necessary to correct K_p

to around 300°K. Taking ΔH as roughly constant we find K_p at 300°K. to be 0.14 atm.⁻¹, and $K_c = 3400$ ml. mole⁻¹.

The effective collision diameter σ_0 for the dissociation was calculated by Rice^{2a} by assuming that the over-all rate constant, k_d , expressed in molal concentration units, was given by

$$k_d = A e^{-\Delta E_{I_2}/kT} \quad (24)$$

where ΔE_{I_2} is the dissociation energy of I_2 and

$$A = 200 \sigma_0^2 N (2\pi RT/\mu)^{1/2} \quad (25)$$

where N is Avogadro's number and μ is the reduced mass in molecular weight units. If we now assume that the activation energy for reaction (b) is equal to¹⁴ ΔE_{I_2} (which is the dissociation energy of an *unattached* iodine) we may write for the over-all rate constant for reactions (a) and (b)

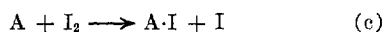
$$k_b K_c = 5\nu_{I_2} K_c e^{-\Delta E_{I_2}/kT} \quad (26)$$

where ν_{I_2} , the frequency of vibration of I_2 in its ground state, which is approximately 6.4×10^{12} sec.⁻¹, is taken as the frequency factor for the rate of decomposition, and the factor 5 allows for the number of energy levels from which I_2 can dissociate, as explained in reference 2a. In order to find the expected value of σ_0 we therefore set

$$200 \sigma_0^2 N (2\pi RT/\mu)^{1/2} = 5\nu_{I_2} K_c \quad (27)$$

Using the value of K_c found above we obtain $\sigma_0 = 13$ Å. It is to be noted that the correction arising from rotation of the iodine molecules^{2b} has not been included in either eq. 25 or eq. 26. This is effectively a correction in the number of states from which decomposition of I_2 can occur, and should affect the value of A and of k_b roughly in the same ratio, so that the calculation of σ_0 from eq. 27 will be affected only slightly. The value $\sigma_0 = 13$ Å. may therefore be compared directly with the corrected experimental values of σ_0 (10 to 14 Å.) given at the beginning of the paper and is seen to be of the same order of magnitude. The van der Waals association can therefore account adequately for the observed rate of reaction. This fact lends some weight to the suggestion of Russell and Simons¹ that there is a relation between the rate of recombination of iodine atoms and the boiling point of the inert substance used to furnish the third body.

If the third body is a monatomic molecule, like argon, a complex between iodine and the inert molecule, having enough energy to dissociate the I_2 , could not be stabilized, since there are no internal degrees of freedom to take care of the excess energy. It has been noted,^{2a} however, that a one step reaction



could result in a lowering of the activation energy. Indeed, since the transition state of reaction (c) would be entirely similar to that of reaction (b) it would appear that (c) would have the same effect as (a) and (b), and that the rate could be calculated as though the reaction took place in two steps. Thus the relation between boiling point and rate of association can reasonably be extended to these cases.

(14) This means that we assume that the energy to split the complex is the same for $C_6H_6 \cdot I_2$ as for $C_6H_5 \cdot I$.

Russell and Simons¹ have measured temperature coefficients for the association of iodine atoms using several different inert gases. They found an activation energy of -2360 cal. per mole-reaction with benzene as the inert gas. If the activation energy for the reverse of reaction (b) is zero, and if our assumption regarding the activation energy of the direct reaction (b) is correct, then this activation energy represents the negative of the heat of dissociation of the complex. It is seen that it is of just the right order of magnitude. The most puzzling feature of Russell and Simons' results is the rather small range of activation energies for the different inert gases. Thus the activation energy with helium is about -1510 cal. per mole-reaction; since the attractive forces in the case of helium would be expected to be very small, the absolute value of the activation energy seems somewhat high. Furthermore, the difference between -2360 and -1510 cal. per mole-reaction would account, through the exponential factor for a difference in the rate of reaction of only about 4-fold at room temperature. Since the rate of association in the presence of benzene is at least 100 times as great as in the presence of helium, this would appear to put too great a burden on the entropy factor, particularly in the light of the analysis of the entropy of the complex given in the following section.

The Structure of the Benzene-Iodine Complex

From the entropy of association ΔS^0 we may obtain a rough pictorial idea of the tightness with which the complex is held together. The value of -12.1 cal. mole⁻¹ deg.⁻¹ is very much lower in absolute value than would be expected if the two molecules were held together by valence-bond forces. We may use the expression

$$-\Delta S^0 = R \ln (v_2' e / v_2) \quad (28)$$

to calculate the volume v_2 in which an iodine molecule is localized in the presence of a benzene molecule. Here v_2' is the molecular volume of free iodine molecules in their standard state, one atmosphere pressure. The factor e takes care of the sharing of the volume by the iodine molecule, *i.e.*, it gives the communal entropy, and it does not appear in the denominator of the fraction because we deal only with the case in which only one iodine is attached to a given benzene molecule.

At 450°K. the value of v_2' is 6.13×10^4 Å.³. Then we find from eq. 28, $v_2 = 370$ Å.³.

We can roughly assume that the center of the I_2 molecule is located somewhere between two spheres, the inner one of which has a volume of $4\pi\sigma_{I_2}^3/3$ or $2b_{I_2}$, which is equal to 400 Å.³, and an outer one of $400 + 370 = 770$ Å.³. The diameter of the inner sphere is $\sigma_{I_2} = 4.57$ Å. and that of the outer sphere is 5.69 Å. The average range of the vibration of the iodine against the benzene is thus, according to this rough calculation about 1.12 Å., as compared to effective distances of the order of a few tenths of an ångström for the relative vibration of the two atoms in a diatomic molecule in which valence-type forces are operative. This, of course, assumes that the I_2 molecule rotates freely when attached to benzene.

A similar calculation could, of course, be made

for the benzene-benzene complex and the iodine-iodine complex, and results of the same order of magnitude would be obtained.

Comparison with Results of Benesi and Hildebrand

Benesi and Hildebrand³ (1949) found that in carbon tetrachloride solution the equilibrium constant K corresponding to a reaction like reaction (a) was $1.72 (\text{mole fraction})^{-1}$ at room temperature. There seems to be no question that this is a different type of complex from that which we have studied in the present paper. In solution in carbon tetrachloride, the I_2 , the C_6H_6 and the complex are all continually under the influence of the van der Waals forces of the surrounding molecules. Only something of a different nature would result in the shift of the absorption band by which the complex was detected.

Carbon tetrachloride has a molar volume of 96.5 ml. In a dilute solution, a given mole fraction x corresponds to a concentration of x moles per 96.5 ml., or, calculating gas pressures as though the other molecules were not there, a pressure of about $254x$ atm. at 25° . Thus on this basis $K_p = 0.68 \times 10^{-2} \text{ atm.}^{-1}$. However in the gas phase K_p would be smaller, since this calculated value takes no account of the fact that the free volume for molecules in solution is less than the total volume. Our value of K_p , even above 400°K. , is around $4 \times 10^{-2} \text{ atm.}^{-1}$. Complexes of the type observed by Benesi and Hildebrand should, therefore, have a completely negligible influence on our experiments.

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FLAME QUENCHING BY A VARIABLE-WIDTH RECTANGULAR-CHANNEL BURNER AS A FUNCTION OF PRESSURE FOR VARIOUS PROPANE-OXYGEN-NITROGEN MIXTURES

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Flame quenching distances for a variable-width water-cooled rectangular-channel burner as a function of pressure for various propane-oxygen-nitrogen mixtures are presented. The relation between pressure p and quenching distance d , is given by dap^{-r} , with $r \approx 1$ for equivalence ratios approximately equal to one (for pressures of 0.1 to 1.0 atm. and for volumetric oxygen fractions of the oxidant mixture of 0.17, 0.21, 0.30, 0.50 and 0.70). For lean and stoichiometric mixtures, it is shown that an equation based on a diffusion mechanism may be used successfully to correlate the observed quenching data.

Various investigators have attempted to relate quenching distance to the fundamental properties characterizing the combustion wave. Reference 1 relates quenching distance to minimum ignition energy and burning velocity by assuming that a consideration of heat-transfer processes alone is sufficient to explain the behavior of the combustion wave. No thorough test of this theory has been made, chiefly because of the lack of low pressure burning velocity data. A quenching theory is proposed in reference 2 in which the diffusion of H, O and OH radicals in the flame front plays the vital role in determining whether or not the flame will be quenched by a given wall geometry. This latter theory can be readily applied (once flame equilibrium radical concentrations are calculated) and has been successful in correlating quenching distance data for propane-air, ethylene-air and iso-octane-air flames over a range of pressures. One objection to this diffusional mechanism for flame quenching is based on the observation that surfaces which may display widely different chain breaking efficiencies all display the same flame quenching effects.³ However, such varying chain breaking wall efficiencies have not been demon-

strated for the case of high temperature flames near cold walls.

The present work, in addition to supplying the data necessary to describe the wall quenching of propane-oxygen-nitrogen flames as a function of fuel-oxidant ratio, oxygen content of the oxidant mixtures, and pressure, is intended as an additional test of this current concept of flame quenching.

Apparatus.—The rectangular channel quenching distance burner used in making these measurements was made of stainless steel. The burner length was 5 inches and the slit width, established by adjusting the movable burner-lip assembly, was never more than $\frac{1}{2}$ inch. Two inside-thickness gages were used at the ends of the rectangular slot to determine the burner wall separation. The burner itself was mounted in a 3.5 cubic foot capacity, pressure-controlled chamber.

The desired fuel-oxidant mixture was introduced through three inlets located at the bottom of the burner channel. Fine glass beads were sandwiched between two layers of 200-mesh stainless steel screen which served both as a flow straightener and as a flame arrestor. The jacketed walls of the burner were kept at 40° by circulating water. This wall temperature was sufficiently high to prevent condensation of water on the burner lip. A spark igniter was used to establish a flame atop the rectangular burner port. A thermocouple was employed to measure local temperatures and to indicate flash back of the flame through the rectangular channel of the burner. Fuel and oxidant were supplied from separate cylinders and were separately metered through critical flow orifices.

Oxygen-nitrogen mixtures for which the volumetric oxygen fraction α was 0.17, 0.21, 0.30, 0.50 and 0.70 were used as oxidants. The supplier's stated accuracy was $\pm 0.1\%$

(1) B. Lewis and G. von Elbe, "Combustion, Flames and Explosion of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 413.

(2) D. M. Simon, F. E. Belles and A. E. Spakowski, "Fourth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, 1953.

(3) R. Friedman and W. C. Johnston, *J. App. Phys.*, **21**, 79 (1950).