Our final parameters and estimated limits of error, as deduced from qualitative comparisons of calculated curves (Fig. 1) and from ratios of calculated to observed positions of maxima and minima (Table I is an example), are the following: C–H/Se–C = 1.09/1.97 (assumed), Se⋯H/Se–C = 1.300 ± 0.017, (∠Se–C–H = 110.5 ± 3.5°), C⋯C/Se–C = 1.51 ± 0.11, (∠C–Se–C = 98 ± 10°), Se–C = 1.977 ± 0.012 Å., Se⋯H = 2.571 ± 0.034 Å., and C⋯C = 2.98 ± 0.23 Å.

Discussion

It seems appropriate to regard the selenium–carbon bonds in unconjugated compounds of bivalent selenium as normal and, therefore, to take 1.98 Å. as the normal Se–C single bond length. With a small (and perhaps unjustifiable) correction for electronegativity difference, the selenium radius then becomes 1.22 Å. (1.98 = 0.77 + 1.22 − (0.09 × 0.1)). This is appreciably greater than Pauling's value 1.17 Å.,[9] which is supported by the bond

(9) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1940, p. 165.

lengths of 2.32 Å. in hexagonal selenium[10] and 2.34 Å. in both α- and β-monoclinic selenium.[11,12] It has been pointed out,[13] however, that nominal single bonds in the heavier elements may actually have appreciable double-bond character; our value for the selenium radius is in agreement with this possibility, which, accordingly, may deserve further consideration.

(10) A. J. Bradley, *Phil. Mag.*, **48**, 477 (1924).

(11) R. Burbank, *Acta Cryst.*, **4**, 140 (1951).

(12) R. E. Marsh, L. Pauling and J. D. McCullough, *ibid.*, **6**, 71 (1953).

(13) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

PASADENA, CAL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF LONDON, KING'S COLLEGE]

The Effect of Solvent in Dipole Moment Measurements

BY N. PILPEL

The apparent dipole moments of acetophenone, phenetole, chlorobenzene, nitrobenzene and benzonitrile have been calculated from solution data by the conventional method, and by employment of the solvent effect equations of Sugden, Smith and Goss. The values differ from the true vapor values by amounts which depend on the method of calculation. These differences can be almost completely eliminated by averaging the values obtained by the four different methods.

The purpose of the present paper is to draw attention to the fact that, by suitable combination of three solvent effect equations—those due to Sugden,[1] Smith,[2] and Goss[3]—with the conventional expression for dipole moments in solution,[4] values of the moments can be obtained which, for five compounds at least, agree very reasonably with the true values which the compounds exhibit when in the vapor state. For the purpose of discussion the following notation is employed.

P_{12} is the total polarization of a two component mixture and is given by

$$P_{12} = [(\epsilon_{12} - 1)/(\epsilon_{12} + 2)](M_1c_1 + M_2c_2)/d_{12} \quad (1)$$

ϵ denotes dielectric constant, d density, M molecular weight, c mole fraction, n refractive index, and the subscripts 1, 2, and 12 refer respectively to the solvent, the solute and the mixture. P_1 and P_2 are the partial polarizations of the solvent and of the solute and are calculated on the assumption that P_1 is independent of c. P_{s1} and P_{s2} are the corresponding partial polarizations obtained by the intercept method,[5] in which P_{s1} is assumed a function of c. μP denotes orientation polarization, P_D distortion polarization. These are related by

$$\mu P = P_{2\infty} - P_D \quad (2)$$

where P_D is given by

$$P_D = 1.05(n_2^2 - 1)/(n_2^2 + 2)M_2/d_2 \quad (3)$$

The subscript ∞ indicates the value of the particular parameter at infinite dilution, μ, the dipole moment is calculated from the Debye equation

$$\mu = 0.0128[T(P_{2\infty} - P_D)]^{1/2} \quad (4)$$

The solvent effect equation of Sugden, which is applicable to the particular case of polar solutes dissolved in the non-polar solvent benzene, may be written

$$P_2 = A + \mu P(\epsilon_{12} - 1)/(\epsilon_{12} + 2) \quad (5)$$

In this A is a constant characteristic of the solute and solvent. Plotting P_2 against $(\epsilon_{12} - 1)/(\epsilon_{12} + 2)$ should therefore yield a straight line of slope μP, and from this μ can be calculated by equations 2 to 4.

The second solvent effect equation considered is that due to Smith.[2,6] This is written

$$P_{2\infty} = B + \mu P(\epsilon_1 - 1)/(\epsilon_1 + 2) \quad (6)$$

where again B is a constant. When polar solvents are used it is necessary to correct the measured $P_{2\infty}$ values for the quantity $\partial P_1/\partial c_2$, i.e., for the variation in P_1 with concentration of the solute. Then plotting $P_{2\infty}$ cor against $(\epsilon_1 - 1)/(\epsilon_1 + 2)$ should yield a straight line from which μP and μ can be calculated as before.

The third solvent effect treatment considered is due to Goss,[3,7] and applies strictly only when the isotropic, non-polar solvent CCl_4 is used. The relevant equations are

$$P_{s2} = P_D + Z\{(\epsilon_{12} - 1)/(\epsilon_{12} + 2)\}^4 + Y/\epsilon_{12} \quad (7)$$

(1) S. Sugden, *Nature*, **133**, 415 (1934).

(2) J. W. Smith, *Trans. Faraday Soc.*, **48**, 802 (1952).

(3) F. R. Goss, *J. Chem. Soc.*, 1915 (1937).

(4) R. J. W. Le Fevre, "Dipole Moments," Methuen & Co., London, 1948, p. 31.

(5) W. J. C. Orr and J. A. V. Butler, *Nature*, **130**, 930 (1932).

(6) J. W. Smith and L. B. Witten, *Trans. Faraday Soc.*, **47**, 1304 (1951).

(7) F. R. Goss, *J. Chem. Soc.*, 752 (1940).

and

$$\mu P = Y/[3\{(Z + P_D)/P_D\}^{1/4} - 2] \qquad (8)$$

in which Y and Z, which are constants for any particular solute, are obtained by the simultaneous solution of

$$(P_{s2})_{c=0} = P_D + Z\{(\epsilon_1 - 1)/(\epsilon_1 + 2)\}^4 + Y/\epsilon_1 \qquad (9)$$

$$(P_{s2})_{c=1} = P_D + Z\{(\epsilon_2 - 1)/(\epsilon_2 + 2)\}^4 + Y/\epsilon_2$$

The experimental results from the present investigation have been combined with literature results and the combined data subjected to the four solvent effect treatments outlined above. The general findings will be discussed shortly.

Experimental

Preparation of Materials.—High grade commercial materials were purified by standard methods taking particular

TABLE 1
DATA AT 20

c_2	$d^{20}{}_4$	$n^{20}{}_D$	ϵ_{12}	P_{12}	P_{s1}	P_{s2}	P_1	P_2
			Acetophenone in benzene					
0.00000	0.87900	1.5011	2.2835	26.62	26.60	211.6	26.62	
.01348	.88180	1.5018	2.453	29.12	26.69	205.0	28.16	212.1
.01550	.88223	1.5019	2.479	29.48	26.70	203.5	28.38	211.1
.01989	.88312	1.5021	2.538	30.28	26.76	201.8	28.89	206.5
.04235	.88761	1.5031	2.829	34.09	27.20	189.4	31.23	203.2
.06055	.89115	1.5040	3.071	36.96	27.78	179.8	32.96	197.4
.09073	.89681	1.5053	3.469	41.23	28.88	165.8	35.47	187.6
.24968	.92548	1.5116	5.754	58.68	36.62	125.2	45.25	155.0
.52597	.96880	1.5222	9.950	77.42	47.80	103.9	53.45	123.2
.66238	.98709	1.5262	12.13	84.59	52.41	100.8	56.25	114.1
.82480	1.00800	1.5303	14.90	91.93	56.73	99.4	58.51	105.8
.90372	1.01736	1.5321	16.17	95.18	59.2	99.1	59.04	102.5
.91644	1.01878	1.5323	16.38	95.65	59.0	99.1	58.60	102.0
.94814	1.02238	1.5331	16.87	96.96	59.2	99.0	59.11	100.8
.96950	1.02466	1.5335	17.23	97.83	59.3	99.0	58.69	100.1
.97240	1.02505	1.5335	17.28	97.95	59.3	99.0	59.90	99.97
1.00000	1.02835	1.5340	17.73	99.03	59.6	99.0		99.03
			Benzonitrile in benzene					
0.00000	0.87892	1.5012	2.2825	26.59	26.58	359.5	26.59	
.00758	.87975	1.5015	2.452	29.02	26.70	331.2	28.54	347.5
.01359	.88051	1.5016	2.588	30.84	26.92	314.9	30.00	338.0
.02300	.88178	1.5020	2.808	33.50	27.41	291.8	32.13	326.0
.03086	.88285	1.5022	2.982	35.56	27.81	277.4	33.79	317.3
.05502	.88650	1.5031	3.536	41.04	29.46	240.0	38.10	289.2
.07414	.88948	1.5036	3.982	44.80	30.98	216.1	41.07	272.2
.10845	.89463	1.5046	4.788	50.39	34.31	182.7	45.40	246.0
.14845	.90045	1.5059	5.749	55.70	38.24	155.4	49.48	222.7
.16773	.90348	1.5065	6.210	57.81	39.89	146.9	51.04	212.7
.23770	.91330	1.5085	7.910	64.17	45.52	124.7	55.68	184.7
.34732	.92846	1.5117	10.60	71.13	52.76	106.3	60.35	154.8
.54281	.95311	1.5172	15.12	79.35	60.51	94.70	65.05	123.8
.77949	.98133	1.5233	20.54	86.22	66.62	91.85	67.94	103.1
.90183	.99446	1.5263	23.29	89.21	68.40	91.54	69.19	96.02
.91411	.99553	1.5266	23.54	89.49	68.58	91.52	69.27	95.39
.94878	.99964	1.5275	24.41	90.29	69.13	91.47	69.92	93.72
.97273	1.00249	1.5282	24.91	90.81	69.44	91.44	70.12	92.61
1.00000	1.00520	1.5289	25.51	91.39	69.70	91.39		91.40
			Phenetole in benzene					
0.00000	0.87903	1.5011	2.2825	26.62	26.62	74.52	26.62	
.00176	.87928	1.5011	2.287	26.70	26.62	74.51	26.63	72.07
.01827	.88129	1.5012	2.329	27.49	26.63	74.50	26.78	74.24
.03170	.88290	1.5013	2.364	28.15	26.64	74.50	26.93	74.57
.05400	.88550	1.5016	2.421	29.21	26.68	74.46	27.14	74.58
.12193	.89280	1.5021	2.595	32.45	26.79	72.99	27.85	74.43
.31486	.91268	1.5036	3.042	40.81	28.05	68.65	29.44	71.69
.46365	.92611	1.5046	3.346	46.70	29.04	67.14	30.40	69.93
.64519	.94033	1.5056	3.684	53.50	30.90	66.39	31.57	68.28
.72488	.94619	1.5061	3.824	56.38	30.58	66.18	32.20	67.67
.90560	.95884	1.5070	4.100	62.54	33.40	65.58	33.58	66.28
.93675	.96101	1.5071	4.141	63.53	33.50	65.57	33.47	66.02
.96994	.96336	1.5073	4.185	64.60	33.55	65.56	33.63	65.78
1.00000	.96538	1.5074	4.225	65.56	33.56	65.56		65.56

TABLE I   (*Continued*)

c_2	d^{20}_4	$n^{20}D$	ϵ_{12}	P_{12}	P_{81}	P_{82}	P_1	P_2
				Benzonitrile in chlorobenzene				
0.00000	1.10628	1.5246	5.698	62.09	62.08	161.2	62.09	
.01077	1.10524	1.5246	5.900	63.11	62.09	156.9	62.81	156.8
.02675	1.10360	1.5247	6.213	64.58	62.19	151.2	63.84	155.2
.05819	1.10060	1.5248	6.832	67.21	62.55	141.0	65.71	150.1
.08222	1.09811	1.5249	7.314	69.00	63.12	134.4	66.91	146.1
.15431	1.09092	1.5252	8.731	73.35	65.07	119.5	70.66	135.1
.18536	1.08778	1.5253	9.339	74.91	65.84	114.9	71.16	131.8
.26403	1.07982	1.5255	10.92	78.27	68.21	106.2	73.56	123.4
.33119	1.07305	1.5258	12.25	80.51	70.12	101.5	75.10	117.7
.66497	1.03915	1.5272	18.90	87.59	77.19	92.68	80.03	100.4
.89469	1.01581	1.5283	23.34	90.35	80.83	91.45	81.43	93.67
.94787	1.01152	1.5284	24.39	90.90	81.60	91.42	81.81	92.48
.97330	1.00778	1.5287	24.91	91.14	81.95	91.41	81.66	91.94
1.00000	1.00523	1.5288	25.49	91.40	82.26	91.40		91.40
				Benzonitrile in nitrobenzene				
0.00000	1.20328	1.5524	35.95	94.23	94.23	90.30	94.23	
.01522	1.20040	1.5522	35.69	94.16	94.22	90.34	94.20	89.63
.05011	1.19358	1.5516	35.10	94.04	94.22	90.52	94.18	90.44
.07940	1.18791	1.5510	34.64	93.93	94.21	90.58	94.15	90.45
.10733	1.18246	1.5502	34.24	93.83	94.21	90.67	94.13	90.51
.22922	1.15872	1.5481	32.56	93.41	94.15	90.97	94.02	90.65
.27275	1.15030	1.5472	32.02	93.26	94.12	91.11	93.97	90.67
.57234	1.09216	1.5396	28.93	92.36	93.97	91.16	93.47	90.96
.79002	1.04849	1.5343	26.95	91.75	93.90	91.17	93.18	91.09
.90535	1.02550	1.5313	26.12	91.47	93.15	91.29	92.43	91.18
.94997	1.01653	1.5301	25.84	91.40	92.59	91.33	91.97	91.25
.97543	1.01095	1.5294	25.66	91.38	92.21	91.35	91.78	91.30
1.00000	1.00555	1.5288	25.51	91.37	91.60	91.37		91.37
				Acetophenone in carbon tetrachloride[11]				
0.00000	1.5943	....	2.2376	28.18	28.24	216.2	28.18	
.00472	1.5911	....	2.292	29.08	28.27	213.5	28.65	218.9
.01068	1.5872	....	2.357	30.12	28.30	209.1	29.37	209.8
.02209	1.5794	....	2.492	32.19	28.36	203.4	30.68	209.7
.04308	1.5655	....	2.743	35.77	28.45	191.8	32.92	204.4
.08458	1.5380	....	3.273	42.32	30.59	172.2	37.36	195.4
.19959	1.4645	....	4.390	56.96	36.21	138.2	46.44	172.4
.44708	1.3166	....	8.823	76.19	49.05	110.1	57.63	135.6
.73426	1.1595	....	13.44	89.70	60.09	100.7	63.62	111.9
.87124	1.0898	....	15.65	94.82	64.13	99.6	65.59	104.7
1.00000	1.0276	....	17.73	99.14	66.00	99.1		99.1
				Benzonitrile in carbon tetrachloride[11]				
0.00000	1.5938	....	2.2436	28.28	28.27	367.7	28.23	
.00703	1.5895	....	2.387	30.48	28.36	341.9	30.05	348.3
.01577	1.5845	....	2.564	33.14	28.56	319.6	32.21	339.6
.02864	1.5766	....	2.840	36.67	29.10	290.0	35.06	322.9
.06286	1.5561	....	3.575	44.72	31.49	235.1	41.59	290.6
.14645	1.5061	....	5.480	58.27	41.18	158.3	52.59	233.4
.27741	1.4283	....	8.572	70.05	51.59	118.3	61.85	179.0
.56660	1.2572	....	15.39	82.40	65.58	94.37	70.63	123.8
.79492	1.1235	....	20.69	87.75	71.73	91.85	73.61	103.1
1.00000	1.0050	....	25.48	91.40	75.39	91.40		91.40
				Phenetole in carbon tetrachloride[11]				
0.00000	1.5937	....	2.2433	28.28	28.31	79.32	28.28	
.00263	1.5916	....	2.251	28.43	28.33	79.01	28.34	85.30
.00755	1.5874	....	2.263	28.67	28.35	78.62	28.39	79.94
.02156	1.5760	....	2.298	29.34	28.38	76.54	28.55	77.45
.04931	1.5535	....	2.363	30.63	28.45	74.30	28.82	75.94
.11971	1.4982	....	2.256	33.76	28.66	72.11	29.44	74.06
.23845	1.4099	....	2.800	38.91	29.40	70.06	30.57	72.86
.47290	1.2532	....	3.306	48.17	30.27	68.00	32.57	70.34
.84180	1.0439	....	3.980	60.70	34.74	66.23	34.84	66.79
1.00000	0.9652	....	4.224	65.56	36.09	65.59		65.56

TABLE II

RECALCULATED POLARIZATION DATA FOR VARIOUS SOLUTES AT 20

Solvent	$(\epsilon_1 - 1)/$ $(\epsilon_1 + 2)$	Benzonitrile			Chlorobenzene			Nitrobenzene		$P_{2\infty}$ cor., cc.
		Data ref.	$P_{2\infty}$, cc.	$P_{2\infty}$ cor., cc.	Data ref.	$P_{2\infty}$, cc.	$P_{2\infty}$ cor., cc.	Data ref.	$P_{2\infty}$, cc.	
C_6H_{14}	0.233	..	...	...	..	..	..	14	380	380
CCl_4	.292	11	368	368	11	84.6	84.6	11	364	364
C_6H_6	.300	16	360	360	15	82.5	82.5	14	361	361
C_6H_5Cl	.610	16	161	228	16	62.0	62.0	14	162	232
C_6H_5CN	.891	16	91.4	91.4	16	82.2	45.7	16	91.7	102
$C_6H_5NO_2$	.921	16	90.5	74.9	15	84.5	48.0	16	94.2	94.2

Solvent	$(\epsilon_1 - 1)/(\epsilon_1 + 2)$	Acetophenone			Phenetole	
		Data ref.	$P_{2\infty}$, cc.	$P_{2\infty}$ cor., cc.	Data ref.	$P_{2\infty}$, cc.	$P_{2\infty}$, cor., cc.
CCl_4	0.292	11	216	216	11	78	78
C_6H_6	.300	16	212	212	16	74.0	74.0
$C_6H_5OC_2H_5$	.518	..	...	...	16	65.5	65.5
$C_6H_5COCH_3$	.848	16	99.0	99.0	..	..	..

care to exclude moisture. The agreement between the measured physical constants (Table I) and reliable literature values was in all cases good.

Measurements.—Binary liquid mixtures over the whole concentration range possible were made up by weight.

Dielectric constants were determined from the variation in electrical capacity of Sayce Briscoe cells (see ref. 4, p. 36) silvered by the method of Sugden,[8] and thermostated in a bath of transformer oil. The circuit used was that of Goss[9] with the ear phone detector replaced by a "magic eye." Dried, filtered air, ϵ_{20} 1.0005, and the following purified liquids were employed as standards for the purpose of cell calibration: benzene ϵ_{20} 2.2825[10]; chlorobenzene ϵ_{20} 5.700[11]; chloroform ϵ_{20} 4.806[11]; benzonitrile ϵ_{20} 25.48[11]; and nitrobenzene ϵ_{20} 35.92.[11]

Densities were measured in an Ostwald Sprengel pycnometer fitted with an overflow expansion bulb.

Refractive indices for the sodium-D line were measured with an Abbe refractometer.

Results

The experimental results are set out in Table I in which the notation used has already been given. P values were calculated in the conventional manner, P_s values by the intercept method.[5] $P_{2\infty}$ values were determined by graphical extrapolation and checked by employment of a number of mathematical extrapolation methods. A more detailed account of this aspect of the work is published elsewhere.[12,13] Orientation polarizations were calculated (a) by use of equations 1 to 3 in the usual manner, (b) by plotting P_2 against $(\epsilon_{12} - 1)/(\epsilon_{12} + 2)$ and taking μP as the slope of the best straight line through the points, (c) by Smith's method. For this the present results were combined in Table II with reliable literature data. The $P_{2\infty}$ values were corrected for the quantity $\partial P_1/\partial c_2$ as described by Smith[2] and then $P_{2\infty}$ cor plotted against $(\epsilon_{12} - 1)/(\epsilon_{12} + 2)$ of the solvent. The slope of the best straight line through the points gave a value for μP. Finally (d) equation 9 was employed on the polarization data for carbon tetrachloride solutions and μP calculated by means of equation 8. The μP values obtained by the four different methods are recorded in columns (a), (b), (c) and (d), respectively, of Table III.

(8) S. Sugden, *J. Chem. Soc.*, 768 (1933).

(9) F. R. Goss, *ibid.*, 1341 (1933).

(10) J. Timmermans "Physicochemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, 1950.

(11) F. R. Goss, private communication.

(12) N. Pilpel, *Research*, **5**, 444 (1952).

(13) N. Pilpel, *ibid.*, **6**, 18S (1953).

TABLE III

ORIENTATION POLARIZATIONS AT 20

Solute	(a) cc.	(b) cc.	(c) cc.	(d) cc.	Mean μP, cc.	μ, D	μvapor, D
$C_6H_5OC_2H_5$	39.5	41.0	48.8	45.8	43.7	1.43	1.40
C_6H_5Cl	49.3	67.3	58.0	56.6	57.8	1.67	1.68
$C_6H_5COCH_3$	175	190	203	204	193	3.02	3.03
$C_6H_5NO_2$	330	420	420	385	389	4.32	4.23
C_6H_5CN	326	430	452	431	410	4.44	4.39

Discussion

Examination of column (a) in Table III shows that for the five solutes now studied μsolution is in all cases less than μvapor, *i.e.*, the solvent effects for all these compounds are negative. The solvent effects are seen to be considerable, particularly for the more polar materials such as acetophenone, nitrobenzene and benzonitrile.

The application of Sugden's method in all cases results in an increase in the apparent orientation polarization of the solute. This is shown by comparison of columns (a) and (b) in Table III. The moments thereby calculated are generally greater than the true vapor ones. However the absolute magnitudes of the solvent effects are reduced. In view of the relative simplicity of Sugden's treatment and the fact that the experimental data obey equation 5 noticeably well, it may be concluded that the treatment represents a definite improvement over the conventional method for calculating dipole moments from solution data.

Sugden's method is restricted solely to the treatment of polarization data obtained in benzene solution. There are many classes of organic compounds, however, for which benzene is not a particularly suitable solvent, and it is here that Smith's treatment is likely to prove more satisfactory.

Examination of column (c) in Table III shows that for all the solutes considered the orientation polarizations obtained by application of Smith's treatment are again higher than those calculated by the conventional method. The treatment thus has the same general effect as Sugden's, *i.e.*, to convert a negative into a positive solvent effect. Once

(14) J. W. Smith and D. Cleverdon, *Trans. Faraday Soc.*, **45**, 109 (1949).

(15) R. J. W. Le Fevre and P. Russell, *J. Chem. Soc.*, 491 (1936).

(16) Present investigation.

again the absolute magnitudes of the solvent effects are reduced, in two cases—phenetole and chlorobenzene—almost to zero. On the whole, however, Smith's treatment gives values for the moments which are further from the true vapor values than Sugden's. On the other hand it does enable a very much larger body of experimental data to be rationalized than can be achieved by employment of equation 5. The plots of $P_{2\infty}$ cor. against volume polarization of the solvent approximate very closely to straight lines and in no case considered, even when highly polar solvents are used, do any of the experimental points lie markedly off these lines. This fact, combined with the improved agreeement between $\mu_{soln.}$ and μ_{vapor} shows that the treatment is one of considerable value.

We now consider the applicability of Goss's treatment of the data obtained in carbon tetrachloride solutions. The orientation polarizations of the five solutes are recorded in column (d) of Table III. It is seen that once again the values obtained are higher than those by the conventional method, and that again the absolute magnitudes of the solvent effects are reduced. Indeed, with the one exception of benzonitrile, it is seen that the agreement between $\mu_{soln.}$ and μ_{vapor} is now in general better than that obtained either by Sugden's or Smith's methods. With all the solutes, however, there is still an appreciable solvent effect.

It cannot therefore be said that any of the treatments that have been discussed are entirely satisfactory in translating the solution data into the true dipole moment of the solute considered. The conventional method leads to values which are too low, the other methods generally to values which are too high.

In view of this fact it has seemed reasonable to try the effect of averaging the polarization values obtained by the four different treatments. These mean values are given in column 5 of Table III and the dipole moments calculated therefrom in column 6.

When these are compared with the true vapor values, given in column 7 of the same table, it is seen that the agreement is in all cases remarkably good. In no instance do the figures in column 6 and 7 differ by more than 0.09 Debye unit. The maximum error involved in taking the value of the moment from column 6 is about 2% (for nitrobenzene), the average error is about 1%. This is considered very reasonable.

Attempts to improve the agreement between the figures in columns 6 and 7 by including in the former values obtained by use of a number of other solvent effect treatments, e.g., Onsager's,[17] and Guggenheim's,[18] were unsuccessful. Such inclusions in general led to poorer agreement.

It is therefore concluded that a likely value of a dipole moment will be obtained from solution data by averaging the values derived from the conventional method and the three solvent effect treatments discussed. Further work, however, will be needed to confirm this finding.

The author wishes to thank Battersea Polytechnic and the Directors of J. Lyons & Co., Ltd., for laboratory facilities.

(17) L. Onsager, THIS JOURNAL, **58**, 1686 (1936).
(18) E. A. Guggenheim, *Nature*, **137**, 459 (1936).

STRAND, W.C. 2, ENGLAND

Diffusion Kinetics of the Photochemical and Thermal Dissociation–Recombination of Trihalide Ions[1]

BY J. C. ROY, W. H. HAMILL AND R. R. WILLIAMS, JR.

RECEIVED JANUARY 10, 1955

A diffusion equation for dissociation–recombination in the non-steady state region is applied to the photodissociation of Br_3^- and I_3^-, using Mn(II) as a radical scavenger. The efficiency of oxidation of Mn(II) is enhanced by additional X^-. If $X_3^- \rightarrow X_2^-\cdot + X\cdot$, the effect of additional X^- is attributable to $X^- + X\cdot \rightarrow X_2^-\cdot$ which hinders recombination. The thermal dissociation of iodine, in the presence of Mn(II) and of I^-, exhibits a similar dependence upon concentration of I^- but different kinetics may apply.

In the preceding paper of this series[2] yields of radiohalogen following neutron capture in several liquid alkyl halides as a function of the concentration of added free halogen were shown to be describable in terms of diffusion controlled dissociation-recombination in a two particle system. The equation appearing below was derived, as an extension of the work of Samuel and Magee,[3] to describe the probability of recombination W of two free radicals

(1) From the doctoral dissertation of Jean-Claude Roy, University of Notre Dame, June, 1954. Presented at the 126th meeting of the American Chemical Society, New York, September, 1954. This work was been supported in part by a grant from the Atomic Energy Commission under contract At(11-1)-38.
(2) J. C. Roy, R. R. Williams. Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954).
(3) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

as modified by a competing reaction with a reactive solute at mole fraction X; the primary dissociation results in an initial mean separation $\bar{R}_0 = n_0^{1/2} L$, where n_0 is the number of displacements of mean free path L, in terms of an equivalent fictitious separation by random walk. Also $\gamma = Ld^{-1}$ and $\rho_0 = \bar{R}_0 d^{-1}$.

$$-\ln (1 - W_\infty(X))(1 - W_0(X))^{-1} =$$
$$\sigma P_1 [\pi L^2 (2\pi n_0)^{1/2}]^{-1}[1 - (\pi n_0 P_2 X)^{1/2}]$$
$$= P_1[2.51\gamma\rho_0]^{-1} - P_1 P_2^{1/2}[1.41\gamma^2]^{-1}X^{1/2} \quad (1a)$$

$$-\log (1 - W_\infty(X)) = -[\log (1 - W_0(X)) +$$
$$P_1(5.75\gamma\rho_0)^{-1}] - P_1 P_2^{1/2}[3.24\gamma^2]^{-1}X^{1/2} \quad (1b)$$
$$= \beta - \mu X^{1/2}$$

In equation 1a, $\sigma = \pi d^2$ is the collision cross section for recombination occurring with probability P_1 per