CCXCIV.—*Electrometric Titration Curves of Dibasic Acids. Part IV. Corrections for Interionic Effects and for Solvent Electrostriction. First and Second Dissociation Constants of some* n-*Paraffin* αω-*Dicarboxylic Acids, Alkyl- and Dialkyl-malonic Acids,* s-*Di- and -tetra-alkylsuccinic Acids,* β-*Alkyl- and* ββ-*Dialkyl-glutaric Acids, and Cyclic* 1 : 1-*Di-acetic Acids. Remarks on the Configurations and Molecular Dimensions of these Acids in Dilute Aqueous Solution.*

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IN our preliminary survey (Part I, J., 1928, 1594) of the possibility of measuring the distance between the carboxyl groups of a dibasic acid by utilising the hydrogen potentials obtaining during neutralisation, in conjunction with Bjerrum's theory concerning the effect of ionic substituents on electrolytic equilibria, we suggested that this theory was much too simple to warrant the expectation of quantitative accuracy. The theory is concerned with the propagation of electrical influences from an ionic centre to a focus of reaction situated elsewhere in the same molecule, and the sources of disturbance to which we referred may be summarised as follows: in the first place, polar transmission through the molecule itself is neglected; secondly, although account is taken of the propagation of the polar field through the medium, local variations in the properties of the medium are neglected.

We have shown, however, that despite these disturbances, measurements made by this method are not devoid of significance; for the direction of the errors and their relative importance in different examples can usually be foreseen on theoretical grounds, and in very many cases the first disturbance is negligible. Nevertheless, in the absence of appropriate corrections, the measurements remain qualitative, and therefore they ought to be used only for purposes of comparison and under certain other limitations which have been stated. We refer to this matter, not only because it is the starting point of the work to be described, but also because our data have been employed by others in contexts which appear to imply the ascription of more precise physical significance than we ourselves would care to claim.

In the previous papers of this series (Part I, *loc. cit.*; Part II, J., 1928, 2267; Part III, J., 1929, 1691) we have been concerned solely with the collation of our data with the available chemical evidence concerning constitutional effects on molecular configuration and valency direction. For that purpose only qualitative data are necessary, because the chemical evidence itself cannot be interpreted otherwise than qualitatively and comparatively. We have shown, however, that the physical data follow the indications of the chemical evidence quite as accurately as the limits of possible comparison allow.

The new method of approach to stereochemical problems having been justified to that extent, the next step appeared to be to attempt to advance it beyond the qualitative stage which at present limits the application of purely chemical arguments; and for that purpose it was necessary to give some attention to the sources of inaccuracy indicated above.

Of these, the first-mentioned disturbance is the less serious because it is the less general. Later in this paper we confirm our previous conclusion that internally transmitted polar effects become negligibly small after propagation through two, or at most three, saturated carbon atoms. Accordingly, a large class of structures exists for which the complication due to internal polar influences may justly be disregarded. These structures being available for the application of theory, we do not in this paper attempt to discuss the first error on quantitative lines, but confine ourselves to the second, more general, source of disturbance.

It may be added that we make no attempt here to discuss the difficulty which Bjerrum's theory and our own calculations share with many other theories that have been justified in application, namely, that of providing a rigidly logical substitute for the application of continuous conceptions to discontinuous matter in local regions. This type of difficulty is very well known; but the precedent for proceeding in spite of it, in the hope that the doubt which an imperfect *a priori* basis creates may be dispelled by *a posteriori* comparison with experience, is also well established.

Methods and Results.

Interionic Effects.—One part of the problem concerning the effect of media relates to the influence of dissolved ions, and it was necessary to consider this before the disturbance due to local variations in the properties of the solvent itself could profitably be attacked. One of the most obvious ways in which we might have dealt with the interionic influences is by modifying the method of calculation (see Part I) by a suitable application of Debye and Hückel's equation for the activities of electrolytes. This plan, however, involves

Table I.

Malonic acid.

Volume of original solution of acid = 150·0 c.c.
Molar concentration of acid solution = *C*.
" " " sodium hydroxide = *N*.

C	0·0500		0·0200		0·0100
N	0·9868		0·3903		0·1974
C.c.	$p_{\rm H}$.	C.c.	$p_{\rm H}$.	C.c.	$p_{\rm H}$.
0·00	2·055	0·00	2·324	0·00	2·457
1·00	2·254	1·06	2·459	1·00	2·602
2·00	2·459	2·03	2·619	2·00	2·787
3·00	2·626	3·01	2·771	3·01	2·860
3·70	2·770	4·04	2·959	4·00	3·022
4·40	2·923	4·96	3·141	5·01	3·218
5·10	3·072	6·01	3·386	6·00	3·460
5·91	3·291	6·98	3·746	7·01	3·861
6·70	3·582	7·53	4·169	8·02	4·494
7·50	4·035	8·02	4·384	9·00	4·908
8·20	4·436	8·60	4·662	10·01	5·194
9·10	4·789	9·00	4·815	11·00	5·418
10·01	5·054	10·11	5·145	12·03	5·646
10·99	5·265	11·02	5·347	13·00	5·888
12·10	5·520	12·08	5·493	14·00	6·203
13·20	5·797	13·06	5·744	14·70	6·448
14·40	6·261	14·00	6·019	14·90	6·800
14·70	6·491	14·58	6·380	15·00	6·971
14·90	6·720	15·07	6·736	15·11	7·188
15·00	6·934	15·38	7·650	15·20	7·789
15·10	7·269	15·63	9·847	15·30	9·397
15·20	7·767				
15·30	10·680				

C	0·0100		0·00400		0·00125
N	0·1951		0·09868		0·02467
C.c.	$p_{\rm H}$.	C.c.	$p_{\rm H}$.	C.c.	$p_{\rm H}$.
0·00	2·460	0·00	2·720	0·00	3·002
1·01	2·597	1·00	2·836	1·00	3·122
2·02	2·724	2·00	2·973	2·00	3·232
2·98	2·863	3·00	3·134	3·00	3·339
3·99	3·027	3·70	3·254	4·00	3·454
5·01	3·212	4·50	3·470	5·00	3·616
6·04	3·442	5·30	3·767	6·00	3·837
7·03	3·822	6·00	4·217	7·00	4·150
7·55	4·178	6·81	4·736	8·00	4·577
8·06	4·470	7·51	5·067	9·00	4·952
8·54	4·690	8·20	5·295	10·00	5·234
9·01	4·850	9·00	5·527	11·01	5·466
10·03	5·171	9·90	5·775	12·00	5·701
11·97	5·380	10·70	6·033	13·01	5·934
11·98	5·608	11·50	6·396	14·01	6·288
13·04	5·870	11·70	6·564	14·80	6·390
14·03	6·170	11·91	6·817	14·94	6·579
14·56	6·413	12·04	7·065	15·05	6·803
15·07	6·759	12·15	8·076	15·21	7·310
15·28	7·231	12·30	9·647	15·30	8·093
15·47	9·162			15·39	9·799
15·56	10·747			15·45	10·812
15·61	11·232				

practical difficulties, and after a brief trial we discarded it in favour of the following empirical process.

This involved the determination of the potentiometric titration curves for each acid for a series of concentrations decreasing to near the limit beyond which the accuracy of the measurement of potential begins to be impaired.

The acids were purified by repeated crystallisation before use (compare Part II, p. 2270, footnote), and the potential measurements were carried out and standardised and the results calculated exactly as described in Part I. We found that the requisite precision was not obtained at concentrations much smaller than $M/1000$, and, accordingly, $M/800$ was taken as our limit of dilution. Table I contains the detailed data for malonic acid, and the corresponding K values (together with the pair recorded in Part I) are shown in Table II.

Table III summarises the results for all the acids which we have examined by the above method, and it includes data relating to a number of acids which have not previously been investigated at all by potentiometric means—for instance, several alkyl-malonic and -glutaric acids and the five symmetrically alkylated succinic acids (stereoisomerides are distinguished by their m. p.'s in the table).

When these data were plotted it was seen that, above a certain dilution, the K's varied slowly and linearly with the concentration. It followed that a linear extrapolation would yield the K values which should pertain to conditions under which interionic effects are negligible. These extrapolated values are collected together in Table III under the heading " corr. to $\mu = 0$."

TABLE II.

Acid.	10^2C.	10^4K_1.	10^7K_2.	Acid.	10^2C.	10^4K_1.	10^7K_2.
			Normal acids.				
Oxalic	1·000	620	845	Glutaric	1·000	0·463	56·5
	0·400	605	730		0·673	0·460	53·4
	0·125	594	674		0·200	0·455	42·1
Malonic	5·000	17·7	41·2		0·125	0·452	40·0
	4·991	17·7	43·7	Adipic	1·000	0·391	60·8
	2·000	15·8	25·5		0·675	0·390	52·9
	1·000	15·3	24·3		0·250	0·385	45·0
	1·000	15·4	23·8		0·125	0·384	41·6
	0·400	15·1	21·1	Pimelic	0·483	0·333	48·7
	0·125	14·9	21·2		0·400	0·330	46·8
Succinic	5·000	0·734	46·1		0·250	0·330	42·6
	4·880	0·736	45·0		0·125	0·327	40·3
	2·000	0·678	37·8	Suberic	0·330	0·307	47·1
	1·000	0·659	36·6		0·125	0·307	42·0
	0·400	0·648	35·0		0·125	0·304	42·5
	0·125	0·644	33·5	Azelaic	0·125	0·281	41·4
					0·125	0·283	40·5

TABLE II (*contd.*).

Acid.	10^2C.	10^4K_1.	10^7K_2.	Acid.	10^2C.	10^4K_1.	10^7K_2.
Substituted malonic acids.							
Methyl-	5·040	10·7	34·3	Dimethyl-	5·560	8·27	15·3
	1·000	9·21	19·2		1·000	7·00	10·0
	0·360	9·02	19·5		0·400	6·97	8·75
	0·125	9·00	18·2		0·125	6·85	9·22
Ethyl-	5·905	12·6	28·1	Methylethyl-	1·000	14·5	4·29
	1·000	10·5	17·2		0·400	13·5	4·00
	0·400	10·5	14·8		0·125	13·7	3·96
	0·125	10·3	15·1	Diethyl	1·060	62·6	0·60
n·Propyl·	1·622	10·7	20·8		0·610	62·3	0·59
	1·000	10·4	16·6		0·420	61·7	0·56
	0·400	10·2	16·3		0·133	61·5	0·51
	0·125	10·2	14·5	Ethyl·*n*-propyl-	1·000	73·5	0·45
*iso*Propyl-	1·000	11·7	17·5		0·400	72·5	0·40
	0·767	11·7	15·9		0·125	71·8	0·38
	0·400	11·5	14·0	Di·*n*-propyl	0·381	86·7	0·34
	0·125	11·5	13·5		0·125	86·1	0·32
Substituted succinic acids.							
αα′·Dimethyl- (209°)	1·000	1·75	13·9	αα′-Diethyl· (192°)	0·750	2·39	3·75
	0·400	1·72	12·1		0·375	2·35	3·73
	0·125	1·70	11·8		0·125	2·34	3·48
αα′·Dimethyl· (129°)	1·000	1·19	7·02	αα′-Diethyl- (129°)	0·750	3·20	2·83
	0·400	1·16	6·74		0·375	3·15	2·71
	0·200	1·18	6·56		0·125	3·14	2·57
	0·125	1·16	6·46	Tetramethyl·	0·750	3·30	0·58
	0·125	1·15	6·44		0·375	3·24	0·56
					0·125	3·21	0·53
Substituted glutaric acids.							
β-Methyl	1·000	0·577	6·37	ββ·Dimethyl·	1·000	2·06	5·53
	0·675	0·575	6·28		0·800	2·03	5·51
	0·200	0·567	6·02		0·250	2·00	5·20
	0·125	0·565	5·99		0·125	1·98	5·16
β·Ethyl-	1·000	0·537	5·10	ββ·Methylethyl·	1·000	2·47	2·16
	0·500	0·528	4·84		0·500	2·42	2·05
	0·250	0·521	4·79		0·250	2·41	2·01
	0·125	0·518	4·74		0·125	2·42	2·01
β·*n*·Propyl·	0·500	0·507	4·52	ββ·Diethyl·	0·545	3·40	0·79
	0·477	0·497	4·32		0·400	3·40	0·78
	0·250	0·492	4·21		0·125	3·38	0·76
	0·125	0·490	4·15	ββ-Di·*n*-propyl·	0·125	2·06	0·51
					0·125	2·04	0·49
Cyclic 1 : 1·*diacetic acids.*							
*cyclo*Pentane-	0·500	1·67	2·65	*cyclo*Hexane-	0·223	3·36	1·03
	0·342	1·68	2·64		0·125	3·34	1·00
	0·250	1·66	2·60		0·125	3·34	0·99
	·125	1·67	2·60	*cyclo*Heptane·	0·125	2·79	1·09
					0·125	2·78	1·11

TABLE III.

	10^4K_1 (25°).			10^7K_2 (25°).
Acid.	Potentiometric (corr. to $\mu = 0$).	Conductivity values (from literature).	References.	Potenti metric (corr. to $\mu = 0$
Normal acids.				
Oxalic	590	380, 570, 570	6, 11, 12	See below
Malonic	14·9	17·1, 15·8, 14·1, 16·3	1, 15, 22, 26	
Succinic	0·641	0·665, 0·652	15, 21	
Glutaric	0·453	0·475, 0·473, 0·469, 0·471	15, 18, 19, 21	
Adipic	0·382	0·371, 0·376, 0·377	15, 18, 21	
Pimelic	0·328	0·348, 0·323, 0·322	2, 18, 21	
Suberic	0·304	0·311, 0·258, 0·299, 0·304	1, 15, 18, 21	
Azelaic	0·281	0·296, 0·253, 0·288	1, 18, 21	
Substituted malonic acids.				
Methyl-	8·92	8·7, 7·99, 8·6	15, 22, 23	17·5
Ethyl-	10·3	12·7, 12·0, 10·3	15, 20, 22	14·7
n-Propyl-	10·1	11·3, 11·5, 11·2	1, 14, 23	14·3
*iso*Propyl-	11·4	12·7, 13·5, 13·2	1, 14, 20	13·2
Dimethyl-	6·83	7·2, 7·2, 6·57	15, 20, 22	8·72
Methylethyl-	13·8	16·7, 16·5, 13·9, 16·1	1, 20, 22, 23	3·86
Diethyl-	61·5	75·0, 85, 63·9	14, 17, 22	0·51
Ethyl-*n*-propyl-	71·6	116, 73·7	14, 22	0·37
Di-*n*-propyl-	85·8	119, 112, 100, 90	14, 18, 20, 22	0·31
Substituted succinic acids.				
αα′-Dimethyl- (209°)	1·70	2·04, 1·91, 1·94, 1·96, 2·08, 1·91	1, 3, 4, 5, 9, 23	11·6
„ (129°)	1·15	1·22, 1·32, 1·23, 1·38	3, 4, 5, 9	6·36
αα′-Diethyl- (192°)	2·33	2·35, 2·45	9, 23	3·47
„ (129°)	3·11	3·47, 3·43	9, 23	2·54
Tetramethyl-	3·19	3·14, 3·11	1, 9	0·52
Substituted glutaric acids.				
β-Methyl-	0·565	0·600, 0·590	19, 23	5·96
β-Ethyl-	0·517	0·529	19	4·69
β-*n*-Propyl-	0·487	—	—	4·11
ββ-Dimethyl-	1·98	2·21, 1·98, 2·00	16, 19, 24	5·10
ββ-Methylethyl-	2·40	2·44	19	2·00
ββ-Diethyl-	2·38	—	—	0·75
ββ-Di-*n*-propyl-	2·05	—	—	0·49
Cyclic 1 : 1-*diacetic acids.*				
*cyclo*Pentane-	1·66	1·73	19	2·58
*cyclo*Hexane-	3·34	—	—	0·99
*cyclo*Heptane-	2·78	—	—	1·10

	10^7K_2 (25°). [See also above, col. 5.]		
Acid.	Potentiometric (corr. to $\mu = 0$).	From literature (salts present).	References and method.
Normal acids.			
Oxalic	640	490, 720, 690	8, 11, 12
Malonic	20·3	20, 21, 13·6	7, 8, 10
Succinic	33·3	29, 27, 43	8, 10, 13
Glutaric	38·0	29	8
Adipic	38·7	—	—
Pimelic	37·7	44	7
Suberic	39·5	28, 33	7, 25
Azelaic	38·5	28·5, 43	8, 25

References and Methods :—(1) Bethmann, *Z. physikal. Chem.*, 1890, **5**, 401. (2) *Idem*, *Annalen*, 1893, **275**, 360. (3) Bischoff and Walden, *Ber.*, 1889, **22**, 1821. (4) Boeseken, Schweizer, and van der Wart, *Rec. trav. chim.*, 1912, **31**, 100. (5) Bone and Sprankling, J., 1899, **75**, 863. (6) Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 713. (7) *Idem*, *ibid.* (by partition). (8) *Idem*, *ibid.* (by conductivity of acid salt). (9) Crum Brown and Walker, *Annalen*, 1893, **274**, 44. (10) Datta and Dhar, J., 1915, **107**, 827 (by solubility of CO_2). (11) Dawson and Smith, J., 1929, 2539 (by catalysis). (12) Drucker, *Z. physikal. Chem.*, 1920. **96**, 381. (13) McCoy, *J. Amer. Chem. Soc.*, 1908, **30**, 692 (by partition). (14) Meldrum, *J. Physical Chem.*, 1911, **15**, 477. (15) Ostwald, *Z. physikal. Chem.*, 1889, **3**, 282. (16) Pfaff, *Annalen*, 1896, **292**, 146. (17) Salm, *Z. physikal. Chem.*, 1908, **63**, 97. (18) Smith, *ibid.*, 1898, **25**, 194. (19) Spiers and Thorpe, J., 1925, **127**, 538. (20) Springer and Jones, *Amer. Chem. J.*, 1915, **48**, 423. (21) Voermann, *Rec. trav. chim.*, 1904, **23**, 277. (22) Vogel, J., 1929, 1476. (23) Walden, *Z. physikal. Chem.*, 1891, **8**, 451. (24) Walker, *Annalen*, 1896, **292**, 146. (25) Wegscheider, *Monatsh.*, 1902, **23**, 625 (by conductivity of acid salt). (26) White and Jones, *Amer. Chem. J.*, 1910, **44**, 171.

Table III also contains a number of previously recorded values of K_1 and K_2 for comparison with our own results. The tabulated values of K_1 are those obtained by the conductivity method * at 25°, and moderately good agreement with our extrapolated values of K_1 is to be expected because the conductivity method is inherently less affected than most others by interionic disturbances. Except in the case of a few of the older determinations, and some of the measurements on the stronger acids (such as oxalic and dipropylmalonic) which give poor results by conductivity, the agreement is moderate to good. The few available values of K_2 which are set out in the lower part of the table include determinations at or about 25° by various methods which are indicated in the references. It is a general defect of these methods that salt effects are present, and for this reason nothing more than a rough comparison of the results with our extrapolated values of K_2 would be justified.

From this point onward discussion will be based on the potentiometric values of K_1 and K_2 " corr. to $\mu = 0$."

Solvent Effects.—The problem presented by the attraction between the solvent molecules and the ions and the consequential changes in the properties of the solvent near ions, cannot readily be solved by any empirical method such as that employed in connexion with interionic effects, and we are forced to rely on the results of calculation. The principal part of such a calculation consists in the evaluation of the electrical potential of an ion in a polar solvent, and this is considered in a separate paper (this vol., p. 2179) since the results have applications which are independent of the subject of the

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* Except that Dawson and Smith's value, obtained from experiments on catalysis, of K_1 for oxalic acid is included, since these authors correct for salt effects.

present series of communications. In that paper the potential is exhibited as a function $\psi(q, r)$ of the charge, q, on the ion and the distance, r, of the field-point from it; and the results of the evaluation of the function, ψ, are expressed partly in formulæ (31) and partly in tabulated numerical data (32). Furthermore, it is shown that the potential energy of a second ion, of charge q', in the field of the first can be represented (35) with sufficient accuracy as $q'\psi(q, r)$ except at distances which are so short that in any application such as that now contemplated the calculation would be vitiated in any case because of the neglect of intramolecular polar transmission.

Knowing the value of the mutual potential energy of the ions at any distance from each other, we are in a position to apply Boltzmann's distribution function and complete the calculation of the relation between the dissociation constants of a dibasic acid on the general lines laid down by Bjerrum. The result may be expressed

$$K_1/K_2 = 4e^{-\frac{q'\psi(q,r)}{kT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From the observational data for K_1 and K_2 ($q = 4{\cdot}774 \times 10^{-10}$, $k = 1{\cdot}371 \times 10^{-16}$, $T = 298{\cdot}2$) we can calculate ψ; and hence we can evaluate r, the distance between the ionic charges on the dibasic anion, by using the relations (31) and (32) referred to above.

Discussion.

(1) *The Normal Acids.*

Preliminary Considerations.—The values of r, computed from the observations in the manner described above, for the normal dicarboxylic acids, $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$, from oxalic acid to azelaic acid ($n = 0$—7), are assembled in Table IV under the heading "r (obs.)." The significance of the columns headed "r (max. ex obs.)" and "r (Calc.)" is explained later. All r-values are in Ångstrom units.

TABLE IV.

Acid.	n.	r (obs.).	r (max. ex obs.).	r (calc.).	Δr.	
Oxalic	0	3·37	—	3·54	− 0·17	
Malonic	1	3·43	—	4·26	− 0·83	
Succinic	2	5·58	7·18	5·87	− 0·29	Sum = + 0·02
Glutaric	3	7·11	9·66	6·84	+ 0·27	
Adipic	4	8·22	11·41	8·36	− 0·14	
Pimelic	5	9·43	13·25	9·43	± 0·00	
Suberic	6	11·07	15·71	10·88	+ 0·19	
Azelaic	7	12·03	17·10	12·04	− 0·01	

In order to compare the values of r based on observation with the indications of the molecular model, we want to know what kind of model to take—whether rigid or flexible. We reflect that the dimension which r represents is the distance between the ionic centres (points at which the net ionic charges may be supposed to be concentrated) in a dipolar ion, and the mutual repulsion of the charges might make an intrinsically flexible polymethylene chain simulate the behaviour of a rigid model. *Prima facie* considerations do not tell us whether the electrostatic repulsion would be strong enough to do this, and to obtain an answer we require to examine the statistics of the flexible model.

Effect of Molecular Pliability on the Dissociation Constants of a Symmetrical Dibasic Acid.—We can picture the ideally pliable molecule as consisting of two carboxyl groups attached to the ends of a string; the size of the carboxyl groups will set a minimal limit, r_1, to the extension, r, of the model, and the length of the string will set a maximal limit r_2. In mathematical terms this means that when $r_1 < r < r_2$ we neglect sources of potential energy of configuration other than that arising from the interaction of the charges on the bipolar ion; and that when r becomes $< r_1$ or $> r_2$ we assume that the potential energy becomes very great. The extension, r, has already been defined for the bivalent ion as the linear distance between the ionic centres; it is now defined for the univalent ion and for the acid molecule as the linear distance between points whose geometrical relation to the carboxyl carbon atoms is identical with that of the ionic centres in the bivalent ion. Under these conditions the equation * connecting the K-ratio with r_1 and r_2 is

$$K_1/K_2 = \frac{4}{3}(r_2^3 - r_1^3) \Big/ \int_{r_1}^{r_2} e^{-\frac{q\psi(q,r)}{kT}} r^2 . dr. \quad . \quad . \quad (2)$$

Now equation (1) is really an equation for rigid molecules, because, in its derivation, it is tacitly assumed that molecules of the same chemical species are geometrically similar; equation (2) pertains

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* Let A, U, and B respectively denote the numbers of acid molecules, univalent ions, and bivalent ions in a given volume; dA, dU, and dB will represent the numbers having extensions between r and $r + dr$, and K_{1r} and K_{2r} may be taken to symbolise the corresponding first and second dissociation constants. Then, having regard to the assumed constitution of the model, the application of statistics gives the relations

$$(dA/A) = (dU/U) = 3r^2 . dr/(r_2^3 - r_1^3)$$

$$dB/B = e^{-\frac{q\psi(q,r)}{kT}} r^2 . dr \Big/ \int_{r_1}^{r_2} e^{-\frac{q\psi(q,r)}{kT}} r^2 . dr$$

Introducing equation (1) (noting that $q' = -q$) in the form

$$K_{1r}/K_{2r} = 4e^{\frac{q\psi(q,r)}{kT}}$$

together with the mass-action relations

$$K_{1r}/K_{2r} = dU^2/dA . dB \quad \text{and} \quad K_1/K_2 = U^2/AB$$

we obtain the necessary equations with which to eliminate the unwanted variables and derive the result in the text.

to the pliable model. Suppose, now, that equation (1) has been applied to the observational data for pliable molecules. We may call the derived value of r the " effective extension " of the pliable molecule and denote it by $r_{\text{eff.}}$. Then, by comparing equation (1) ($r_{\text{eff.}}$ being written for r) with equation (2) (in which r_2 and r_1 are rewritten $r_{\text{max.}}$ and $r_{\text{min.}}$ respectively), we obtain a relation between the " effective extension " and the " maximal " and " minimal extension " of the molecule :

$$\psi(q, r_{\text{eff.}}) = \frac{kT}{q} \log_e\left[\frac{r^3{}_{\text{max.}} - r^3{}_{\text{min.}}}{3} \Big/ \int_{r_{\text{min.}}}^{r_{\text{max.}}} e^{-\frac{q\psi(q,r)}{kT}} r^2 \, . \, dr\right] \qquad (3)$$

Equation (3) can be solved graphically after the function ψ has been obtained from the accompanying paper (*loc. cit.*) and the definite integral has been evaluated by Runge's process. Corresponding values of $r_{\text{eff.}}$ and $r_{\text{max.}}$ have been calculated by assuming (i) $r_{\text{min.}} = 0$, and (ii) $r_{\text{min.}} = 3$ Å.U., and a selection of figures is given in Table V. From these it will be seen that for maximal extensions between 4 and 18 Å.U. the effective extensions range from about 70% to about 90% of the maximal extensions; it is also evident that the relationship between these two quantities is little sensitive to the assumed value of the minimal extension provided that this lies within reasonable limits.

TABLE V.

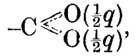
$10^8\, r_{\text{eff.}}$	4·00	5·00	6·00	7·00	8·00
$10^8\, r_{\text{max.}}$ ($r_{\text{min.}} = 0$)	4·79	6·48	8·13	9·76	11·30
$10^8\, r_{\text{max.}}$ ($r_{\text{min.}} = 3$ Å.U.)	4·56	6·22	7·89	9·49	11·06
$10^8\, r_{\text{eff.}}$	9·00	10·00	11·00	12·00	13·00
$10^8\, r_{\text{max.}}$ ($r_{\text{min.}} = 0$)	12·88	14·37	15·87	17·32	18·78
$10^8\, r_{\text{max.}}$ ($r_{\text{min.}} = 3$ Å.U.)	12·63	14·12	15·61	17·06	18·53

In applying these calculations to our experimental results, we have used $r_{\text{min.}} = 3$ Å.U. (which should not be very far from the truth), and the smallness of the difference caused by the use of the zero value shows that the effect of the uncertainty about the precise value of $r_{\text{min.}}$ is unimportant. On this basis, the values headed " r (obs.) " of Table IV have been treated as values of $r_{\text{eff.}}$ and translated, by means of Table V, into values of $r_{\text{max.}}$, which in Table IV are recorded under the heading " r (max. ex obs.)."

The Pliable Model.—When the values of " r (max. ex obs.) " are plotted against n, the number of polymethylene groups, the points approximate to a straight line the slope of which indicates a mean increase per methylene group of 1·9 Å.U. Now there are at least three conceivable types of pliable model, *viz.*, (1) " rotation-pliable " —those in which rotation around the valencies does not contribute appreciably to the energy of configuration, whilst the resistance to valency-deflexion and valency-extension is very great; (2) " deflexion-pliable"—those in which neither rotation nor alteration of the inter-valency angles sensibly affects the energy, whilst the resistance to valency-extension is great; and (3) "extension-pliable"—those in which rotation, deflexion, and a limited amount of extension make no great contribution to the molecular energy. In the first case the increase in $r_{\text{max.}}$ per methylene group should be $1{\cdot}54\ \sin(\theta/2)$ Ångstrom units, where θ is the angle between the carbon valencies of the methylene group; *i.e.*, it should be considerably less than 1·54 Å.U. In the second case the increase should be equal to 1·54 Å.U. Only in the third case can the increase be greater than 1·54 Å.U., and the application of this model to our results requires the assumption that there is no perceptible energy contribution due to distortion until the valencies have been pulled into a straight line and then *stretched* by over 20% of their original length. The intrinsic improbability of this is so great that we are compelled to give consideration to the rigid model.

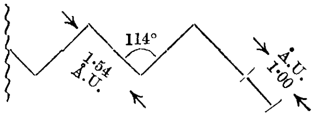
The Rigid Model.—When we plot the values of "r (obs.)" from Table IV against n, the points (except for $n = 1$) lie close to the straight line $10^8 r = 2{\cdot}98 + 1{\cdot}29n$. The figure 1·29 Å.U. for the mean increase in length for each added methylene group is a possible value, because it is close to that (1·27 Å.U.) found by Müller (*Proc. Roy. Soc.*, 1928, **120**, 437) by X-ray methods for long-chain hydrocarbons in the crystalline state. Also, the value of θ which satisfies the equation $1{\cdot}29 = 1{\cdot}54 \sin(\theta/2)$ is 114°, and this is a possible value for the intervalency angle, because we should expect this angle to be a little greater than the tetrahedral angle, $\cos^{-1}(-\frac{1}{3}) = 109{\cdot}5°$ (Ingold, J., 1920, **119**, 305).

Further Comparisons with the Model.—It will be realised that the pliable and rigid models represent limiting cases, the former implying that non-ionic resistance to flexure is negligible in comparison with ionic resistance, and the latter the converse relation. The conclusion to be drawn from our investigation of the two models is, then, that the non-ionic sources of potential energy of configuration are not only not negligible but are actually large enough to dominate the ionic sources. Accordingly, for the purpose of further comparisons with the experimental data, we must adopt the rigid model as the more appropriate to our problem.

(i) *Structure of the carboxylate ion.* The value 2·98 Å.U. given by the intercept of the linear graph on the axis $n = 0$ enables us to make an approximate estimate of the distance of the ionic centres in the carboxylate ions from the centres of the carboxyl carbon atoms. For reasons fully explained elsewhere, we regard the carboxylate ion as possessing an axis of symmetry,  $-\mathrm{C}\!\begin{smallmatrix}\nearrow \mathrm{O}(\frac{1}{2}q)\\ \searrow \mathrm{O}(\frac{1}{2}q)\end{smallmatrix}$, and it is therefore necessary only to locate the effective ionic centre on that axis. The distance of such a centre from the centre of the corresponding carboxyl carbon atom is, then,

$$\tfrac{1}{2}(2{\cdot}98 - 1{\cdot}29)/\sin\,(114^\circ/2) = 1{\cdot}00\ \text{Å.U.}$$

(ii) *Structure of the polymethylene chain.* The approximate conformity of the r–n relation to a straight-line law implies that the most appropriate model is the plane zig-zag, which is the familiar result of the X-ray examination of many normal-chain aliphatic compounds in the crystalline state. But the graph of the relationship between r and n required by this model is not accurately a straight line; it is a zig-zag the form of which can be calculated trigonometrically from the data expressed in the following diagram :



It is in this way that values tabulated under the heading " r (calc.) " are obtained for Table IV; the differences between these and values headed " r (obs.) " are also shown. The comparison is exhibited graphically in a later paper (this vol., p. 2178).

The r value for oxalic acid follows the indications of the model fairly closely, but this is probably an accidental result of the balancing of the various disturbances which affect this case (compare this vol., p. 2177). Malonic acid shows a deviation from the model which is well beyond experimental error. From succinic acid to azelaic acid, however, the divergences are comparatively small, the mean deviation from the mean being only 0·15 Å.U., *i.e.*, less than 2% of the mean computed distance. We deduce from this that, as the polymethylene chain grows, the internal transmission of polar influences from one carboxyl group to the other becomes so rapidly damped out that in succinic acid it has already become quite subsidiary to the effect of the external electric field. It will be appreciated that we are here studying on quantitative lines an important special case of what has been termed the " direct polar effect."

Comparison with X-*Ray Results.*—A number of the normal dibasic acids have been examined by the powder method by Trillat (*Compt. rend.*, 1925, **180**, 1330) and by Henderson (*Proc. Roy. Soc. Edin.*, 1928, **48**, 20). Both authors obtained a mean increase in the *principal spacing* of about 1·1 Å.U. per carbon atom. Müller and Shearer had found a similarly small value (1·0 Å.U.) for the mean increase for monobasic fatty acids (J., 1923, **123**, 2043, 3152, 3156), but, as the former author showed subsequently in the case of stearic acid, this is due to tilt between the axes of the zig-zags and the cleavage planes (*Proc. Roy. Soc.*, 1927, **114**, 542). Caspari's investigation of single crystals of adipic acid and a number of its higher normal homologues (J., 1928, 3235) shows that the same explanation applies to Trillat's and Henderson's results on these substances. For the mean increase in the *length of the molecule* for each added carbon atom, Caspari found 1·27 Å.U., which agrees well with our 1·29 Å.U., having regard to the difference of physical condition and of method.

Origin of the Forces Inhibiting Free Rotation.—The conformity of our results to the requirements of the rigid model does not, of course, imply complete molecular rigidity; but it does suggest that departures from the uniplanar zig-zag form are only brief occurrences.

The idea that a molecule, which is theoretically flexible on account of free rotation around the bonds, actually assumes a particularly simple and symmetrical geometrical form in the crystal is now a commonplace, and the result is usually ascribed to " packing," that is, to a form of *inter*molecular action. We know, moreover, again through X-ray diffraction experiments, that there are close analogies in the matter of molecular form between the crystalline state and the liquid state. For instance, Steward and Morrow showed for normal primary alcohols (*Physical Rev.*, 1927, **30**, 232), and Morrow showed for normal monocarboxylic acids (*ibid.*, 1928, **31**, 10), both in the state of liquid, that the mean spacing is a linear function of the number of carbon atoms in the chain. Moreover, the latter investigator found, for liquid monocarboxylic acids, that the mean increase *of spacing* per added methylene group was 1·0 Å.U.—exactly the same spacing difference as that which Müller and Shearer had observed for monocarboxylic acids in the crystalline state. The explanation was obviously the same, *viz.*, that in the liquid state the molecular axes are tilted to the effective planes, the angle of tilt being the same as that which obtains in the crystal. The analogies are, in fact, so close that it is difficult to avoid carrying over to the liquid state the ideas, originally applied to the crystal, about why theoretically flexible molecules assume a definite geometrical form; indeed, in a pure liquid the molecules are nearly as close to one another as they are in the solid, and hence, so far as *pure* liquids are concerned, there is no obvious need for supplementing the explanation based on intermolecular action. But this theory can hardly be still further extended to cover the case of a dilute solution, and thus our results, which relate to dilute solutions, very strongly suggest that, contrary to the general view, an important part (if not the whole) of the forces which in the crystal, in the liquid, *and in dilute solution*, inhibit rotation and tend to maintain a geometrically simple, favoured configuration, is *intra*molecular in origin. Some further discussion of the matter is contained in a later paper (this vol., p. 2179).

It may be added that our results contain evidence that the particular geometrical configuration here considered is essentially a property of the methylene group, and becomes modified in the presence of tertiary or quaternary carbon atoms.

The Malonic Acids.

The series of acids studied in Part III (*loc. cit.*) has been extended by the inclusion of methylethyl- and ethyl-*n*-propyl-malonic acid. The observational data, when reduced by means of formula (1), lead to the following values of the distance, r, between the carboxyl groups of malonic acids $RR'C(CO_2H)_2$.

		Monosubstituted.				Disubstituted.				
Type. RR′......	H_2.	MeH.	EtH.	$Pr^{\alpha}H$.	$Pr^{\beta}H$.	Me_2.	MeEt.	Et_2.	$EtPr^{\alpha}$.	Pr^{α}_2.
r (Å.U.)	3·43	3·51	3·44	3·42	3·38	3·40	3·15	2·75	2·70	2·67

This is a series of compounds in which internal polar effects inevitably influence the dissociation constants and hence cause a disturbance to configurational relationships deduced from these constants.

The theory of this case is explained in Part III, in which it is shown, *inter alia*, that the spatial sequence indicated by the hypothesis of valency deflexion, *viz.*,

$$\left.\begin{matrix} r \\ \text{large}\end{matrix}\right\} \cdots\cdots\cdots \overbrace{\mathrm{H_2}}^{A}>\overbrace{\mathrm{MeH}>\mathrm{EtH}>\mathrm{Pr^{\alpha}H}>\mathrm{Pr^{\beta}H}}^{B}>\overbrace{\mathrm{Me_2}>\mathrm{MeEt}>\mathrm{Et_2}>\mathrm{EtPr^{\alpha}}>\mathrm{Pr^{\alpha}_2}}^{C} \cdots\cdots\cdots \left\{\begin{matrix} r \\ \text{small}\end{matrix}\right.$$

should be modified owing to the polar influences by the displacement of series B, without internal derangement, to the left relatively to A, and by the displacement of series C, again without internal derangement, to the left relatively to the altered position of group B. The observed order illustrates these deductions :

$$\left.\begin{matrix} r \\ \text{large}\end{matrix}\right\} \cdots\cdots\cdots \underbrace{\mathrm{MeH}>\mathrm{EtH}>\overbrace{\mathrm{H_2}}^{A}>\mathrm{Pr^{\alpha}H}>\mathrlap{\overbrace{\phantom{\mathrm{Me_2}>\mathrm{Pr^{\beta}H}>\mathrm{MeEt}>\mathrm{Et_2}>\mathrm{EtPr^{\alpha}}>\mathrm{Pr^{\alpha}_2}}}^{C}}\mathrm{Me_2}>\mathrm{Pr^{\beta}H}}_{B}>\mathrm{MeEt}>\mathrm{Et_2}>\mathrm{EtPr^{\alpha}}>\mathrm{Pr^{\alpha}_2} \cdots\cdots\cdots \left\{\begin{matrix} r \\ \text{small}\end{matrix}\right.$$

Part III also contains a statement of theoretical requirement with regard to the relative intervals between the r-values of the different members of the series, and with regard to the effects to be expected from the superposition of polar and spatial influences on the first and second dissociation constants, considered individually. All that need be stated here is that the whole of that discussion is borne out, both in general and in detail, by the extended and more accurate results now submitted.

The Succinic Acids.

The symmetrical dialkyl and tetra-alkyl succinic acids have not been previously studied in the present connexion. The distances (in Å.U.) for acids $CO_2H{\cdot}CRR'{\cdot}CRR'{\cdot}CO_2H$, calculated from the experimental results by means of formula (1), are as shown in the following table :

	Un-substituted.	*s*-Disubstituted.				Tetra-substituted.
RR′	H.	MeH.		EtH.		Me_2.
(m. p.)		(209°)	(129°)	(192°)	(129°)	
r	5·58	3·87	3·80	3·40	3·32	3·07
r (mean)	5·58	3·83		3·36		3·07

From the argument of Part III, it will readily be seen that this is not a series in which internal polar disturbances are expected noticeably to affect the results : those alkyl groups which are near enough to the first-ionised carboxyl group to have their polarity modified by its dissociation are not near enough to the second carboxyl group to propagate the effect of the modification, and those which are sufficiently close to the second carboxyl to transmit such an influence are too remote from the other one to acquire the effect appreciably in the first place.

There is another difference between this series and the malonic acid series. In the malonic acids the model is unambiguously determined by the chemical formula, and it has not a sufficient number of degrees of freedom to enable the distance between the ionic centres to be changed by rotation around the linkings. The simplest normal dibasic acid whose structure permits the possibility of a change of geometrical type through rotation is succinic acid; and the same possibility obviously applies throughout the succinic acid series. Now, we have already observed that succinic acid, in common with all its higher normal homologues, gives an r distance corresponding fairly closely with the requirements of the uniplanar zig-zag model; for succinic acid the model requires $r = 5{\cdot}87$ Å.U. (Found : 5·58 Å.U.). When, however, we examine the r distances assembled in the preceding table, we see that the fall (nearly 2 Å.U.) between the values for $RR' = H_2$ and $RR' =$ MeH is much too great to be accounted for solely on the basis of valency deflexion, and this indicates that we should compare the data for the substituted succinic acids with the requirements of the other simple geometrical model to which they might tend to conform, *viz.*, the uniplanar coil For inter-valency angles of 114°, this model requires $r = 3{\cdot}61$ Å.U., whilst if the angles were 109° 28′ the distance would be $r = 3{\cdot}23$ Å.U. The results are therefore consistent with the suggestion that whilst succinic acid itself favours the uniplanar zig-zag model, the alkylated succinic acids tend to conform to the uniplanar coil. The smallness of the r value for tetramethylsuccinic acid suggests the operation of valency deflexion in addition, and a comparison of the results for the dimethyl-, diethyl-, and tetramethyl-acids is not inconsistent with this hypothesis. Further discussion of the effects due to valency deflexion in relation to those attributable to a change of geometrical type arises most appropriately in connexion with the substituted glutaric acids.

The Glutaric Acids.

The series of β-substituted glutaric acids which we studied in Part II has, in the present work, been expanded by the inclusion of β-ethyl- and β-methyl-β-ethyl-glutaric acid. The values (Å.U.) of the intercarboxyl distances of the acids $RR'C(CH_2{\cdot}CO_2H)_2$, calculated from the observations by means of equation (1), are as follows :

Type		β-Mono-substituted.			ββ-Disubstituted.				Cyclic 1 : 1-diacetic acids.		
RR′	H_2.	MeH.	EtH.	Pr^aH.	Me_2.	MeEt.	Et_2.	Pr^a_2.	$(CH_2)_4$.	$(CH_2)_5$.	$(CH_2)_6$.
r	7·11	4·06	3·99	3·97	3·58	3·33	3·12	3·12	3·45	3·16	3·20

The two most obvious features presented by these results are, first, that the distance for glutaric acid is very much larger than for any of the substituted acids, and secondly, that, apart from this, the data are in agreement with the valency-deflexion hypothesis with regard both to the order of the compounds and to the relative magnitudes of their differences in respect of the property considered.

Concerning the first point, it was suggested in Part II that the substitution of the β-carbon atom in glutaric acid would cause a departure from the zig-zag form characteristic of polymethylene dicarboxylic acids. The new measurements appear to bear this out since there seems to be no other way of accounting for the much smaller distances given by the alkylglutaric acids than by glutaric acid.

Fuller explanation is required of the second statement, namely, that the remaining results show agreement with the valency-deflexion hypothesis. With that hypothesis *in its original form* the correspondence is only general; what is more important is that new data show agreement, both in general and as to detail, with the *chemical observations* on ring closure which have been used to illustrate that hypothesis and have caused it to be modified in certain important particulars. As instances of unexpected chemical observations which have led to the adoption of a modified form (dynamical) of the valency-deflexion hypothesis, reference may be made to the larger effect of the *cyclo*pentane ring than of the *gem*-dimethyl substituent, the larger effect of the *gem*-diethyl group than of the *cyclo*pentane ring, and especially the smaller effect of the *cyclo*heptane ring than of the *cyclo*hexane ring : all these results have their counterpart in the distance measurements recorded above. It is unnecessary to go through the remaining details of the comparison since this ground has already been traversed in Part II (except as regards the ethyl- and methylethyl-acids which fit perfectly into the general scheme). Reference may, however, more usefully be made to our citation in Part II of the correspondence between the chemical results on ring closure and the *r*-distance measurements as evidence of valency deflexion, since this point seems to have been misunderstood. The argument is not the one (illogical as a general proposition) that a conformity between structural relations deduced from two kinds of evidence necessarily confirms the presumed cause of the said relations : any supposed cause, *e.g.*, that the whole of both the phenomena compared is due to restricted rotation, could thus be defended. It is to the geometry of the problem that the comparison appeals : the experiments on ring-formation relate to the degree of juxtaposition of *a certain pair* of C_α- and $C_{\alpha'}$-substituents; in the present investigations we are concerned with the distance between *a different pair* of C_α- and $C_{\alpha'}$-substituents (the carboxyl groups); but the two sets of results run parallel, even to the duplication of the irregularities; the parallel cannot be explained by rotation around the $C_\alpha C_\beta$-bonds since this would cause one pair of $C_\alpha C_{\alpha'}$-substituents to diverge whilst the other pair converged; only the approximation of the α- and α′-carbon atoms themselves can explain the *universally conjunctural* approximation of the different pairs of substituents attached thereto. This is the basis on which we regarded our results as confirming the valency-deflexion hypothesis—in the dynamical form in which its authors have applied it since 1923 (see Ingold and Thorpe, J., 1928, 1318, and cited references). It is not surprising that, as methods become more refined, additional stereochemical factors should emerge; but the circumstance that these investigations lead to the recognition of such a factor in restricted rotation is not considered to obliterate either the mass of chemical evidence underlying the hypothesis of valency deflexion or the independent confirmation of it which our results themselves provide.

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