THE ELECTROMETRIC TITRATIONS OF SOME UNSATURATED DICARBOXYLIC ACIDS.

By H. W. Ashton and J. R. Partington.

The present communication deals with an aspect of the internal electrostatic field of a molecule which has been the subject of other researches by entirely different methods made in this laboratory.[1] These have dealt with the pyrone compounds, the molecules of which are capable of existing in two forms (I. and II.), and the facility of polarisation

[1] Mitchell and Partington, *J. Chem. Soc.*, 1562, 1929 ; Johnson and Partington, *ibid.*, 86, 1931 ; Hunter and Partington, *ibid.*, 87, 1933.

of the double bonds of which is modified by substitution in the manner expected. These measurements are being continued with thiopyrones.

$$
\begin{array}{ccc}
\text{I.} & & \text{II.}
\end{array}
$$
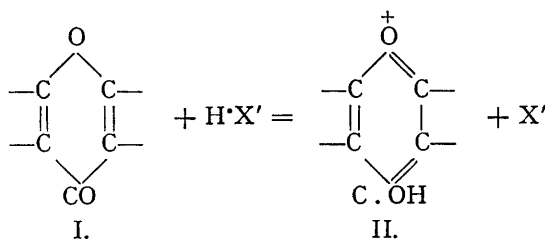
In the present work the effect of substitution on the strengths of some unsaturated dicarboxylic acids has been examined, and it has been demonstrated that the results again point to the existence of important electrostatic effects transmitted through the unsaturated linkages, the effects caused by fields external to the molecules being, in comparison, of minor interest and importance. The strengths of the acids have been measured by means of electrometric titration.

The electrometric titration of maleic and fumaric acids, using the hydrogen electrode, was carried out by Hildebrand [2] who gives no details of the results and does not mention any difficulty in obtaining satisfactory curves. It appeared very improbable on chemical grounds that this method would be suitable for unsaturated acids, owing to the possibility of reduction of the acids by hydrogen in the presence of platinum, but some experiments were made with a modification of the hydrogen electrode described by Lewis, Brighton and Sebastian.[3] The electrode was of platinised platinum and also of iridised gold, of the same type as the silver electrode previously described.[4] In the preparation of the iridised gold electrodes, gold foil was used and it was found necessary first to clean this very thoroughly by scraping, sandpapering and immersion in chromic acid solution. A very small current, with electrolysis in a 5 per cent. solution of iridium chloride prolonged for 12 to 20 hours, was found to give a satisfactory deposit of iridium. Very pure hydrogen was prepared by the electrolysis of baryta solution and freed from oxygen by passing over heated platinum wire, but was found to give the same results as cylinder hydrogen passed through alkaline pyrogallol. The second source of the gas was mostly used. The potentials were determined by means of a Tinsley three-range potentiometer with eighteen coils and enclosed slide wire, with an arrangement such that potential differences between the ends of the slide wire of 0·1, 0·01 or 0·001 volt could be used at will. A moving coil mirror galvanometer and standard Weston cell were used. A system of electrical shielding was adopted in which the accumulator, galvanometer, Weston cell, potentiometer and the stand carrying the experimental cell rested on a sheet of tinfoil covered with shellac varnish, all the pieces of apparatus being connected together and all connecting wires not supported by their own rigidity rested on insulating stands.

With hydrochloric acid in the cell, steady and reproducible potentials were obtained in half to two hours, with either type of electrode, but when a solution of maleic or fumaric acid was used in the half-cell, variable potentials were found, the rate of change depending on the rate of passage of hydrogen and on the depth of immersion of the electrode. The results indicated that reduction of the unsaturated acid was probably occurring, and it was clear that the hydrogen electrode could not be used with these acids.

[2] J. Amer. Chem. Soc., 35, 847, 1913.   [3] Ibid., 39, 2245, 1917.
[4] Partington and Simpson, Trans. Faraday Soc., 26, 147, 1930.

Attention was therefore directed to the quinhydrone electrode and this was found to give excellent results with all the acids investigated. The reference electrode was a calomel electrode made up with very pure materials.   In the earlier experiments mechanical stirring of the solution in the quinhydrone half-element was used, but during the course of the work the method of stirring with a current of nitrogen recommended by Morgan, Lammert and Campbell [5] appeared and was adopted, the advantages claimed by these authors being confirmed.   The electrode was a piece of bright platinum foil, 1·5 cm. square, welded to platinum wire sealed through glass tubing to a mercury contact.   Great care is necessary in avoiding possible mercury leakage to the electrode, and any electrode showing abnormal behaviour was at once rejected. Little trouble, however, was experienced in this direction.

With the quinhydrone electrode, steady and reproducible potentials were set up in a few minutes and did not alter after several hours.   In all measurements a steady potential, which could be maintained for several hours, was attained.

In some preliminary measurements the p_H values of maleic and fumaric acids were determined at 18° C., the reference electrode being a saturated calomel electrode, the potential of which was taken as 0·2503 volt,[6] and the formula of the quinhydrone half-element was taken as :

$$E = E_0 + (RT/F) \log a_H = 0{\cdot}7044 + (RT/F) \log a_H \text{ at } 18° \text{ C.}$$

Hence $$E = E_{obs} + 0{\cdot}2503 = 0{\cdot}7044 + 0{\cdot}0577 \log a_H$$

and $$- \log a_H = p_H = \frac{0{\cdot}4541 - E_{obs}}{0{\cdot}0577}.$$

The potential at the boundary between the saturated calomel solution and the acid was, as usual, neglected.   The results at various concentrations are given in Table I.   The values of p_H when plotted against log $(1/c)$ give straight lines.

TABLE I.

Fumaric Acid.

c mol./lit.	.	.	0·01	0·005	0·0025	0·001	0·0005	0·00025	0·0001
p_H	.	.	2·42	2·62	2·85	3·10	3·33	3·59	3·90

Maleic Acid.

c mol./lit.	.	.	.	0·10	0·01	0·005	0·001	0·0005	0·0001
p_H	.	.	.	1·40	2·06	2·36	2·95	3·24	3·76

In the electrometric titrations the vessel shown in Fig. 1 with the connection to the *normal* calomel electrode was used.   The U-shaped connecting tube was filled with saturated potassium chloride solution. The solution in the reference electrode (N KCl saturated with HgCl), and 10 ml. of the acid solution in the half-element, respectively, were poured in over the plugs, and, by gently turning the latter, contact between the solutions was established.   The open arm of the normal calomel electrode dipped into the vessel shown during the titrations, but was otherwise kept immersed in N KCl solution saturated with HgCl.   Such calomel electrodes agree with one another to within 0·1 millivolt over periods of several months ; any electrode showing a change of potential in frequent checking was at once rejected.

The titration vessel was fitted with a rubber bung supporting the electrodes, the nitrogen inlet and a burette provided with a potash guard

[5] *J. Amer. Chem. Soc.*, **53**, 454, 1931.
[6] Clark, *Hydrogen Ions,* 1928 ; Sörensen and Linderström-Lang, *Compt. rend. Lab. Carlsberg,* **15,** 1924.

tube.   The bung also had openings for introducing the acid solution and the solid quinhydrone.   This bung and all others used was first boiled with caustic soda solution and then with dilute nitric acid, and finally about twenty times with distilled water.   The nitrogen used in stirring was from a cylinder and was passed successively through alkaline pyro-gallol and the solution under investi-gation before it entered the half element.   The platinum foil electrode, which was kept half immersed in the solution during titration by raising it as required, was first cleaned by immersion in warm chromic acid solution, in which it was allowed to cool, then well washed with distilled water and 96 per cent. alcohol.   It was then dried in the oven and kept in a vacuum desiccator until re-quired.   The whole apparatus was carefully checked before use with standard buffer solutions and was found completely satisfactory.

All titrations were carried out at 25° C. ; in the first experiments the cell was immersed in an oil bath con-tained in a water bath and connected
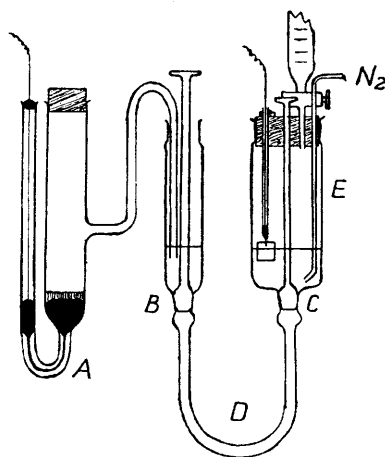
A = Normal calomel electrode.
D = Saturated KCl solution.
BC = Liquid junctions.
E = Titration cell.

FIG. 1.

with the electrical shielding system, but in later experiments the cell was contained in an air thermostat maintained constant to half a degree.   All solutions were made up by weight, their molarities (mol./lit.) being cal-culated from the densities measured at 25° C.   Equilibrium conductivity water was used throughout and all volumetric apparatus was calibrated. The glass cell was soaked in chromic acid solution, and then distilled water, and dried before each experiment.

Preparation of the Acids and other Materials.

Sodium hydroxide solutions for the titrations were prepared (*a*) from Kahlbaum's purest caustic soda, and (*b*) from pure sodium and water in a platinum dish.   Both, frequently checked by titration, gave identical results.

Succinic acid was several times recrystallised and dried in a vacuum desiccator.   M.-pt., 185°.

Maleic and Fumaric acids were Kahlbaum's " für Analyse " recrystal-lised several times and dried in a vacuum desiccator.   M.-pt. maleic, 131° ; fumaric sublimed at 200°.

Acetylene dicarboxylic acid was prepared from dibromosuccinic acid.[7] M.-pt., 179°.

Itaconic, Citraconic and Mesaconic acids were prepared from citric acid.[8] M.-pts., itaconic 162° with signs of decomposition ; citraconic 91° with decomposition ; mesaconic 202°.

Bromomaleic acid was prepared by Walden's method.[9]   M.-pt., 138°.

Bromofumaric acid was prepared by McKenzie's method [10] with very pure bromine, ether and maleic acid.   No deposition of fumaric acid during the preparation was noticed.   M.-pt., 186°.

[7] Bandowski, *Ber.*, **10**, 839, 1877 ; Baeyer, *ibid.*, **18**, 677, 1885.
[8] Sheiner, Ford and Rollen, *Organic Syntheses*, vol. 11, 1931.
[9] *Ber.*, **30**, 2886, 1897.   [10] *J. Chem. Soc.*, 1200, 1912.

Chloromaleic acid was prepared from *s*-dichlorosuccinic acid, obtained from fumaric acid [11] by refluxing with sodium acetate solution, extracting with ether and recrystallising several times. M.-pt., 115°.

Chlorofumaric acid was prepared by evaporating down chloromaleic acid several times with concentrated hydrochloric acid and recrystallising from water.[12] M.-pt., 192°.

Results.

The values of p_H were calculated from the formula for the quin-hydrone electrode :

$$E = E_o + (RT/F) \log a_H$$

where $E_o = 0.6990$ volt at 25° C., at which temperature the potential of the N calomel electrode was taken as 0.2824 volt. Hence :

$$E = E_{obs} + 0.2824 = 0.6990 + 0.0591 \log a_H$$

$$- \log a_H = p_H = \frac{0.4166 - E_{obs}}{0.0591}.$$

Table II. gives the concentrations of the acid and of the alkali used for

TABLE II.

Acid.			Original Acid Molality M.	Alkali Conc. N.	K_1.	K_2.
1. Succinic	.	.	.	0·0100	0·0200	8.85×10^{-5}	4.99×10^{-6}
2. ,,	.	.	.	0·00253	0·00613	8.57×10^{-5}	4.46×10^{-6}
3. Maleic	.	.	.	0·0105	0·0197	1.41×10^{-2}	8.69×10^{-7}
4. ,,	.	.	.	0·00228	0·00590	1.43×10^{-2}	8.71×10^{-7}
5. ,,	.	.	.	0·00101	0·00206	1.43×10^{-2}	8.31×10^{-7}
6. Fumaric	.	.	.	0·0110	0·0237	9.48×10^{-4}	4.58×10^{-5}
7. ,,	.	.	.	0·00206	0·00431	9.51×10^{-4}	5.03×10^{-5}
8. ,,	.	.	.	0·000932	0·00227	8.53×10^{-4}	3.25×10^{-5}
9. Citraconic	.	.	.	0·0101	0·0195	5.45×10^{-3}	7.16×10^{-7}
10. ,,	.	.	.	0·00111	0·00240	5.05×10^{-3}	7.14×10^{-7}
11. Mesaconic	.	.	.	0·00984	0·0330	8.22×10^{-4}	1.74×10^{-5}
12. ,,	.	.	.	0·00242	0·00845	8.24×10^{-4}	1.84×10^{-5}
13. ,,	.	.	.	0·000974	0·00254	7.21×10^{-4}	1.76×10^{-5}
14. Itaconic	.	.	.	0·00104	0·00433	1.40×10^{-4}	3.56×10^{-6}
15. Monochloromaleic.		.	0·0102	0·0252	1.92×10^{-2}	1.38×10^{-4}
16. ,,	.	.	.	0·00316	0·00950	1.91×10^{-2}	1.37×10^{-4}
17. ,,	.	.	.	0·00130	0·00520	1.88×10^{-2}	1.35×10^{-4}
18. Monochlorofumaric		.	0·0105	0·0260	1.72×10^{-2}	1.55×10^{-4}
19. ,,	.	.	.	0·00318	0·0102	1.66×10^{-2}	1.57×10^{-4}
20. ,,	.	.	.	0·00105	0·00285	1.64×10^{-2}	1.52×10^{-4}
21. Monobromomaleic		.	0·0101	0·0201	3.48×10^{-2}	2.51×10^{-5}
22. ,,	.	.	.	0·00308	0·00808	3.76×10^{-2}	2.41×10^{-5}
23. ,,	.	.	.	0·00110	0·00253	3.49×10^{-2}	2.30×10^{-5}
24. Monobromofumaric		.	0·0102	0·0266	3.54×10^{-2}	2.72×10^{-4}
25. ,,	.	.	.	0·00258	0·00940	3.48×10^{-2}	2.70×10^{-4}
26. ,,	.	.	.	0·00103	0·00360	3.38×10^{-2}	2.71×10^{-4}
27. Acetylenedicarboxylic	.		0·0101	0·0314	1.82×10^{-2}	4.20×10^{-5}
28. ,,	.			0·00202	0·00720	1.88×10^{-2}	3.85×10^{-5}

its titration, and the values of the first and second dissociation constants of the acid as calculated by the method explained below. The details of the titrations, which would be required in correcting for ionic strength, are given in Table III. The numbers in the first column of Table II.

[11] Kirchhoff, *Lieb. Ann.*, **280**, 211, 1894 ; van der Riet, *ibid.*, 216.
[12] Perkin, *J. Chem. Soc.*, **53**, 706, 1888.

TABLE III.—DETAILS OF ELECTROMETRIC TITRATIONS.

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
			Succinic Acid (1).					
0·00	2375	3·03	5·00	1398	4·69	9·27	609	6·02
0·15	2329	3·11	5·51	1320	4·82	9·91	239	6·65
0·30	2279	3·20	6·00	1241	4·95	10·02	129	6·83
0·50	2217	3·30	6·55	1150	5·11	10·07	− 42	7·12
1·00	2082	3·53	7·01	1078	5·23	10·15	− 353	7·65
1·75	1921	3·80	7·49	1003	5·36	10·22	− 706	8·24
2·50	1796	4·01	7·98	912	5·51	10·40	−1066	8·85
3·01	1710	4·16	8·37	838	5·63	10·60	−1224	9·12
4·02	1560	4·41	8·75	755	5·78			
			Succinic Acid (2).					
0·00	2230	3·28	4·22	1376	4·72	7·98	328	6·50
0·41	2115	3·47	4·66	1292	4·87	8·24	65	6·94
1·02	1970	3·73	5·20	1181	5·05	8·30	−88	7·20
1·78	1863	3·91	5·76	1068	5·24	8·38	−348	7·64
2·16	1786	4·03	6·20	968	5·41	8·50	−521	7·93
2·65	1691	4·19	6·64	865	5·59	8·60	−596	8·06
3·23	1574	4·39	7·21	707	5·86	9·08	−888	8·57
3·78	1474	4·67	7·58	575	6·08	9·65	−1060	8·85
			Maleic Acid (3).					
0·00	2889	2·16	4·83	1442	4·61	8·20	326	6·50
0·96	2812	2·29	5·07	1221	4·98	8·78	73	6·93
1·97	2708	2·47	5·43	1025	5·32	9·10	−112	7·24
2·81	2589	2·67	5·77	902	5·53	9·25	−330	7·61
3·34	2488	2·84	6·29	751	5·78	9·45	−719	8·25
3·80	2362	3·06	6·79	639	5·97	9·84	−1008	8·76
4·28	2136	3·44	7·25	535	6·15	10·09	−1097	8·91
4·55	1881	3·87	7·75	417	6·35	10·92	−1236	9·14
			Maleic Acid (4).					
0·00	2573	2·70	4·60	1130	5·14	7·74	−13	7·07
1·02	2470	2·87	4·80	1050	5·27	7·88	−266	7·50
2·00	2324	3·12	5·11	952	5·44	8·02	−507	7·91
2·78	2195	3·34	5·82	763	5·76	8·26	−714	8·38
3·42	1950	3·75	6·16	671	5·92	8·72	−980	8·74
4·00	1460	4·58	6·40	609	6·14	9·10	−1058	9·01
4·22	1300	4·85	6·92	461	6·27	10·01	−1232	9·14
4·41	1189	5·04	7·42	239	6·65			
			Maleic Acid (5).					
0·00	2384	3·02	5·27	1100	5·19	9·15	175	6·75
0·93	2304	3·15	5·58	988	5·38	9·46	70	6·93
1·98	2196	3·34	6·13	829	5·65	9·80	−40	7·12
2·93	2062	3·56	6·76	692	5·88	10·11	−300	7·56
3·46	1960	3·74	7·31	581	6·07	10·35	−419	7·76
4·12	1755	4·08	7·88	471	6·25	10·77	−560	8·00
4·63	1477	4·58	8·36	370	6·42	11·13	−661	8·17
4·96	1254	4·93	8·79	267	6·60			
			Fumaric Acid (6).					
0·00	2665	2·54	5·65	1800	4·01	9·25	250	6·63
0·98	2527	2·78	5·97	1744	4·10	9·35	−266	7·50
1·98	2384	3·02	6·27	1699	4·18	9·45	−525	7·94
3·01	2264	3·22	6·75	1610	4·33	9·65	−750	8·32
3·99	2085	3·52	7·27	1515	4·49	9·95	−990	8·73
4·50	2003	3·66	8·28	1264	4·91	10·20	−1055	8·84
4·99	1921	3·80	8·76	1023	5·32	10·49	−1160	9·01
5·49	1838	3·94	9·10	704	5·88			

TABLE III.—(*Continued.*)

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
			Fumaric Acid (7).					
0·00	2405	2·98	7·92	1415	4·66	9·73	−227	7·44
1·02	2323	3·12	8·43	1238	4·96	10·14	−492	7·85
2·04	2229	3·28	8·66	1139	5·12	10·43	−587	8·04
3·02	2122	3·46	8·89	1046	5·28	10·86	−660	8·23
4·01	2010	3·65	9·16	833	5·64	11·25	−708	8·26
5·02	1881	3·87	9·35	680	5·90	11·83	−765	8·35
6·00	1737	4·11	9·44	310	6·53			
7·03	1572	4·39	9·55	±0	7·05			
			Fumaric Acid (8).					
0·00	2260	3·23	5·83	1514	4·49	8·52	−166	7·35
1·04	2165	3·39	6·26	1424	4·64	8·80	−274	7·52
1·94	2071	3·55	6·82	1328	4·80	9·11	−353	7·65
2·96	1951	3·75	7·22	1182	5·05	9·40	−402	7·73
4·00	1882	3·87	7·64	938	5·46	9·78	−460	7·83
4·82	1693	4·19	7·91	667	5·92	10·02	−472	7·85
5·19	1630	4·29	8·10	354	6·45			
5·49	1578	4·38	8·22	117	6·85			
			Citraconic Acid (9).					
0·00	2810	2·30	5·59	1280	4·90	8·97	448	6·29
0·94	2733	2·43	5·82	1182	5·04	9·53	266	6·60
2·02	2631	2·60	6·00	1116	5·16	9·83	90	6·87
3·00	2512	2·80	6·20	1050	5·27	10·04	−105	7·23
3·98	2331	3·11	6·45	965	5·42	10·28	−540	7·96
4·57	2143	3·43	6·99	864	5·60	10·38	−742	8·31
4·84	1888	3·86	7·50	764	5·76	10·51	−900	8·57
5·05	1692	4·19	8·01	662	5·93	10·73	−1024	8·82
5·35	1380	4·72	8·54	546	6·05	11·04	−1175	9·03
			Citraconic Acid (10).					
0·00	2379	3·03	4·44	1252	4·93	8·05	168	6·77
1·03	2300	3·16	4·74	1123	5·15	8·36	−50	7·14
1·99	2205	3·32	5·11	989	5·39	8·76	−322	7·60
2·34	2133	3·44	5·41	910	5·51	9·12	−490	7·85
2·66	2080	3·53	5·80	802	5·69	9·34	−584	8·04
2·86	2024	3·63	6·13	720	5·83	10·01	−674	8·19
3·56	1798	4·01	6·65	597	6·04	10·61	−820	8·44
4·04	1484	4·54	7·16	473	6·25	11·25	−915	8·60
4·22	1357	4·76	7·57	350	6·46	12·16	−1009	8·76
			Mesaconic Acid (11).					
0·00	2658	2·57	4·34	1398	4·69	5·71	−261	7·49
1·00	2430	3·01	4·78	1252	4·93	5·81	−562	8·00
2·01	2166	3·39	5·15	1075	5·23	5·90	−709	8·25
2·54	1990	3·68	5·40	916	5·50	6·00	−790	8·39
3·05	1818	3·98	5·53	862	5·60	6·17	−887	8·55
3·51	1676	4·22	5·61	704	5·86	6·28	−950	8·66
3·91	1542	4·44	5·66	562	6·10			
			Mesaconic Acid (12).					
0·00	2431	2·94	4·69	1220	4·99	5·76	−140	7·29
1·01	2241	3·26	5·09	1027	5·31	5·84	−301	7·46
2·06	2000	3·66	5·32	857	5·60	5·96	−348	7·64
2·67	1843	3·93	5·43	699	5·87	6·17	−509	7·91
3·16	1711	4·16	5·52	510	6·19	6·44	−687	8·21
3·80	1525	4·47	5·60	261	6·61	6·70	−797	8·40
4·20	1392	4·70	5·70	6	7·04	6·97	−885	8·55

TABLE III.—(Continued.)

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.

Mesaconic Acid (13).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2238	3·27	4·99	1487	4·53	7·75	−159	7·32
0·94	2151	3·41	5·53	1371	4·71	7·84	−315	7·58
2·00	2022	3·63	6·11	1234	4·96	8·01	−538	7·96
2·72	1915	3·81	6·62	1075	5·23	8·16	−638	8·13
3·51	1774	4·05	7·13	826	5·65	8·30	−709	8·25
3·92	1701	4·17	7·38	611	6·02	8·52	−780	8·37
4·44	1598	4·35	7·59	199	6·73	9·01	−884	8·53

Itaconic Acid (14).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2142	3·43	2·92	1179	5·06	4·99	−299	7·56
0·50	1993	3·68	3·36	1022	5·32	5·32	−565	8·01
0·91	1884	3·86	3·66	917	5·52	5·69	−713	8·26
1·36	1756	4·08	3·86	822	5·66	5·98	−782	8·34
1·76	1613	4·32	4·20	655	5·94	6·61	−911	8·59
2·19	1445	4·61	4·53	370	6·42	7·52	−1017	8·77
2·58	1307	4·84	4·82	−143	7·31			

Monochloromaleic Acid (15).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2897	2·15	4·69	2310	3·14	7·96	560	6·10
0·50	2839	2·24	5·36	2172	3·30	8·05	−142	6·81
0·82	2802	2·31	6·00	1972	3·72	8·12	−478	7·86
1·20	2785	2·34	6·55	1803	4·00	8·18	−703	8·24
1·62	2732	2·43	7·06	1541	4·44	8·25	−840	8·47
2·60	2630	2·60	7·36	1380	4·72	8·53	−1091	8·86
3·00	2584	2·68	7·66	1175	5·06	8·92	−1316	9·28
4·21	2403	2·99	7·82	987	5·37			

Monochloromaleic Acid (16).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2654	2·56	5·12	1689	4·19	6·38	−270	7·52
1·01	2563	2·71	5·43	1536	4·45	6·52	−563	8·00
2·00	2444	2·91	5·63	1422	4·65	6·65	−680	8·20
2·99	2298	3·18	5·81	1295	4·86	6·78	−798	8·40
3·48	2206	3·32	5·98	1128	5·14	7·22	−972	8·70
3·96	2103	3·49	6·09	905	5·42	8·08	−1090	8·86
4·30	2006	3·66	6·22	595	6·04			
4·89	1791	4·02	6·30	83	6·91			

Monochloromaleic Acid (17).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2451	2·90	3·99	1539	4·45	5·20	−177	7·35
1·02	2327	3·11	4·20	1360	4·75	5·32	−245	7·46
1·71	2235	3·27	4·37	1189	5·04	5·54	−315	7·60
2·29	2115	3·47	4·67	687	5·89	5·83	−378	7·72
2·70	2017	3·64	4·74	465	6·26	6·38	−533	7·95
3·22	1854	3·91	4·87	148	6·80	6·94	−644	8·14
3·59	1690	4·19	5·00	27	7·10			

Monochlorofumaric Acid (18).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2908	2·13	5·52	2148	3·42	7·97	102	6·88
0·60	2866	2·22	6·42	1918	3·81	8·02	−200	7·39
0·89	2841	2·25	6·91	1725	4·13	8·08	−721	8·27
1·42	2788	2·33	7·29	1537	4·45	8·15	−847	8·48
2·42	2668	2·54	7·65	1228	4·97	8·29	−983	8·71
3·41	2519	2·79	7·80	1065	5·25	8·46	−1018	8·77
4·41	2370	3·04	7·92	822	5·66			

TABLE III.—(Continued.)

Monochlorofumaric Acid (19).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2653	2·56	3·40	2219	3·30	6·10	468	6·24
0·50	2591	2·67	3·79	2144	3·42	6·24	−200	7·39
1·02	2547	2·74	4·42	1975	3·71	6·32	−325	7·77
1·80	2456	2·90	5·00	1779	4·04	6·41	−632	8·13
2·24	2402	2·99	5·36	1660	4·34	6·60	−847	8·48
2·72	2318	3·13	5·68	1330	4·82	6·90	−977	8·70
3·05	2281	3·19	5·94	975	5·40	7·20	−1082	8·88

Monochlorofumaric Acid (20).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2420	2·96	6·17	1445	4·61	7·83	−860	8·51
1·02	2340	3·09	6·56	1140	5·12	7·99	−927	8·62
2·09	2252	3·24	6·75	1005	5·52	8·32	−990	8·73
3·08	2143	3·43	6·86	587	6·06	8·88	−1082	8·88
4·09	2018	3·64	7·03	−30	7·10	9·60	−1168	9·05
4·72	1902	3·83	7·18	−507	7·91			
5·66	1668	4·23	7·42	−732	8·29			

Monobromomaleic Acid (21).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2930	2·09	4·59	1806	4·00	7·45	615	6·01
1·34	2864	2·21	5·01	1671	4·22	7·58	408	6·36
2·32	2710	2·47	5·43	1541	4·44	7·69	−329	7·61
3·12	2539	2·75	5·82	1441	4·61	7·91	−744	8·31
3·39	2428	2·94	6·39	1261	4·92	8·02	−871	8·53
3·69	2281	3·19	6·66	1168	5·07	8·30	−1027	8·79
4·05	2070	3·55	7·03	977	5·40			
4·23	1972	3·72	7·27	788	5·72			

Monobromomaleic Acid (22).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2667	2·54	5·55	1463	4·58	7·73	−315	7·58
1·07	2573	2·70	5·85	1382	4·71	7·82	−562	8·00
2·10	2444	2·92	6·35	1237	4·96	7·97	−732	8·29
2·78	2325	3·12	6·66	1094	5·20	8·16	−809	8·42
3·16	2228	3·28	6·93	968	5·41	8·39	−880	8·54
3·55	2106	3·49	7·16	781	5·73	8·70	−947	8·65
4·27	1842	3·93	7·36	586	6·06			
4·97	1625	4·30	7·54	178	6·75			

Monobromomaleic Acid (23).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2408	2·98	4·14	1606	4·33	7·03	−458	7·82
1·06	2308	3·15	4·76	1422	4·65	7·40	−519	7·93
2·02	2158	3·40	5·33	1252	4·93	7·83	−646	8·14
2·41	2062	3·56	5·97	943	5·46	8·27	−725	8·28
2·73	1981	3·70	6·03	931	5·48	8·71	−798	8·40
2·98	1917	3·81	6·37	148	6·07	9·76	−948	8·65
3·29	1810	3·99	6·60	55	6·80			
3·60	1748	4·09	6·73	−165	7·33			

Monobromofumaric Acid (24).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2938	2·08	5·93	2086	3·52	7·65	59	6·95
1·04	2850	2·23	6·71	1775	4·05	7·74	−565	8·01
2·14	2735	2·42	7·01	1537	4·45	7·80	−715	8·26
2·95	2638	2·59	7·17	1352	4·76	7·86	−864	8·50
3·41	2564	2·71	7·36	1111	5·17	8·01	−937	8·64
4·01	2472	2·87	7·47	916	5·50	8·13	−1046	8·82
4·76	2351	3·07	7·55	690	5·88	8·30	−1143	8·98

H. W. ASHTON AND J. R. PARTINGTON

TABLE III.—(Continued.)

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.

Monobromofumaric Acid (25).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2662	2·55	5·46	1749	4·09	6·43	−403	7·84
1·04	2567	2·71	5·82	1514	4·49	6·50	−565	8·01
2·04	2460	2·82	6·06	1290	4·87	6·60	−632	8·12
3·04	2333	3·11	6·14	1040	5·29	6·68	−709	8·25
4·04	2166	3·39	6·27	532	6·15	6·88	−809	8·42
4·50	2087	3·52	6·30	178	6·75	7·37	−1020	8·78
5·02	1950	3·75	6·36	−301	7·56			

Monobromofumaric Acid (26).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2455	2·90	5·01	1455	4·59	5·96	−351	7·65
1·04	2356	3·07	5·20	1425	4·64	6·08	−434	7·79
2·04	2251	3·24	5·34	1188	5·04	6·28	−525	7·94
3·06	2106	3·49	5·45	829	5·65	6·54	−622	8·10
3·55	1998	3·67	5·55	440	6·31	6·90	−701	8·24
4·09	1891	3·85	5·70	±0	7·05	7·40	−785	8·38
4·45	1809	3·99	5·87	−174	7·35	8·42	−951	8·64

Acetylenedicarboxylic Acid (27).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2908	2·18	3·83	2011	3·65	6·17	916	5·50
0·96	2808	2·30	4·13	1860	3·90	6·40	296	6·55
1·95	2671	2·53	4·42	1750	4·09	6·46	−375	7·69
2·49	2578	2·69	4·79	1607	4·33	6·54	−840	8·47
2·86	2468	2·94	5·20	1467	4·57	6·61	−922	8·61
3·14	2375	3·03	5·60	1320	4·82	6·65	−937	8·64
3·39	2262	3·23	5·92	1151	5·10	6·84	−1163	9·02

Acetylenedicarboxylic Acid (28).

Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.	Titre.	E.M.F.	p_H.
0·00	2550	2·74	4·26	1451	4·60	5·56	−200	7·39
1·04	2455	2·90	4·52	1375	4·73	5·60	−370	7·68
2·06	2273	3·21	4·84	1216	5·11	5·77	−645	8·14
2·57	2127	3·47	5·17	898	5·45	5·83	−575	8·30
2·96	1992	3·68	5·30	728	5·84	6·03	−845	8·48
3·34	1838	3·94	5·40	532	6·15	6·27	−1002	8·75
3·54	1753	4·09	5·47	110	6·86			
3·93	1580	4·38	5·53	−10	7·07			

correspond with those in Table III., and in the latter the values of the observed E.M.F. are in volts × 10^4. The titre is in ml. of the alkali specified in Table II.

A combined diagram of the titration curves is shown in Figs. 2 and 3. from which the different behaviour of the acids is apparent. Maleic acid, with the *cis*-configuration, gives a curve having an inflexion in the middle part, whilst fumaric, with the *trans*-configuration, gives a curve without inflexion similar to that of a monobasic acid. This behaviour implies [13] that in the case of maleic acid the first dissociation constant is much larger than the second, whilst in the case of fumaric acid the two constants are not very different. Similar curves, corresponding with the molecular configurations, are obtained with citraconic (*cis*) and mesaconic (*trans*) acids, in which methyl substitution has occurred, and also in the case of bromomaleic and bromofumaric acids. In these cases, however, the inflexion characteristic of maleic acid is less pronounced, so that substitution by methyl or bromine has brought the

[13] Auerbach and Smolczyk, *Z. physikal. Chem.*, **110**, 65, 1924.
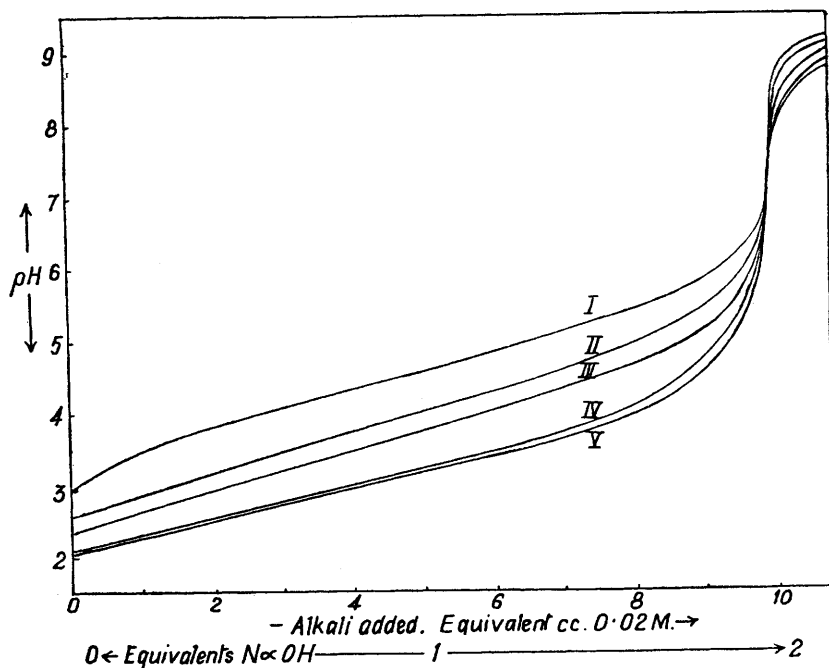
I. Succinic acid.   II. Mesaconic acid.   III. Fumaric acid.   IV. Brom.-fumaric acid.   V. Chlor.-fumaric acid.
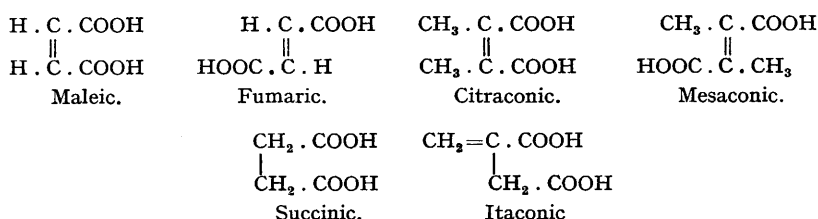
FIG. 2.
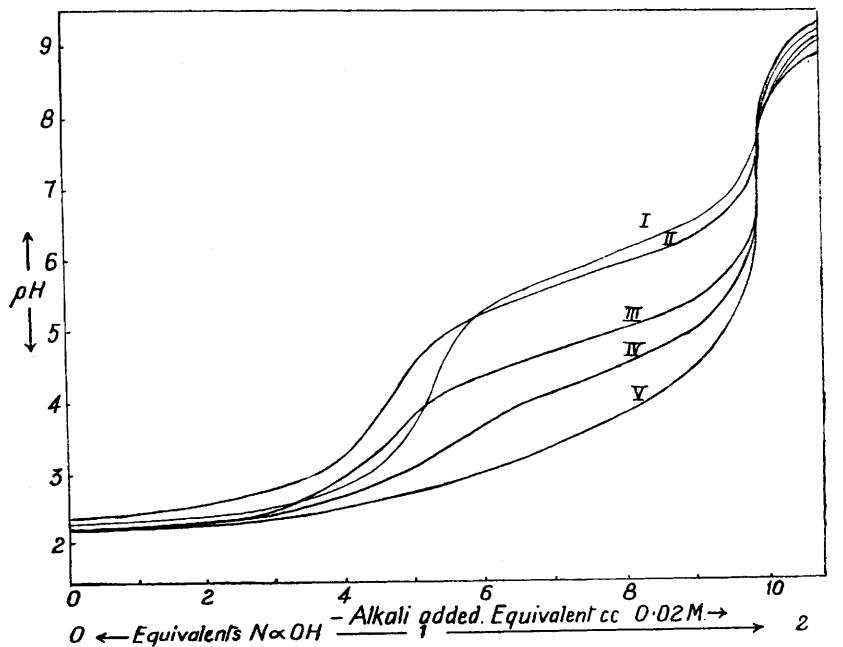
I. Maleic acid.   II. Citraconic acid.   III. Brom-maleic acid.   IV. Acetylene dicarboxylic acid.   V. Chlor-maleic acid.

FIG. 3.

two dissociation constants closer together. In the case of the chloro-substituted acids the curve, both for *cis*- and *trans*-acids, is of the same type and lacks an inflexion ; the curves for chloromaleic and chloro-fumaric acids are of the same type as that for bromofumaric acid. Such a behaviour, in which substitution markedly reduces the separation of the first and second dissociation constants, is also reported for some hydroxy-substituted acids.[14]

H . C . COOH	H . C . COOH	CH$_3$. C . COOH	CH$_3$. C . COOH
‖	‖	‖	‖
H . C . COOH	HOOC . C . H	CH$_3$. C . COOH	HOOC . C . CH$_3$
Maleic.	Fumaric.	Citraconic.	Mesaconic.

CH$_2$. COOH	CH$_2$=C . COOH
|	|
CH$_2$. COOH	CH$_2$. COOH
Succinic.	Itaconic

Certain negative substituents thus increase the strength of the acids and also cause a considerable increase in the second stage of dissociation, so that the ratio K_1/K_2 for the two isomers becomes much smaller than the value for the unsubstituted acids.

The large values of K_1/K_2 for the *cis*-isomers are usually explained by a mutual influence of adjacent carboxyl groups, so that when one hydrion has been detached the ionisation of the second is greatly depressed on account of the negative charge on the COO′ residue from the first group. In the case of *trans*-isomers, the carboxyl groups are widely separated, so that each hydrogen may ionise practically independently, and in consequence the values of K_1 and K_2 are not so very different.

The general results shown in the curves are confirmed by the actual values of K_1 and K_2, which have been calculated from the results of the titrations.[15] If c is the total concentration of acid, a the total concentra-tion of added alkali, and h the hydrion concentration of the solution, then for any corresponding values we have :

$$K_1 = \frac{D}{K_2 B - A} \quad \text{and} \quad K_2 = \frac{D + K_1 A}{K_1 B}$$

where :

$$A = ah + h^2 - hc ; \quad B = 2c - a - h ; \quad D = h^2(a + h).$$

Thus the values of K_1 and K_2 may be calculated from any two points on the titration curve, and by taking several pairs of points, mean values may be obtained.

It should be noticed that, since the values of p_H have been calculated from the electrode potentials, they correspond with the hydrion activities, $p_H = - \log a_H$, whilst the remaining molecular species enter the equa-tions as concentrations. The dissociation constants so calculated are " incomplete."[16] The ionisation of a monobasic acid may be ex-pressed by the following equations :

$$K_o = \frac{a_H \cdot a_{A'}}{a_{HA}} ; \quad K_i = \frac{c_H \cdot c_{A'}}{c_{HA}} ; \quad K_u = \frac{a_H \cdot c_{A'}}{c_{HA}}$$

[14] Wohl and Claussmann, *Ber.*, **40**, 2308, 1907.
[15] Britton, *J. Chem. Soc.*, 1896, 1925 ; *ibid., Hydrogen Ions*, 2nd ed., 168, 1932.
[16] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab.*, **9**, 11, 1929.

in which K_o, expressed in terms of the activities, is the thermodynamic dissociation constant and is independent of total concentration; K_i is the constant which would correspond with Ostwald's Dilution Law and, even with moderately weak acids, is a function of total concentration; and K_u is the "incomplete" (unvollständige) dissociation constant, which is not independent of total concentration since, although it involves hydrion activity, it also contains the concentrations of anion and undissociated acid. Since the activity coefficient f is defined as a/c, we find that:

$$K_o = K_u \frac{f_{A'}}{f_{HA}} = K_i \frac{f_H \cdot f_{A'}}{f_{HA}}.$$

With an obvious extension of the notation we have, for a dibasic acid, the equations:

$$K_{o,1} = \frac{a_H \cdot a_{HA'}}{a_{H_2A}}, \qquad K_{o,2} = \frac{a_H \cdot a_{A''}}{a_{HA'}},$$

$$K_{i,1} = \frac{c_H \cdot c_{HA'}}{c_{H_2A}}, \qquad K_{i,2} = \frac{c_H \cdot c_{A'}}{c_{HA'}},$$

$$K_{u,1} = \frac{a_H \cdot c_{HA'}}{c_{H_2A}}, \qquad K_{u,2} = \frac{a_H \cdot c_{A''}}{c_{HA'}},$$

$$K_{o,1} = K_{u,1} \frac{f_{HA'}}{f_{H_2A}} = K_{i,1} \frac{f_H \cdot f_{HA'}}{f_{H_2A}},$$

$$K_{o,2} = K_{u,2} \frac{f_{A''}}{f_{HA'}} = K_{i,2} \frac{f_H \cdot f_{A''}}{f_{HA'}}.$$

In the case of a symmetrical dicarboxylic acid, HAAH, each hydrogen of which may ionise quite independently, it follows from statistical considerations [17] that $K_1/K_2 = 4$, a result which has been found experimentally in many cases.[18] In other cases the ratio is greater than 4, which may be explained by an interaction between the carboxyl groups, the two hydrogens no longer ionising independently. This deviation may be expressed in terms of a magnitude n, defined by the equation:

$$n = P_2 - P_1 - \log 4 \simeq P_2 - P_1 - 0.6$$

where $P_2 = -\log K_2$ and $P_1 = -\log K_1$. Bjerrum [19] has shown from the experimental results for acids that n is a function of the distance of separation of the carboxyl groups and not much dependent on substitution in the acid. Discrepancies were found for phthalic and maleic acids, the value of n for the latter being much larger than for oxalic and malonic acids, in which the carboxyl groups are similarly situated.

oxalic   malonic   maleic   phthalic
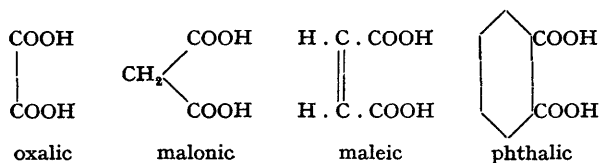
Bjerrum has also given a semi-quantitative treatment of the relation between the ratio K_1/K_2 and the distance between the carboxyl groups.

[17] Wegscheider, Monatsh., 16, 153, 1895; Adams, J. Amer. Chem. Soc., 38, 1503, 1916.
[18] Chandler, ibid., 30, 702, 1908.   [19] Z. physikal. Chem., 106, 219, 1923.

The influence of the dissociation of one carboxyl group on that of the second may depend both on intramolecular disturbances and also on local accumulation of hydrogen ions around the negative COO' group, this accumulation leading to an excess over the average distribution in the solution. The second effect only was considered by Bjerrum, who derives the equation :

$$K_1/K_2 = 4 \log \frac{\epsilon}{DTkr}$$

by a simple application of Boltzmann's equation, D being the dielectric constant, ϵ the electronic charge, k Boltzmann's constant, T the absolute temperature and r the distance between the COO' rest and the H atom of the second carboxyl group. For aqueous solutions at $25°$ this gives :

$$n = P_2 - P_1 - \log 4 = 3 \cdot 1 \times 10^8/r.$$

The values of r so calculated may be compared with the distances between the carboxyl groups deduced from the atomic dimensions and the chemical structural formulæ on the assumption of a straight chain configuration. Fair agreement is obtained except in the case of succinic and higher acids, for which bent chains are assumed. The values of r found are usually only about half the values calculated for the distance between the carboxyl groups.

The experimental data and the relevant theory have been much extended for such types of acids by Gane and Ingold,[20] who attempt to take into consideration certain factors neglected by Bjerrum, including in particular a semi-quantitative discussion of the effect of the internally propagated field, which tends to make the calculated values of r too small. The influence of this internal field in the molecules, particularly in the case of the acids dealt with in the present communication, is important. These acids have an unsaturated linkage between two adjacent atoms carrying the carboxyl groups, and the internal effect should, therefore, be very marked. The deviations from the theory of Gane and Ingold which we have found are, therefore, what would be expected, since their theory contains no allowance for such an effect. Distortion of the molecules, leading to the bending of chains which may occur with intervening CH_2 groups has, however, been considerably reduced by the stiffness conferred by the double bond, although some degree of distortion is probably present in some cases.

Gane and Ingold's modification of Bjerrum's equation, in which the change in the properties of the solvent are taken into account but the inductive influence is still neglected, takes the form [21] for a dicarboxylic acid :

$$K_1/K_2 = 4e^{-\epsilon\psi/kT}$$

where ψ is a function both of the charge ϵ of the ionised group and the distance r. The values of ψ are calculated from the experimental values of K_1 and K_2, and thence the values of r are calculated from theoretical considerations [22] connecting ψ and r. Table IV. gives the distances r calculated both by Bjerrum's (B) formula and by that of Gane and Ingold (G. and I.). As Gane and Ingold show, the distance between the centres of the carboxyl groups in succinic acid, assuming a rigid zig-zag

[20] J. Chem. Soc., 1594, 2267, 1928 ; 1691, 1929 ; 2153, 2179, 1931.
[21] Ibid., 2160, 1931.   [22] Ingold, ibid., 2179, 1931.

configuration and the usual angles and atomic dimensions, is 5·87 Å.U., which is in sufficiently good agreement with the value 5·67 Å.U. found. Although the separate values of K_1 and K_2 for this acid given by Gane and Ingold are somewhat different from ours, owing to the adoption of a different method of calculation, their ratio K_1/K_2 is substantially the same as ours.

In the case of maleic and fumaric acids, the angle in $C\diagup_{\diagdown C}^{C}$ may be calculated as 125° (180° — $\tan^{-1}\sqrt{2}$) by assuming that the double bond is represented by two tetrahedra with an edge in common. On the approximate assumptions that the distance between adjacent carbons is the same, 1·54 Å.U., both in single and double bonds, and that the distance from carbon to the effective centre of the carboxyl group is 1·00 Å.U., this gives the distance between the carboxyls as 4·50 Å.U. in maleic acid and 6·13 in fumaric acid.

TABLE IV.

Acid.	K_1.	K_2.	n.	r Å.U. (B.).	r Å.U. (G. and I.).
Succinic	$8·71 \times 10^{-5}$	$4·77 \times 10^{-6}$	0·6594	4·70	5·67
Maleic	$1·42 \times 10^{-2}$	$8·57 \times 10^{-7}$	3·617	0·86	2·95
Fumaric	$9·50 \times 10^{-4}$	$4·80 \times 10^{-5}$	0·6940	4·47	5·53
Itaconic	$1·40 \times 10^{-4}$	$3·56 \times 10^{-6}$	0·9933	3·11	4·62
Acetylene-dicarboxylic	$1·85 \times 10^{-2}$	$4·02 \times 10^{-5}$	2·061	1·50	3·53
Citraconic	$5·14 \times 10^{-3}$	$7·15 \times 10^{-7}$	3·25	0·95	3·05
Mesaconic	$8·22 \times 10^{-4}$	$1·78 \times 10^{-5}$	1·062	2·99	4·48
Bromomaleic	$3·58 \times 10^{-2}$	$2·40 \times 10^{-5}$	2·572	1·21	3·27
Bromofumaric	$3·47 \times 10^{-2}$	$2·70 \times 10^{-4}$	1·507	2·06	3·93
Chloromaleic	$1·90 \times 10^{-2}$	$1·37 \times 10^{-4}$	1·540	2·01	3·90
Chlorofumaric	$1·67 \times 10^{-2}$	$1·54 \times 10^{-4}$	1·433	2·16	3·82

The agreement with Gane and Ingold's formula is much better in the case of maleic and fumaric acids than with Bjerrum's, although both formulæ represent correctly the qualitative distinction.

In the case of itaconic acid the double bond is not in the carbon chain but is attached to it, so that the molecule may be regarded as a substituted succinic acid. The value of r shows, in fact, that the structure of itaconic acid is of the fumaric or succinic *trans*-type, and different from the maleic type. The molecule probably has a zig-zag and not a coiled chain. This conclusion is confirmed by the comparatively low value of the first dissociation constant.

The assumption that the triple bond in acetylenedicarboxylic acid, $HOOC . C{\equiv}C . COOH$, is represented by two tetrahedra having a face in common leads to the angle 180°, *i.e.*, the molecule is linear and the distance between the effective centres of the carboxyl groups would be 6·62 Å.U. The much smaller distance found, 3·53 Å.U., may be explained by the very large intramolecular interaction through the triple bond, and the assumption of a coiled or maleic structure seems unnecessary.

In the alkyl substituted acids, citraconic and mesaconic, the distinction between the *cis-* and *trans*-isomers is clearly revealed in the values of

r, although the divergence from the values calculated from the model is greater than in the case of the unsubstituted acids, pointing to the expected enhancement of the intramolecular effects by substitution and suggesting that some dissymmetry may also have been introduced.

The halogen substituted acids show some residue of the difference of structure in the case of the bromo-acids, but none in the case of the chloro-acids, the *cis-* and *trans*-forms of which behave as if they were identical.   In reality it is almost certain that the abnormalities in the r values point to severe intramolecular disturbances set up by the substituents and to some dissymmetry.   The structure of the unsubstituted acids has probably been at least approximately preserved after substitution.   Identity of the acids is, of course, excluded on the grounds of the difference in physical properties such as the melting-point.

If we accept the assumption that a change of log K of less than a unit corresponds with only a small change of acidity, the results show quite clearly that, whereas the value of K_1 is very little affected by substitution in the case of acids of the maleic (*cis-*) type, a marked change

TABLE V.

Acid.			Effective Charge in Multiples of Charge on Electron.	Acid.			Effective Charge in Multiples of Charge on Electron.
Succinic	.	.	1·1	Chlorofumaric	.	.	2·5
Fumaric	.	.	1·2	Bromofumaric	.	.	2·5
Chloromaleic	.	.	1·45	Citraconic	.	.	3·1
Itaconic	.	.	1·6	Maleic	.	.	3·5
Mesaconic	.	.	1·8				
Bromomaleic	.	.	2·4				

in the strength of the acid occurs with acids of the fumaric (*trans-*) type. This is what would be expected from the relative positions of the carboxyl groups.   Where these are close together, their mutual influence is already strong and is little further affected by substitution, whereas when the groups are widely separated the effect of substitution can be appreciable.   The effect on the second dissociation constant is also the one expected, since here the dissociation of hydrogen proceeds more easily the smaller the dissociation in the first stage, so that the effects are reversed.

In all cases of a substituted acid of the maleic type the value of r is greater for the substituted than for the unsubstituted acid, whereas the naïve valency deflexion hypothesis would predict a smaller value.   This is merely another example of the failure of the merely geometrical significance of this hypothesis, which is now generally admitted.   In the case of the fumaric acids the values of r diminish on substitution, but to a much greater extent than would be expected from the valency deflexion which would be caused by the introduction of larger groups.

The deviations of the values of K_1/K_2 calculated according to the formula of Gane and Ingold from those found experimentally might be explained by assuming that the value of r was that given by the molecular model but the charge on the carboxyl group had been increased above the electronic charge ϵ owing to electronic drift.   A calculation

of the charge necessary to explain the results shows, however, that it is often unreasonably large, and also that, whereas the substitution of a positive methyl group might be expected to change the effective charge in the opposite sense from that produced by a negative halogen, in both cases an increase of charge is found.   The results are shown in Table V.

East London College,
   University of London.