

**238.** *The Electric Polarizations of some Metallic Acetylacetonates.*

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The electric dipole moment of a molecule is a measure of its electrical asymmetry, and usually can be related to its structural symmetry. In a number of instances, however, molecules which should, from their accepted structure, be non-polar appear to be polar. From time to time various explanations of these anomalies, some general, some specific, have been proposed; but so far no certain solution of the problem has been found, largely because no very intensive experimental attack has been made on it.

In this paper there are described measurements on some acetylacetonates which are very anomalous. The results eliminate some explanations, but do not give a final answer. They show that these compounds do not owe their abnormality to incomplete chelation, or to the chelate rings having lower symmetry than that required by modern theory, and that solvent effects are not likely to be the cause.

One admissible explanation is that there is a transitory electric moment arising from slow bending within the molecule caused by thermal bombardment, but rough calculations indicate that the frequency of bending would be too high for the molecule to orient while bent. The only other explanation is that the field can induce con-

siderable moments by causing inter-nuclear movements, a process usually called "atom polarisation."

The second of the two following papers continues the investigation from this point.

In 1932 Smith and Angus (*Proc. Roy. Soc.*, 1932, A, **137**, 372) observed that for both beryllium acetylacetonate and basic beryllium acetate there are definite differences between the total and the electron polarisations measured at one temperature. These differences, if dipole orientation polarisations, would correspond to permanent electric dipole moments of 1.07D. and 1.35D. respectively.

It is of some importance that the origin of these polarisations should be decided, for if it should be shown that they are due to fully chelated molecules being polar, then modern molecular structure theory would be proved seriously in error. If, however, this should prove not to be so, then it is essential for the proper understanding of polarisation phenomena that the true cause should be discovered: there are numerous other instances of compounds which should be non-polar but appear to be polar.

The earliest explanation offered for such polarisation differences was that they are atom polarisation ( $A_P$ ) which, since it would contribute to the polarisation at low field frequencies but not at visible frequencies, would appear as a difference between the total and the electron polarisations ( $P$  and  $E_P$ ) as measured by the dielectric constant for radio-frequencies and by the refractive index for visible light. Since 1932, increasing doubt has been cast upon the existence of large atom polarisations by Van Vleck ("The Theory of Electric and Magnetic Susceptibilities," Oxford, 1932, pp. 45—54), Sugden (*Trans. Faraday Soc.*, 1934, **30**, 734), H. O. Jenkins (*idem*, p. 739), Wolf and Fuchs ("Dielektrische Polarisation," Leipzig, 1935, pp. 262, 299), and Groves and Sugden (J., 1937, 1779). The last-named authors have suggested that as an empirical rule  $A_P$  may be taken as 5% of  $E_P$ : the unexplained polarisations for the beryllium compounds are about 50% of  $E_P$ .

In 1936, H. O. Jenkins (J., 1936, 862) pointed out that all the anomalies were shown by measurements made in solution, and proceeded to develop a theory to explain them as solvent effects. Later, Frank and Sutton (*Trans. Faraday Soc.*, 1937, **33**, 1307) showed that an alternative solvent effect is possible.

In order to provide more data the present authors have made measurements on beryllium acetylacetonate in a variety of solvents, and over a range of temperature in one solvent. The polarisations of several other acetylacetonates also have been measured in benzene solution. The best ones for this purpose are those of metals whose normal valency is half the maximum covalency on the Sidgwick rule. Of the others, those which are not salts are usually too sparingly soluble or are very easily hydrolysed. The compounds examined were therefore aluminium, ferric, cobaltic, chromic, thorium, and zirconium acetylacetonates; and what measurements were possible were made on the cupric and zinc derivatives.

The paper following this one describes work on quinones, with a similar bearing, carried out independently by Hammick, Hampson, and G. I. Jenkins, and the one following it describes polarisation measurements in the vapour intended to settle the questions left outstanding by the first two papers.

#### EXPERIMENTAL.

*Preparation and Purification of Materials.*—Benzene, carbon tetrachloride, and *n*-hexane were purified as described previously (Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, A, **143**, 147; Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945).

Chloroform of A. R. quality was twice distilled from phosphoric oxide, in a stream of dry air, the second distillation being made just before use.

Decalin, of a specially pure grade obtained from L. Light, was fractionated between 180—190°, and then finally again, in dry air, the fraction boiling at 180—185° being taken (cf. Sutton, New, and Bentley, J., 1933, 652).

Beryllium acetylacetonate was prepared by Jaeger's method (*Rec. Trav. chim.*, 1914, **33**, 394) and recrystallised several times from ligroin (b. p. 40—60°). The substance is dimorphic, m. p.'s 103—103.6° and 108.1—108.6° (corr.); cf. 108° (Combes, *Compt. rend.*, 1894, **119**, 1222).

Aluminium acetylacetonate. Preparation from commercial anhydrous aluminium chloride and acetylacetone in chloroform solution gave a product containing iron which could not be removed. A sample prepared from aluminium hydroxide, obtained from A. R. quality potash alum, contained only a negligible amount of iron, and was used after several recrystallisations from ligroin. M. p. 192—193° (corr.); cf. 193—194° (Combes, *Compt. rend.*, 1889, **108**, 406), 191° (Gach, *Monatsh.*, 1900, **21**, 99).

Ferric acetylacetonate was prepared as described by Urbain (*Compt. rend.*, 1899, **129**, 303) and Hantzsch and Desch (*Annalen*, 1902, **323**, 13), and was recrystallised twice from benzene-ligroin: m. p. 181.3—182.3° (corr.); cf. 184° (Urbain, *loc. cit.*), 179° (Hantzsch and Desch, *loc. cit.*).

Cobaltic acetylacetonate was prepared by the action of acetylacetone on an aqueous suspension of freshly precipitated cobalt sesquioxide, and was recrystallised from benzene-ligroin: m. p. 240°; cf. 240° (Urbain and Debiegne, *Compt. rend.*, 1899, **129**, 304), 241° (Gach, *Monatsh.*, 1900, **21**, 105).

Chromic acetylacetonate was prepared as described by Urbain (*loc. cit.*) and by Gach (*Monatsh.*, 1900, **21**, 116), and recrystallised from ethanol: m. p. 216°; cf. 214° (Urbain and Debiegne, *loc. cit.*), 216° (Gach, *loc. cit.*).

Zirconium acetylacetonate was prepared as directed by Biltz and Clinch (*Z. anorg. Chem.*, 1904, **40**, 219). It was dehydrated by several recrystallisations from absolute alcohol.

Thorium acetylacetonate was prepared as directed by Biltz (*Annalen*, 1904, **331**, 336), and recrystallised from ethanol: m. p. 169°; cf. 168—169° (Morgan and Moss, J., 1914, **105**, 197); 171—172° (Urbain, *Bull. Soc. chim.*, 1896, **15**, 348).

Cupric acetylacetonate was prepared by treating an aqueous solution of cupric sulphate with an ethanolic solution of acetylacetone, and recrystallised from benzene-chloroform.

Zinc acetylacetonate was prepared by refluxing a benzene solution of acetylacetone with zinc oxide. The substance was difficult to purify because of the great ease with which it hydrolysed, and because it decomposed on being sublimed in a vacuum.

*Physical Measurements.*—Dielectric constants were measured with essentially the same heterodyne beat apparatus as that previously described (Sutton, *Proc. Roy. Soc.*, 1931, **A**, **133**, 668; Hampson, Farmer, and Sutton, *loc. cit.*). It was used in conjunction with a solution condenser of the type described by Jenkins and Sutton (J., 1935, 609) for the measurements at 25°; and with the one described by Hampson (*Trans. Faraday Soc.*, 1934, **30**, 877) for the measurements at higher temperatures.

The experimental methods and techniques were those used before.

Refractive indices were measured as before.

Densities at 25° were measured by a Sprengel-Ostwald pyknometer; those at higher temperatures with the one described by Hampson (*loc. cit.*).

As before, all dielectric constants are based upon an assumed standard value of 2.2727 for that of pure dry benzene at 25° (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, **A**, **123**, 664; Sugden, J., 1933, 768). Refractive indices of pure solvents were measured absolutely, and those of solutions differentially, relative to solvent. The symbols used have the following meaning:  $f_2$ , molecular fraction of solute;  $d_4^t$ , density at  $t^\circ$ ;  $n_4^t$ , refractive index at  $t^\circ$  for wave-length  $\lambda$ ;  $P_2$ , molecular total polarisation of solute;  ${}_E P_2$ , molecular electron polarisation of solute.

The visible absorption spectra of the coloured acetylacetonates were investigated by Mr. M. W. Lister, using a Hilger-Nutting spectrophotometer. He found that the ferric compound has a maximum absorption at  $\lambda < 5300$  Å., the cobaltic compound one at 5900 Å., and a minimum at 5135 Å., and the chromic compound a maximum at 5600 Å. and a minimum at 4870 Å. The refractivities of solutions of the ferric and chromic compounds were measured for the mercury yellow line (5780 Å.) and that of the cobaltic one for the mercury green line (5461 Å.); hence, from the usual dispersion theory, it may be seen that the observed electron polarisations may be somewhat high for the ferric and chromic compounds, but low for the cobaltic one. The true  $P_2 - {}_E P_2$  values, for  $\lambda = \infty$ , may therefore be more than those given for the first two compounds, but less for the last one. They would be still more diverse, in fact, though to no great extent, since the corrections are not likely to be more than a few c.c.

#### DISCUSSION.

The results of the measurements at 25° are summarised in Table XI;  $\mu$  is the apparent dipole moment.

TABLE I.  
*Beryllium Acetylacetonate.*

(a) In benzene.					
$f_2$ .	$d_{42}^{25}$ .	$\epsilon$ .	$n_{5461}^2$ .	$P_2$ .	$\epsilon P_2$ .
0.0000	0.8733	—	2.25712	—	—
0.01076	0.8781	2.2944	2.25918	86.73	60.04
0.01458	0.8803	2.3029	2.26000	86.44	58.78
0.020785	0.8828	2.3181	2.26117	88.86	59.22
$P_2 = 87.34$ c.c.; $\epsilon P_2 = 59.35$ ; $P_2 - \epsilon P_2 = 27.99$ c.c. $\mu = 1.16 \times 10^{-18}$ e.s.u.					
(b) In carbon tetrachloride.					
0.0000	1.5845	2.2261	2.1329	—	—
0.01028	1.5746	2.2463	2.1386	87.45	61.75
0.01122	1.5740	2.2488	—	88.22	—
0.01474	1.5706	2.2533	2.1389	87.57	59.27
0.021165	1.5643	2.2682	2.1435	88.00	60.87
0.02769	1.5580	2.2795	2.1468	87.21	61.03
$P_2 = 87.7$ c.c.; $\epsilon P_2 = 60.9$ c.c.; $P_2 - \epsilon P_2 = 26.8$ c.c.					
(c) In <i>n</i> -hexane.					
0.0000	0.6641	1.8876	1.8998	—	—
0.01043	0.6704	1.9051	1.9070	87.41	61.49
$P_2 = 87.4$ c.c.; $\epsilon P_2 = 61.5$ c.c.; $P_2 - \epsilon P_2 = 26.5$ c.c.					
(d) In chloroform.					
0.0000	1.4795	—	2.0920	—	—
0.00565	1.4747	4.6865	2.0965	68.58	61.62
0.00994	1.4711	4.6569	2.1001	64.60	61.87
0.01122	1.4701	4.6457	2.1008	65.44	61.30
0.01808	1.4641	4.5947	2.1049	64.26	60.66
$P_2 = 64.8$ c.c.; $\epsilon P_2 = 61.4$ c.c.; $P_2 - \epsilon P_2 = 3.4$ c.c.					
(e) In carbon disulphide (measurements by Mr. N. Davidson).					
0.0000	1.2662	2.6332	—	—	—
0.00912	1.2496*	2.6541	—	88.0	—
0.01400	1.2461	2.6611	—	85.9	—
0.01491	1.2454	2.6644	—	86.9	—
$P_2 = 87$ c.c.					

TABLE II.  
*Beryllium Acetylacetonate in Decalin.*

$f_2$ .	$T$ , K.	$d_{42}^{25}$ .	$\epsilon$ .	$P_2$ .	$f_2$ .	$T$ , K.	$d_{42}^{25}$ .	$\epsilon$ .	$P_2$ .
0.0000	298°	0.8625	2.1608	—	0.01889	298°	0.8671	2.1830	86.91
	338	0.8318	2.1076	—		338	0.8364	2.1285	86.63
	373	0.8050	2.0614	—		373	0.8094	2.0808	86.24
	415	0.7729	2.0059	—		415	0.7771*	2.0233	85.10
* From graph.									

TABLE III.  
*Aluminium Acetylacetonate, at 25°.*

(a) In benzene.					
$f_2$ .	$d_{42}^{25}$ .	$\epsilon$ .	$n^2$ .	$P_2$ .	$\epsilon P_2$ .
0.0000	0.8735	—	2.2571	—	—
0.00582	0.8790	2.2932	2.2619	133.45	—
0.00826	0.8816	2.3009	2.2627	131.16	90.73
0.01092	0.8840	2.3106	2.2656	132.23	92.17
0.01468	0.8876	2.3231	2.2669	131.70	90.25
$P_2 = 134.0$ c.c.; $\epsilon P_2 = 91.1$ c.c.; $P_2 - \epsilon P_2 = 42.9$ c.c.					
(b) In chloroform.					
0.0000	1.4794	—	2.0920	—	—
0.00425	1.4754	4.6828	2.0978	120.73	92.50
0.00777	1.4723	4.6662	2.1020	121.72	91.07
0.01139	1.4690	4.6508	2.1051	122.89	89.26
0.01402	1.4664	4.6399	2.1088	132.93	90.33

TABLE IV.

*Zinc Acetylacetonate, in Benzene at 25°.*

$f_2$ .	$d_{42}^{25}$ .	$\epsilon$ .	$n^2$ .	$P_2$ .	$\epsilon P_2$ .
0-00568	0-8795	2-2876	—	97-74	—
0-00653	0-8803	2-2948	—	108-94	—
0-00742	0-8812	2-2980	—	109-38	—

TABLE V.

*Copper Acetylacetonate, in Chloroform at 25°.*

0-0000	1-4795	—	2-0920	—	—
0-00415	1-4791	4-6913	2-0969	66-67	65-73
0-00486	1-4792	4-6765	2-0972	67-96	63-66
0-00736	1-4789	4-6725	—	67-04	—
0-00998	1-4788	4-6487	—	68-96	—

 $P_2 = 67.7$  c.c.;  $\epsilon P_2 = 65.7$  c.c.;  $P_2 - \epsilon P_2 = 2.0$  c.c.

TABLE VI.

*Ferric Acetylacetonate, in Benzene at 25°.* $(\lambda = 5780)$ .

0-0000	0-8733	—	2-2580	—	—
0-00318	0-8774	—	2-2624	—	91-54
0-00400	0-8784	2-2909	—	148-35	—
0-00639	0-8815	2-3018	—	148-07	—
0-01201	0-8886	2-3270	—	147-79	—
0-01447	0-8918	2-3382	—	147-67	—

 $P_2 = 148.6$  c.c.;  $\epsilon P_2 = 91.5$  c.c.;  $P_2 - \epsilon P_2 = 57.1$  c.c.

TABLE VII.

*Cobaltic Acetylacetonate, in Benzene at 25°.*

0-0000	0-8734	—	2-2571	—	—
0-00371	0-8788	2-2854	2-2627	127-25	100-16
0-00552	0-8814	2-2927	2-2650	130-34	98-55
0-00920	0-8866	2-3047	—	128-56	—
0-01082	0-8888	2-3115	—	130-45	—

 $P_2 = 129.5$  c.c.;  $\epsilon P_2 = 99.4$  c.c.;  $P_2 - \epsilon P_2 = 30.1$  c.c.

TABLE VIII.

*Chromic Acetylacetonate, in Benzene at 25°.* $(\lambda = 5780)$ .

0-0000	0-8735	—	2-2580	—	—
0-00484	0-8797	2-2910	2-2634	135-48	95-64
0-00655	0-8819	2-2982	2-2651	137-03	95-06
0-00851	0-8844	2-3064	2-2665	138-08	(93-74)
0-01256	0-8894	2-3214	—	137-25	—

 $P_2 = 137.5$  c.c.;  $\epsilon P_2 = 95.3$  c.c.;  $P_2 - \epsilon P_2 = 42.2$  c.c.

TABLE IX.

*Thorium Acetylacetonate, in Benzene at 25°.*

0-0000	0-8736	—	2-2571	—	—
0-00522	0-8910	2-3025	2-2628	195-67	127-53
0-00703	0-8970	2-3124	2-2649	194-58	127-19
0-00826	0-9008	2-3194	2-2662	195-59	127-72
0-01252	0-9144	—	2-2710	—	127-57

 $P_2 = 195.6$  c.c.;  $\epsilon P_2 = 127.5$  c.c.;  $P_2 - \epsilon P_2 = 67.8$  c.c.

TABLE X.

*Zirconium Acetylacetonate, in Benzene at 25°.*

0-0000	0-8736	—	2-2571	—	—
0-01050	0-8933	0-3276	2-2686	185-44	123-52

 $P_2 = 185.4$  c.c.;  $\epsilon P_2 = 123.5$  c.c.;  $P_2 - \epsilon P_2 = 61.9$  c.c.

TABLE XI.

Metal.	Solvent.	$P_2$ .	${}_E P_2$ .	$P_2 - {}_E P_2$ .	$\mu$ .	$100(P_2 - {}_E P_2)/{}_E P_2$ .
Be	Benzene	87.3	59.4	28.0	1.16	47.1
	Carbon tetrachloride	87.7	60.9	26.8	1.14	44.0
	<i>n</i> -Hexane	87.4	60.9	26.5	1.13	43.5
	Decalin	86.9	(61)	25.9	1.12	42.5
	Chloroform	64.8	61.4	3.4	0.4	5.5
	Carbon disulphide	87	(61)	26	1.12	42.5
Zn	Benzene	(100)	(62)	(38)	(1.35)	(61)
Cu <sup>II</sup>	Chloroform	67.7	65.7	2.0	0.31	3.0
Al	Benzene	134.0	91.1	42.9	1.44	47.1
	Chloroform	122.3	90.8	31.5	1.23	34.7
Fe <sup>III</sup>	Benzene	148.6	91.5	57.1	1.66	62.4
Co <sup>III</sup>	"	129.5	99.4	30.1	1.20	30.3
Cr <sup>III</sup>	"	137.5	95.3	42.2	1.43	44.3
Th	"	195.6	127.5	67.8	1.81	53.2
Zr	"	185.4	123.5	61.9	1.73	50.1

The large differences between  $P_2$  and  ${}_E P_2$ , especially those for the ferric, thorium, and zirconium compounds, show beyond doubt the reality of the phenomenon which we set out to discuss, and emphasise the need for its explanation. It will be noticed that, provided we exclude results in polar solvents, the following generalisations hold:

(1)  $P_2 - {}_E P_2$  is as much as 60% of  ${}_E P_2$  in one case, and is about 45% of it in most of the others.

(2)  $P_2 - {}_E P_2$  shows only second order dependence on the solvent.

(3) The  $P_2 - {}_E P_2$  values fall into three groups having rough ratios of 2 : 3 : 4 (taking that for the beryllium compound as 28, the values would be 28, 42, 56) as the compounds have two, three, or four chelate rings; but there are considerable variations in each group.

There are five possible explanations of these facts:

(1) That the compounds, although fully chelated, are polar because the chelate rings lack sufficient symmetry.

(2) That the compounds are not fully chelated.

(3) That these compounds have very large atom polarisations.

(4) That the molecules bend considerably under thermal collisions, and remain bent long enough to orient as dipoles in the field applied for measurement of total polarisation.

(5) That there is a solvent effect, either of the Jenkins-Bauer type or of the Sutton-Frank type, or both.

We may consider the implications of these, one by one.

*Polar Chelate Molecules.*—As previously remarked, the first possibility has an important bearing on modern molecular structure theory, because this predicts that the fully chelated compounds would be non-polar. One older representation of a  $\beta$ -diketone chelate ring (Sidgwick, "The Electronic Theory of Valency," Oxford, 1927, p. 120) shows it as being asymmetric about at least two of three mutually perpendicular planes, the XZ and XY planes (Fig. 1). Another, the structure with three-electron and one-electron

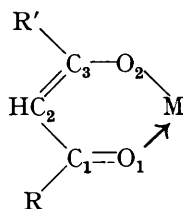
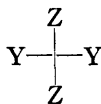


FIG. 1A.



X axis perpendicular to plane of paper.

FIG. 1.

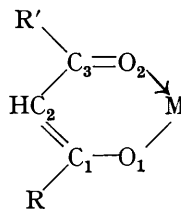


FIG. 1B.

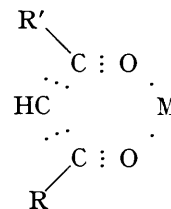


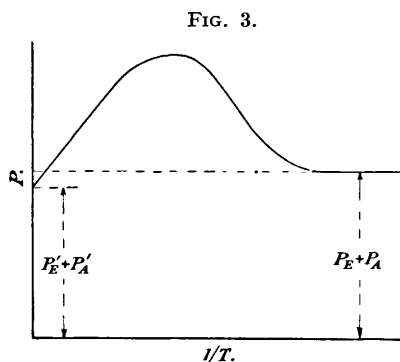
FIG. 2.

bonds (Fig. 2), is asymmetric only about the XZ plane, but is highly improbable on modern theory (Pauling, *J. Amer. Chem. Soc.*, 1931, 53, 3225). What is now considered to be the true state of affairs is that the molecule may be thought of as a hybrid derived from both structures 1A and 1B. On modern theory such "resonance" is not merely

possible but inevitable, because the energy contents of the two are similar (are equal if  $R = R'$ ), the positions of the atomic nuclei are much the same in both, and the number of unpaired electron spins is equal in both (to zero) (see Sidgwick, J., 1936, 533; 1937, 694). There should therefore be no asymmetry about the XY plane. Moreover, it is improbable that there is any about the YZ plane, for on classical stereochemical principles structure 1A requires that atoms M, O<sub>1</sub>, C<sub>1</sub>, C<sub>2</sub> be coplanar, likewise C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, O<sub>2</sub>; while structure 1B requires that O<sub>1</sub>, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, likewise C<sub>2</sub>, C<sub>3</sub>, O<sub>2</sub>, M, be coplanar. The only way in which all four requirements may be satisfied is for all the atoms to be coplanar. This argument may be criticised for its being based on a mixture of classical and wave-mechanical principles, but the conclusion is nevertheless very probable.

The acetylacetonate ring, with  $R = R'$ , should be derived equally from structures 1A and 1B, and so should have a moment only along the Y axis. Thus, compounds with two such rings on four tetrahedral or square diagonal bonds, three on octahedral bonds, or four on cubic diagonal bonds, should be non-polar.

If, however, the ring were polar perpendicular to the Y axis, and the several rings in a molecule had equal moments, the resultant moments would be in the ratio  $\sqrt{2} : \sqrt{3} : 2$ , and the orientation polarisations in the ratio 2 : 3 : 4, for compounds with two, three,



and four rings respectively. The polarisation would obey the Debye law, that  $P = A + B/T$  ( $T =$  absolute temperature) in solution, although the slope  $B$  would not be exactly that for the moment obtained at one temperature from the total and the electron polarisations because of solvent effects (see H. O. Jenkins, *Trans. Faraday Soc.*, 1934, 30, 739).

*Incomplete Chelation.*—On general chemical grounds it seems unlikely that incompleteness of chelation would be so extensive as to account for the moments, particularly in such a stable compound as beryllium acetylacetonate, but Sugden has tentatively suggested that this might be the cause of parachor anomalies in some beryllium  $\beta$ -diketone derivatives (J., 1929, 322), and we must consider its consequences.

The polarisation would not obey the Debye law, because the completeness of chelation would vary with temperature, almost certainly decreasing as the temperature rises, and so would the effective moment of the un-chelated molecules, owing to the possibilities of change of moment with change of configurational potential energy. Thus, at low temperatures the only polarisations would be those of deformation, and at an infinitely high temperature this would again be true, so the  $P-1/T$  curve would be qualitatively as represented in Fig. 3.

Absence of any simple relation between the number of rings and the polarisation, and considerable dependence of the latter upon the solvent, would also be predicted.

*Atom Polarisation.*—At present too little is definitely known about atom polarisation for the inherent probability of the third explanation to be estimated. Van Vleck (*loc. cit.*) has shown that it is certainly very small in some simple di- and tri-atomic molecules, but he does not rule out the possibility that it may be considerably greater in more complex molecules, such as are all those which concern us. The largest atom polarisation determined directly by refractivity measurements in the infra-red is 11.7, for glycerol (Cartwright and Errera, *Proc. Roy. Soc.*, 1936, A, 154, 138).

Atom polarisation would be independent of solvent or of temperature. Regarding its variation in the acetylacetonates, it is difficult to say more than that it should increase when the number of rings increases, but that it should also depend upon the nature of the central atom.

*Moment by Bending.*—This theory was advanced by Hampson (*Trans. Faraday Soc.*, 1934, 30, 877) to explain the apparent moments of diphenylmercury and some derivatives: it is closely related to the theory advanced by Meyer (*Z. physikal. Chem.*, 1930, B, 8, 27) to explain the temperature variation of the moments of ethylene dichloride and similar

compounds, and which has been developed by Smyth, Dornste, and Wilson (*J. Amer. Chem. Soc.*, 1931, **53**, 4242), by Lennard-Jones and Pike (*Trans. Faraday Soc.*, 1934, **30**, 830), and by Altar (*J. Chem. Physics*, 1935, **3**, 460).

Molecules such as the acetylacetonates may be non-polar in their configurations of minimum potential energy, but certainly are not so when bent out of these. Hence, the average value of  $\mu^2$  for a vibrating molecule is not zero, nor therefore is the polarisation. If we suppose the molecule to be vibrating in simple harmonic motion of small amplitude then the average polarisation,  $\bar{P}$ , may readily be calculated by classical methods.

Let the angle between two dipoles, each of magnitude  $\mu_1$ , be  $\pi - \phi$ ; then the resultant moment is  $2\mu_1 \sin \phi/2$ , and the potential energy may be written  $V_0 \phi^2/2$ . Applying Maxwell-Boltzmann statistics to the vibrational degree of freedom, we have

$$\bar{P} = \frac{4\pi N}{9kT} \bar{\mu}^2 = \frac{4\pi N}{9kT} \cdot \mu_1^2 \frac{\int_{-\infty}^{+\infty} \phi^2 e^{-V_0 \phi^2/2kT} d\phi}{\int_{-\infty}^{+\infty} e^{-V_0 \phi^2/2kT} d\phi} = \frac{4\pi N \mu_1^2}{9V_0} * \dots \quad (1)$$

Thus, the mean polarisation would be independent of temperature. It should be affected by solvent like the polarisation caused by a permanent, constant moment (for which, see Müller, *Trans. Faraday Soc.*, 1934, **30**, 729; H. O. Jenkins, *Nature*, 1934, **133**, 106; Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284; Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171), *i.e.*, the greater the dielectric constant of the solvent, the greater the departure from the polarisation in the vapour. Furthermore, if  $\bar{P}$  be observed and  $\mu_1$  be known,  $V_0$  can be calculated, and for the theory to be acceptable this force constant would have to be of reasonable magnitude for the molecule in question.

It is obvious that the period of vibration must be large compared with the time of relaxation, so that the molecule may have time to orient in the field as a dipole, while still bent one way. This time, for medium-sized molecules in the common non-polar solvents, is of the order  $10^{-11}$  to  $10^{-12}$  seconds (Debye, *Trans. Faraday Soc.*, 1934, **30**, 679; see also Cartwright and Errera, *loc. cit.*); the oscillation period would therefore have to be  $10^{-10}$  to  $10^{-11}$  seconds. Substances with polarisations arising from this cause should, therefore, absorb in the corresponding range of wave-length, *i.e.*, in the ultra-short wireless wave region of 3 — 30 mm.

For the theory to be consistent it is essential that the force constant calculated from equation (1) should give an admissible order of frequency for the vibration.

The polarisations of chelate compounds should be in the ratio of the number of rings, but be also dependent upon the nature of the central atom.

If the vibration is anharmonic, the problem approximates very closely to that of the polarisation of ethylene dichloride and like molecules, the chief difference being the precise form of the potential function. As will be shown in a later paper (p. 1279), the polarisation may increase or decrease with rise of temperature according to the sign of the anharmonic force constant. Treatment of this related problem by wave-mechanics (Lennard-Jones and Pike, *loc. cit.*) made very little difference except at very low temperatures, where the effect of zero-point energy becomes apparent. Owing to it, no molecule is ever still, and  $(\bar{\mu}^2)$  is never zero; so the  $P-1/T$  curve rises for large  $1/T$  values. This does not mean, as might appear, that for no molecule save a diatomic one can  $P = P_E + P_A$ , for when the period of vibration is less than the time of relaxation, the low-frequency polarisation depends not upon  $(\bar{\mu}^2)$  but upon  $(\bar{\mu})^2$  which, for a harmonic oscillator, or for an anharmonic one with only even-powered terms in the potential function, is zero.

*Solvent Effects.*—Any explanation of the abnormal polarisations based on solvent effect obviously requires that the anomalies should vanish in the vapour phase. The

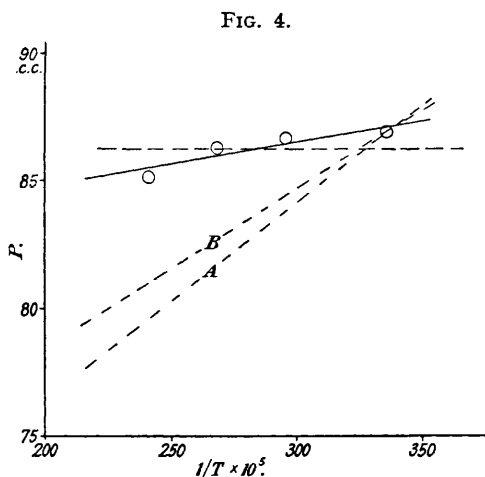
\* This relation is the limiting form of that obtained for an ethylene dichloride type of molecule by Lennard-Jones and Pike (*loc. cit.*, p. 849), when the temperature is low and the amplitude of the oscillations small.



two mechanisms for solvent effects so far considered require also that the polarisations should be much the same in *n*-hexane, benzene, and carbon tetrachloride, but that they should be about 30% higher in carbon disulphide; and that they should increase rapidly with increase of temperature, the coefficient for benzene or carbon tetrachloride solutions being + 0.0055°, *i.e.*, an increase of 55% for a 100° rise. Further, they require that the polarisations of the acetylacetonates should be in the ratio of the numbers of rings.

The data in Table XI obviously are insufficient to show which of these five theories is right; it is necessary in addition that measurements over a range of temperature should be made in solution and, ultimately, in the vapour phase. Such data for beryllium acetylacetonate in decalin solution are shown graphically in Fig. 4: vapour-phase results are described in a later paper by Coop and Sutton (p. 1269).

The mean-line change of  $P$  is a drop of 1.6 c.c. between 25° and 142.4°; but if a mean line parallel to the  $1/T$  axis be drawn, the average deviation from it is only 0.6 c.c., which is within the limit of experimental error. There is, therefore, no definite evidence for any temperature dependence of  $P$ . Curve  $A$  is the Debye curve for a moment of 1.12D: it corresponds to a change of 7.3 c.c. over the temperature range used. Curve  $B$  shows



the result of allowing for the effect of change of dielectric constant of solvent on polarisation: it corresponds to a change of about 5.85 c.c. Both theoretical curves are much steeper than the experimental one. High-frequency dispersion measurements made by Dr. F. C. Frank (private communication) on solutions of this substance in benzene show independently that the permanent moment is certainly less than 0.4D.

The absence of definite temperature dependence makes it most improbable that chelation is incomplete to any considerable extent; and it also throws doubt upon the theories of solvent effect so far advanced, although of course it does not rule out some other solvent effect. Another prediction of the Jenkins-Bauer and Sutton-Frank theories, *viz.*, that the polarisation should be higher in carbon disulphide than in other non-polar solvents (see above), is, as Table I shows, not fulfilled. The drop of  $P_2 - \epsilon P_2$  in chloroform is almost certainly due to drop in polarisation of the *solvent*, owing to dipole saturation in the neighbourhood of the local dipoles of the solute molecules (Frank, *loc. cit.*).

The remaining possibilities are atom polarisation and orientation polarisation by bending. If the latter is the cause, the vibrations must be nearly harmonic because of the temperature invariance, and we may therefore estimate  $V_0$ , the force constant. Equation (1) must be modified for beryllium acetylacetonate, because vibrations of the rings are at right angles instead of being coplanar: there are, in effect, two independent oscillators, each with a force constant  $V_0$ , and it may readily be shown that  $P = 8\pi N\mu^2/9V_0$ . Since there are both co-ordinate links and carbonyl groups in the rings,  $\mu_1$  is probably large, say 7.5D. (see p. 1284). Hence, since  $P = 27$  c.c.,  $V_0 = 3.7$  ergs/radian<sup>2</sup>/molecule. By assuming that the rings bend about the beryllium atom as a centre, a rough calculation of the period of oscillation may now be made and it gives a value of  $1 - 2 \times 10^{-12}$  sec. The time of relaxation of nitrobenzene in decalin or in benzene is  $4 - 5 \times 10^{-12}$  sec., so in order to suit the thermal polarisation theory the period of vibration should be not less than  $4 - 5 \times 10^{-11}$  sec. Actually it is at least thirty times less, *i.e.*, the ratio of force constant to reduced mass is at least nine hundred times greater than would be permitted on this theory.

As a result of the foregoing process of elimination we are led to conclude that the most probable cause of the anomalous polarisations of the acetylacetonates is the one originally suggested. The arguments are not conclusive, but the remaining uncertainties cannot

be settled without using vapour polarisation data. Such data are described and discussed later (p. 1269).

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