LXIV.—*The Solubility of Isomeric Organic Compounds and of Mixtures of Sodium and Potassium Nitrates, and the Relation of Solubility to Fusibility.*

By THOS. CARNELLEY, D.Sc., and ANDREW THOMSON, D.Sc., M.A.,
University College, Dundee.

NEARLY seven years ago (1881) one of us showed in an opening address given to the Owens College Chemical Society, and subsequently published in the *Philosophical Magazine* [5], **13**, 180, that solubility and fusibility were very closely related to one another, so that of two or more isomeric bodies, that dissolves the most easily which has the lowest melting point, and in which the atomic arrangement is the least symmetrical. Very shortly after Dr. Tilden, in a paper in the *Philosophical Transactions*, 1884, Part I, p. 23, also this Journal, **45**, 266, proved that there was a similar connection between the solubility and fusibility of inorganic compounds.

At that time the investigation had included only a comparatively small number (58) of compounds taken at random from *Watts's Dictionary of Chemistry*, and involved no original experiments made with special reference to the subject. We have now extended the investigation so as to include all isomeric sets of carbon compounds whatever. Our data have been obtained partly from literature and partly as the results of our own determinations.

Before giving the results of our work it will be necessary to describe the method we have employed for the estimation of the solubilities of any set of isomeric organic compounds, and for the other cases referred to in the present paper. For this purpose it was absolutely necessary that for each set of isomerides the determinations should be carried out under identically the same conditions, and to attain this we have in all cases made the determinations for the several members of a set of isomerides simultaneously. The results, however, are not only strictly comparable, but are likewise as absolutely correct as we could make them.

A set of long (110 mm.) and narrow (14 mm. outside diameter) glass phials, accurately stoppered, were employed to hold the solvent and various isomerides under investigation. These bottles were about two-thirds filled with the solvent, and such a quantity of each of the isomerides respectively as would be more than sufficient to form a saturated solution at a temperature 10° above that at which the solubility was to be determined. The stoppers were then firmly inserted and the bottles fixed in suitable clips attached to an axis

passing through the centre of a bath filled with water, and so arranged that the phials were completely immersed. The axis could be kept in regular rotation any length of time by means of a small water motor, whilst the bath was maintained at a constant temperature by a thermo-regulator. The following sketch will represent the arrangement. ABCD is a bath made of tin-plate and standing on a tripod. To the axis E are soldered six brass clips, by means of which as many bottles may be fixed on the axis at the same time. FF represents six such phials, containing the solvent and substances under investigation. Six determinations could thus be made simultaneously. GG and H is a pair of pulleys connected by a cord, H being fixed on

About $\frac{1}{4}$ th the actual size.

the axis of the small water-motor for driving the apparatus. L is the thermo-regulator to be used in connection with the lamp for heating the bath, and K the thermometer for indicating the temperature. All our determinations, contained in the present paper, were made at 20° C. In order, therefore, to obtain thoroughly saturated solutions the bath was heated to about 30°, and the phials kept immersed and in continual motion for about two hours, matters being so arranged that some at least of the compounds remained still undissolved at 30°, in order to avoid supersaturation. At the end of that time the lamp was turned out and the bath allowed to cool down

to exactly 20° C., the phials being kept in continual motion throughout. This usually took about two hours. After standing for a few minutes so as to allow the still undissolved portions to settle to the bottom of the phials, a quantity of the saturated liquid from each was withdrawn into a small tared glass bottle and weighed. This gave the weight of the solvent and substance dissolved. To determine the quantity of the latter, the solution was evaporated to dryness and the residue weighed. If, however, the substance was volatile when evaporated, this method could not be employed, and in some cases very great difficulty has been experienced in making an exact determination. But when the compound was coloured, the quantity in solution could be easily estimated colorimetrically by titrating it against a standard solution of the same substance in the same solvent. In the case of acids or alkalis also, the amount could be determined by means of a standard acid or alkali, certain modifications, however, being necessary in the presence of some of the solvents. The difference between the total weight of the solution and that of the substance dissolved gave the weight of the solvent which had been required to dissolve that weight of substance at the given temperature. By the above method results are obtained which are strictly comparable, because each set of isomerides can be worked simultaneously, whilst complete saturation is ensured and supersaturation avoided. Special tests made for the purpose showed that the phials were thoroughly tight at the stoppers, even when such a volatile solvent as ether was employed. Altogether we have found the arrangement to answer admirably.

I. (a.) *Determination of the Solubilities of 1 : 3 and 1 : 4 Nitranilines*
(m. p. 114° and 147°).

The quantity of these compounds dissolved by a given solvent could not be determined by evaporating a weighed quantity of the saturated solution to dryness on the water-bath, as both of them were slightly volatile under these circumstances. Thus, 0.7015 gram of the 1:3 compound, after solution in water and evaporation to dryness, weighed only 0.6280 gram, or had lost nearly 15.0 per cent. in weight, while the 1:4-compound, though not nearly so volatile, still suffered a perceptible loss. Therefore, as both meta- and para-nitraniline form coloured solutions, the quantity of these compounds, dissolved by a given solvent, was estimated colorimetrically by titration against a standard solution of the nitraniline in the solvent under investigation. That this method gives good results was shown by the following test determinations of the nitraniline dissolved in solutions containing known quantities:—

Experiment		Weight of nitraniline taken.	Weight found by experiment.
I.....		0.0162 gram	0.0165 gram.
„	II.....	0.0030 „	0.0029 „
„	III.....	0.0075 „	0.0075 „
„	IV.....	0.0099 „	0.0100 „

As the colour of the solution pales somewhat when kept for more than a day, especially on exposure to light, it is necessary that the determinations should be made as soon as possible, and that the standards should be freshly prepared.

By the above method we have determined the solubility of the meta- and para-nitranilines in 13 different solvents, with the results given in Table I, p. 786. All the determinations refer to 20° C. Column I gives the solvent; Column II the modification of nitraniline referred to; Column III the number of the experiment, each of which is the result of an entirely independent determination. The determinations in a given solvent, to which the same number is attached, were always made simultaneously, and in all respects under the same conditions. Column IV gives the weight of the solution taken saturated at 20° C; Column V the strength of the standard employed; Column VI the number of c.c. of this standard required to produce a colour in 50 c.c. of the solvent, equal to that of the weight of liquid in Column IV, also made up to 50 c.c.; Column VII the solubility represented in parts by weight dissolved in 100 parts by weight of the solvent; and Column VIII the mean of the results in Column VII.

(b.) *Determination of the Solubility of Mixtures of Sodium and Potassium Nitrates in Water.*

The results were obtained with the apparatus above described, and in the manner already detailed, except that the mixed salts were exposed to the action of the solvent for four instead of two hours. Those experiments to which the same number is attached were made simultaneously. (See Table II, p. 789.)

The composition of the dissolved portion of the mixed salts was ascertained:—(a.) By finding the weight of mixed sulphates obtained from a known weight of the mixed nitrate residue left on evaporating the several saturated solutions to dryness; (b.) By determining the melting and solidifying points of the several mixed nitrate residues. Reference to the curves in Diagram I then gave the composition corresponding to a given melting or solidifying point.

The melting and solidifying points of the original mixtures before solution, and of the dissolved portion after solution and evaporation,

TABLE I.

I. Solvent.	II. Substance:— Nitraniline.	III. No. of experiment.	IV. Weight of solu- tion taken, saturated at 20° C.	V. 1 c.c. of standard solution con- tained of nitraniline. gram.	VI. c.c. of standard required.	VII. Solubility. Parts by weight in 100 parts of solvent.	VIII. Mean solubility at 20°.
Water, H ₂ O	meta	1	4.839	0.00081	7.2	0.120	} 0.114
	"	2	4.716	0.00068	8.1	0.112	
	"	3	3.605	0.00098	4.3	0.117	
	"	4	5.022	0.00098	5.6	0.109	} 0.077
	para	1	4.859	0.00080	4.7	0.078	
	"	2	4.870	0.00114	3.2	0.075	
	"	3	4.521	0.00062	5.5	0.076	
Methyl alcohol, CH ₃ -OH..	"	4	4.959	0.00062	6.3	0.079	} 11.06
	meta	1	2.592	0.02208	11.9	11.28	
	"	2	2.412	0.01585	14.9	10.85	
	para	1	2.522	0.02789	8.0	9.70	
Ethyl alcohol, C ₂ H ₅ -OH ..	"	2	2.069	0.01338	13.4	9.48	} 7.05
	meta	1	2.393	0.02208	7.1	7.01	
	"	2	2.565	"	7.8	7.15	
	"	3	2.595	"	7.6	6.99	} 5.84
	para	1	3.929	0.02789	7.6	5.70	
	"	2	2.540	"	5.0	5.81	
	"	3	2.388	"	5.0	6.02	
Propyl alcohol, C ₃ H ₇ -OH..	meta	1	2.472	0.02053	6.3	5.52	} 5.65
	"	2	2.662	"	7.1	5.79	
	para	1	2.795	0.01391	8.8	4.58	} 4.35
	"	2	2.840	"	8.1	4.13	

TABLE I—continued.

I. Solvent.	II. Substance :— Nitraniline.	III. No. of experiment.	IV. Weight of solu- tion taken, saturated at 20° C.	V. 1 c.c. of standard solution con- tained of nitraniline.	VI. c.c. of standard required.	VII. Solubility. Parts by weight in 100 parts of solvent.	VIII. Mean solubility at 20°.
Isobutyl alcohol, $C_4H_9\cdot OH$.	meta	1	2.685	gram. 0.02000	3.4	2.60	} 2.61 } } 1.91
	"	2	2.378	"	3.1	2.68	
	para	1	2.414	0.01356	3.3	1.89	
	"	2	2.288	"	3.2	1.94	
Isoamyl alcohol, $C_5H_{11}\cdot OH$	meta	1	3.339	0.02208	12.0	8.46	} 8.51 } } 6.29
	"	2	2.715	"	9.7	8.56	
	para	1	3.059	0.02780	6.4	6.19	
	"	2	2.680	"	5.8	6.39	
Ethyl Ether (C_2H_5) ₂ O . . .	meta	1	2.426	0.01587	11.2	7.91	} 7.89 } } 6.10
	"	2	2.606	"	12.0	7.88	
	para	1	2.930	0.01278	12.9	5.96	
	"	2	2.365	"	10.9	6.25	
Benzene, C_6H_6	meta	1	2.705	0.01576	4.3	2.57	} 2.45 } } 1.98
	"	2	3.726	"	5.4	2.34	
	para	1	2.413	0.00698	7.2	2.13	
	"	2	3.700	"	9.5	1.83	
Toluene, C_7H_8	meta	1	3.052	0.01576	3.2	1.68	} 1.71 } } 1.31
	"	2	3.212	"	3.5	1.75	
	para	1	2.962	0.00698	5.6	1.34	
	"	2	3.417	"	6.2	1.29	

33

C

C

TABLE I—continued.

I. Solvent.	II. Substance:— Nitriline.	III. No. of experiment.	IV. Weight of solu- tion taken, saturated at 20° C.	V. 1 c.c. of standard solution con- tained of nitriline.	VI. c.c. of standard required.	VII. Solubility. Parts by weight in 100 parts of solvent.	VIII. Mean solubility at 20°.
Cumene, C_9H_{12}	meta	1	3.119	gram. 0.01660	2.2	1.18	} 1.15
	"	2	3.086	"	2.1	1.11	
	para	1	3.520	0.01158	2.8	0.93	} 0.90
	"	2	3.120	"	2.3	0.86	
Chloroform, $CHCl_3$	meta	1	5.487	0.01660	9.9	3.09	} 3.01
	"	2	3.846	"	6.6	2.94	
	para	1	4.329	0.01158	8.0	2.42	} 2.31
	"	2	4.790	"	8.9	2.20	
Carbon tetrachloride, CCl_4 .	meta	1	5.178	0.01660	0.65	0.21	} 0.21
	"	2	5.992	"	0.80	0.22	
	para	1	4.878	0.01158	0.70	0.17	} 0.17
	"	2	3.450	"	0.55	0.18	
Carbon disulphide, CS_2	meta	1	4.854	0.01660	0.95	0.33	} 0.33
	"	2	5.138	"	1.05	0.34	
	para	1	2.906	0.01158	0.65	0.26	} 0.26
	"	2	3.416	"	0.80	0.27	

TABLE II.

I. No. of experi- ment.	II. Composition of mixed salts sub- mitted to the action of the solvent.	III. Weight of solu- tion taken saturated at 20°.	IV. Weight of residue obtained.	V. Solubility. Parts by weight of mixed salts in 100 parts of water.	VI. Mean solubility at 20°.
1 4	100 p. c. NaNO ₃ " "	5·036 6·614	2·372 3·057	89·04 84·7	86·8
1 2	90 p. c. NaNO ₃ + 10 p. c. KNO ₃ " "	4·509 4·807	2·339 2·537	107·9 111·4	109·6
1 3 4 5	80 p. c. NaNO ₃ + 20 p. c. KNO ₃ " " " " " "	4·407 9·6005 8·083 5·778	2·523 5·566 4·629 3·352	133·9 138·0 134·0 138·1	136·5
1 3 4 5	70 p. c. NaNO ₃ + 30 p. c. KNO ₃ " " " " " "	4·548 6·019 3·351 2·817	2·574 3·5095 1·939 1·635	130·7 139·8 136·7 138·3	136·3
1 3 4	60 p. c. NaNO ₃ + 40 p. c. KNO ₃ " " " " " "	4·978 5·573 4·354	2·868 3·268 2·530	135·4 141·7 138·7	137·6
1 2	50 p. c. NaNO ₃ + 50 p. c. KNO ₃ " "	3·898 4·364	2·001 2·254	105·4 106·9	106·1
1 2	45·7 p. c. NaNO ₃ + 54·3 p. c. KNO ₃ = molecular proportions " "	5·727 4·167	2·669 1·959	87·2 88·7	88·0

TABLE II—*continued*.

I. No. of experi- ment.	II. Composition of mixed salts sub- mitted to the action of the solvent.	III. Weight of solu- tion taken saturated at 20°.	IV. Weight of residue obtained.	V. Solubility. Parts by weight of mixed salts in 100 parts of water.	VI. Mean solubility at 20°.
1 2	40 p. c. NaNO_3 + 60 p. c. KNO_3 " "	4.761 3.614	2.159 1.594	82.9 79.3	} 81.1
1 2	30 p. c. NaNO_3 + 70 p. c. KNO_3 " "	3.837 5.663	1.643 2.368	74.9 72.1	
1 2	20 p. c. NaNO_3 + 80 p. c. KNO_3 " "	4.102 4.149	1.429 1.469	53.4 54.8	} 54.1
1 2	10 p. c. NaNO_3 + 90 p. c. KNO_3 " "	5.189 4.456	1.534 1.263	41.9 39.9	
1 2	100 p. c. KNO_3 "	2.626 3.466	0.668 0.864	34.1 33.2	} 33.6

were determined in the ordinary way by heating small quantities of the substance in somewhat large capillary glass tubes, attached to a thermometer immersed in a bath of strong sulphuric acid. In the case of the pure nitrates, for which an ordinary thermometer cannot well be used, the specific heat method formerly described (this Journal, 29, 489) by one of us was employed.

The results obtained are given in Table III (p. 792).

The relation between the composition of various mixtures of sodium and potassium nitrates, and the corresponding melting or solidifying points, is shown in Diagram I, the thick broken curve being for the melting points, and the thin broken curve for the solidifying points. By reference to these curves the composition of any mixture of the nitrates may be determined approximately if the melting or solidifying point of the mixture be known. The form of the curves, however, shows that in nearly all cases there are two different mixtures which have the same melting and solidifying points, while mixtures containing from 40 to 50 per cent. of NaNO_3 all have the same melting and solidifying points, these points not being affected by alterations in composition between those limits.

II. *Relation of the Solubility to the Fusibility of Isomeric Organic Compounds.*

Raoult Pictet has shown (*Compt. rend.*, 88, 855), *first*, that the lower the melting point of a solid the longer are the oscillations of its molecules; and *second*, that the melting points of solids correspond to equal lengths of oscillation, so that $t \times w = c$, where t is the melting point measured from the absolute zero, w the length of oscillation, and c a constant.

Of two isomeric bodies, therefore, the one with the lower melting point will, at any given temperature below the melting point, have its molecules moving with oscillations of greater amplitude than the one with the higher melting point. The molecular weights being equal, the force of restitution will be less in the case of the more fusible compound, and hence its molecules will be in a less stable condition, and be the more readily separated from their fellows than those of the less fusible compound. Now in order that a solid may dissolve in any liquid it is necessary that its molecules should undergo a sort of unloosening process, and we should therefore conclude that of two isomeric compounds, that would dissolve the more easily in which the attraction or the force of restitution to the mean position of oscillation was the least, *i.e.*, the one which is the more easily fusible. This argument shows:—

Rule (1.) *That for any series of isomeric organic compounds the order*

TABLE III

Per cent. NaNO ₃ in original mixture <i>before</i> solution.	Mixed nitrates <i>before</i> solution.				Mixed nitrates <i>after</i> solution and evaporation to dryness.				Per cent. of NaNO ₃ in the mixture <i>after</i> solution and evaporation to dryness, as found :—			
	Uncorrected.		Corrected.		Uncorrected.		Corrected.		From the melting point.	From the solidifying point.	From analysis.	Average §
	Melting point.	Solidifying point.	Melting point.	Solidifying point.	Melting point.	Solidifying point.	Melting point.	Solidifying point.				
100	303*	—	316†	—	303	—	316	—	100	100	100	100
90	288	286	298	296	284	282	294	292	87.5	88	88.5	88
80	274	266	283	275	259	255	267	263	70	70	75.5	71.8
70	260	255	268	263	—	—	—	—	—	—	—	—
60	238	230	242	237	250	245	256	251	65.5	66	64.7	65.4
50	225	220	231	226	241	236	247	242	61	62.5	63.2	62.2
45.7	225	220	231	226	235	230	242	237	58	60	63.9	60.6
40	225	219	231	226	231	226	238	233	55	56.5	57.0	56.2
30	235	230	242	237	—	—	—	—	—	—	—	—
20	275	275	284	284	225	221	231	227	40	38.5	36.9	38.5
10	295	290	306	300	269	266	278	275	22	22	24.6	22.9
0	—	—	339†	—	—	—	339	—	0	0	0	0

* By thermometer.

† By specific heat method, or 319° by thermometer.

§ In taking these averages, no greater weight has been given to the results from analysis than to those deduced from the melting and solidifying points, because the method of analysis employed does not admit of very great exactness, since a very slight error in the weight of mixed sulphates obtained makes a rather large error in the final result.

Note.—M. p. of pure NaNO₃ = 314° (Braun, *Pogg. Ann.*, 154, 120); = 310° (Person, *Ann. Chim. Phys.*, 1847, 22, 329); = 316° (Carnelley, *Jour. Chem. Soc.*, 33, 276). S. p. of pure NaNO₃ = 298° (Mauenné, *Compt. rend.*, 97, 45). M. p. of pure KNO₃, 342° (Braun, *loc. cit.*); 339° (Carnelley, *loc. cit.*); 339° (Person, *loc. cit.*). S. p. of pure KNO₃ = 32° (Mauenné, *loc. cit.*); 320° (Guthrie, *Phil. Mag.* [5], 18, 114). Schaffgotsch (*Pogg. Ann.*, 102, 293) gives the following as the solidifying points (corrected) of mixtures of sodium and potassium nitrates:—100 per cent. NaNO₃ = 313°; 90 per cent. = 298°; 80 per cent. = 281°; 70 per cent. = 262°; 60 per cent. = 244°; 50 per cent. = 229°; 45.7 per cent. (molec. proportion) = 225.6°; 40 per cent. = 230°; 30 per cent. = 250°; 20 per cent. = 280°; 10 per cent. = 311°; pure KNO₃ = 338.3°.

TABLE IV.

Formula.	Substance.	Constitution.	M. p.	Order of solubility.	One part dissolved by parts solvent.	Solvents.	Authority.
C ₂₀ H ₁₄	Dinaphthyl	$\alpha; \beta$	76°	1	—	usual solvents	Smith, <i>Chem. Soc. Jour.</i> , 32 , 562.
	Dinaphthyl	$\alpha; \alpha$	154	2	—	"	"
	Phenylanthracene	—	152	2	—	"	Schellinger, <i>Annalen</i> , 202 , 61.
	Dinaphthyl	$\beta; \beta$	187	4	—	"	Smith, <i>Chem. Soc. Jour.</i> , 32 , 562.
C ₁₄ H ₁₂ Cl ₂	β -Stilbene dichloride	Ph·C ₂ H ₂ Cl ₂ ·Ph	94	1	all proportions in alcohol	alcohol	Zincke, <i>Ber.</i> , 10 , 999.
	α - " "	"	192	2	10 of alcohol	"	" "
C ₁₀ H ₆ Br ₂	Dibromonaphthalene	—	61	1	—	alcohol	Magatti, <i>Gazzetta</i> , 11 , 357.
	"	—	82	2	16·5 alcohol at 56°	"	Guareschi, <i>Annalen</i> , 222 , 262.
	"	—	131	3	50·0 "	"	" " "
C ₄ H ₆ O ₄	Dimethyloxalate	(CO ₂ CH ₃) ₂	51	1	—	water, alcohol, ether	<i>Watts' Dict.</i> , 4 , 272.
	Isosuccinic acid	CO ₂ H·CH(CH ₃)·CO ₂ H	130	2	5·5 cold water	water	Wichelhaus, <i>Zeit. f. Ch.</i> (2), 3 , 247.
	Succinic acid	CO ₂ H·(CH ₂) ₂ ·CO ₂ H	180	3	20·0 "	water, alcohol, ether	" " "
C ₆ H ₁₄ O ₆	Sorbitol	—	110	1	0·5 water	water; alcohol	<i>Watts' Dict.</i> , 5 , 353; 7 , 1093.
	Isodulcitol	—	110 ^d	2	2·1 "	"	" 5 , 1091.
	Mannitol	—	162	3	6·5 "	"	" 3 , 823.
	Dulcitol	—	182	4	31·0 "	"	" 2 , 349.
	"	—					
C ₉ H ₆ O ₄	Aldehydohydroxybenzoic acid	CO ₂ H : OH : COH = 1 : 2 : 3	166	1	1500 water at 25°	water, alcohol, ether, chloroform	Tiemann, <i>Ber.</i> , 10 , 1562.
	" "	" = 1 : 3 : 4	234	2	—	"	" <i>Ber.</i> , 12 , 1334.
	" "	" = 1 : 4 : 5	244	3	—	"	" <i>Ber.</i> , 9 , 1268.
	" "	" = 1 : 2 : 5	249	4	2600 water at 25°	"	" <i>Ber.</i> , 10 , 1562.
C ₈ H ₈ O ₄	Methoxyhydroxybenzoic acid	CO ₂ H : OH : OMe = 1 : 4 : 5	207	1	39 water at 100°	water	Matsmoto, <i>Ber.</i> , 11 , 122.
	" "	" = 1 : 3 : 4	250	2	155 " "	"	" "
C ₉ H ₈ O ₂	Tropic acid	Ph·C(CO ₂ H)·CH ₂	106	1	692 water at 19°	water	<i>Watts' Dict.</i> , 6 , 249.
	Cinnamic acid	Ph·CH·CH·CO ₂ H	133	2	3500 " 17	"	" "
C ₉ H ₈ O ₅	Methoxyphthalic acid	(CO ₂ H) ₂ : OMe = 1 : 2 : 4	141	1	—	water, ether	Schall, <i>Ber.</i> , 12 , 829.
	Methoxyisophthalic acid	" = 1 : 3 : 2	217	2	—	"	" "
	"	" = 1 : 3 : 4	261	3	—	"	" "
	Methoxyterephthalic acid	" = 1 : 4 : 5	278	4	—	"	<i>Ibid.</i> ; Paternò, <i>Gazzetta</i> , 9 , 455.
C ₉ H ₁₀ O ₃	Hydrocoumaric acid	OH : (CH ₂ ·CH ₂ ·CO ₂ H) = 1 : 2	82	1	20 water at 18°	water	<i>Watts' Dict.</i> , 6 , 715.
	Tropic acid	HO·CH ₂ ·CHPh·CO ₂ H	118	2	49 " 14·5°	"	" 6 , 249.
	Hydroxyxylic acid	Me ₂ : OH : CO ₂ H = 1 : 2 : 4 : 5	199	3	—	"	Jacobsen, <i>Ber.</i> , 12 , 434.
C ₉ H ₁₀ O ₃	Methoxytoluic acid	OMe : Me : CO ₂ H = 1 : 4 : 6	67	1	—	water	Schall, <i>Ber.</i> , 12 , 825.
	"	" = 1 : 2 : 6	81	1	—	"	" "
	"	" = 1 : 3 : 6	103	1	—	"	" "
	"	" = 1 : 2 : 5	156	2	—	"	Gerichten, <i>Ber.</i> , 11 , 1587.
	"	" = 1 : 3 : 4	176	3	—	"	Schall, <i>Ber.</i> , 12 , 825.
	"	" = 1 : 2 : 4	192	4	—	"	" "
C ₁₀ H ₄ Br ₂ O	α -Dibromocamphor	—	59	1	4·5 alcohol at 20°	alcohol	Swarts, <i>Ber.</i> , 15 , 1662.
	β - "	—	114	2	26·7 " "	"	" "
C ₁₁ H ₁₂ Br ₂ O ₃	Methyl- β -methoxyphenyldibromopropionate	MeO·C ₆ H ₄ ·C ₂ H ₂ Br ₂ ·CO ₂ Me = 1 : 2	68	1	28·9 vols. CS ₂	carbon disulphide; alcohol	Perkin, <i>Chem. Soc. Jour.</i> , 39 , 426.
	Methyl- α -methoxyphenyldibromopropionate	" " = 1 : 2	125	2	29·6 "	"	" " "
C ₆ H ₄ O ₄ N ₂	Dinitrobenzene	(NO ₂) ₂ = 1 : 3	90	1	16·9 alcohol at 24·6°	alcohol, chloroform, ether, benzene, water	Körner, <i>Gazzetta</i> , 4 , 305.
	"	" = 1 : 2	118	2	26·3 " 24·8	"	" "
	"	" = 1 : 4	172	3	—	"	Rinne, <i>Ber.</i> , 7 , 869.
C ₆ H ₅ O ₅ N ₃	Amidodinitrophenol	OH : NH ₂ : (NO ₂) ₂ = 1 : 2 : 4 : 6	165	1	714 water at 22°	water; alcohol	Dabney, <i>Amer. Chem. J.</i> , 5 , 20.
	"	" = 1 : 4 : 2 : 6	170	2	1219 " "	"	" " "
	"	NH ₂ : (NO ₂) ₂ = consec.	202	3	—	"	" " "
C ₆ H ₁₃ O ₂ N	Amidocaproic acid	—	170	1	27 cold water	water	<i>Watts' Dict.</i> , 3 , 581.
	"	—	subl. 210	2	43·6 water at 14·5°	"	Nencki, <i>J. pr. Chem.</i> [2], 15 , 390.
C ₆ H ₁₄ O ₂ N	Amylearbamide	NH ₂ ·CO·NH·CH ₂ ·Bu	120	1	28 water at 27°	water	<i>Watts' Dict.</i> , 6 , 1116.
	"	NH ₂ ·CO·NH·CHMePr	151	2	79·3 " "	"	" "
C ₇ H ₅ O ₄ N	Nitrobenzoic acid	CO ₂ H : NO ₂ = 1 : 3	140	1	400 water at 10°	water	<i>Watts' Dict.</i> , 1 , 555.
	"	" = 1 : 2	147	2	400 " 22	—	" 7 , 947.
	"	" = 1 : 4	238	3	1327 " 16	—	" 6 , 314.
C ₇ H ₆ O ₅ N ₂	Dinitranisole	OMe : (NO ₂) ₂ = 1 : 2 : 4	86	1	64 of 90 p. c. alcohol at 21°	alcohol	Salkowski, <i>Ber.</i> , 7 , 370.
	"	" = 1 : 2 : 6	116	2	110 " "	"	" "
C ₉ H ₁₁ O ₂ N	Ethamidobenzoic acid	NH ₂ ·CO ₂ H = 1 : 3	112	1	—	alcohol	Griess, <i>Ber.</i> , 5 , 1038.
	Phenyl- β -amidopropionic acid	Ph·CH(NH ₂)·CH ₂ ·CO ₂ H	121	1	—	"	Posen, <i>Annalen</i> , 195 , 143.
	Phenyl- α -amidopropionic acid	Ph·CH ₂ ·CH(NH ₂)·CO ₂ H	250	2	—	"	Schulze, <i>Ber.</i> , 14 , 1785.
	α -Amidohydratropic acid	CH ₃ ·CPh(NH ₂)·CO ₂ H	w. m. 260°	3	—	"	Tiemann, <i>Ber.</i> , 14 , 1976.
	Phenylmethamidooacetic acid	NHMe·CHPh·CO ₂ H	274°	3	—	"	" <i>Ber.</i> , 14 , 1982.
C ₁₄ H ₁₀ O ₅ N ₂	α -Dinitrodesoxybenzoïn	—	115	1	12 alcohol at 78°	alcohol	Golubeff, <i>Bull. Soc. Chim.</i> [2], 34 , 345.
	β - "	—	126	2	24 "	"	" " "
C ₁₉ H ₂₂ ON ₂	Cinchonidine	—	206	1	76·4 ether at 10°	ether	Hesse, <i>Watts' Dict.</i> , 6 , 463.
	Cinchonine	—	245	2	2118·0 " at 17	"	" "
C ₁₀ H ₆ Cl ₂ O ₄ S ₂	α -Naphthalenedisulphonyl chloride	C ₁₀ H ₆ (SO ₂ Cl) ₂	158	1	7·5 benzene at 14°	benzene, and other solvents	Ebert, <i>Ber.</i> , 9 , 598.
	β - "	"	226	2	221·0 " "	"	" "
C ₇ H ₉ ClO ₃ N ₂	Chlorotoluidine nitrate	Me : Cl : NH ₂ = 1 : 4 : ?	165	1	19·9 water at 17°	water	Wroblewsky, <i>Annalen</i> , 168 , 147.
	"	" = 1 : 4 : ?	179	2	35·5 " "	"	" " "
	"	" = 1 : 3 : 4	189	3	38·5 water at 19°	"	" " "

of solubility is the same as the order of fusibility, i.e., the most fusible compound is likewise the most soluble.

In order to test this rule we have collected from literature all the statements which have been made as regards the solubility of isomeric compounds (a task which has involved a very large amount of labour and time), and we have found as follows:—Out of 752 cases in which the rule can be applied, there are 736 in which the order of fusibility and of solubility is the same, and only 16 exceptions (= 2 per cent.) in which the more fusible compound is the less soluble. This is with reference to one solvent in each case, whereas by taking all the solvents into account which have been tried, we have found that out of 1778 cases in which the rule can be applied, there were 1755 which agreed with the rule, and only 23 exceptions (= 1¼ per cent.).

The following may be taken as examples (see Table IV).

This table shows with what a great variety of compounds the rule holds good. Not only do compounds having a similar constitution obey the rule, but compounds likewise which have nothing in common but their isomerism.

The application of the rule, however, does not stop here, for we find that—

Rule (2). *In any series of isomeric acids, not only is the order of solubility of the acids themselves the same as the order of fusibility, but the same order of solubility extends to all the salts of the several acids, so that the salts of the more soluble and more fusible acids are also more easily soluble than the corresponding salts of the less fusible and less soluble acids.*

We have been able to apply this rule in 143 cases, of which 138 agree with the rule, so that there are only five exceptions, or about 3½ per cent. The following may be given as examples* (see Table V, p. 794).

The above is probably but part of a very general law, viz., that the properties of the corresponding derivatives of two or more isomeric compounds are related to one another in the same way as those of the primitive isomers themselves.

Discussion of Exceptions.—As we have already seen, there are only 28 exceptions out of 1921 cases in which we can apply the rule as to the order of solubility of a series of isomers being the same as the order of fusibility. A list of these exceptions is given in Table VI. In this table the statements as to the solubilities are as nearly as possible verbatim with those given in the original papers.

Of the above 28 exceptions, 12 (viz., Nos. 1, 2, 3, 4, 5, 6, 7, 12, 13, 14, 20, and 21), or nearly one-half, refer to only five sets of isomerides.

* In some instances the melting points of the acids are not known, in which case we have given those of the corresponding acid chlorides or amides instead.

TABLE V.

Formula of acid.	Salt.	Constitution.	M. p.	Order of solubility.	One part of salt dissolved by parts water.	Authority.
$C_9H_8O_2 \dots$	Ca-atropate	$Ph \cdot C(CO_2H) \cdot CH_3 \dots$	of acid 106°	1	43 at 18°	<i>Watts' Dict.</i> , 6 , 249.
$C_{11}H_8O_2 \dots$	Ca-cinnamate	$Ph \cdot CH_2 \cdot CH \cdot CO_2H \dots$	133	2	608 "	" "
	Ca- α -naphthoate.	$C_{10}H_7 \cdot CO_2H \dots$	160	1	93 at 15°	<i>Watts' Dict.</i> , 6 , 851.
	Ca- β - "	"	183	2	1800 "	" "
$C_7H_4Cl_2O_2$	Ba-dichlorbenzoate	$CO_2H : Cl_2 = 1:2:6 \dots$	126	1	21.3 at 4°	<i>Watts' Dict.</i> , 8 , 264.
	"	"	156	2	37.9 at 16°	" "
	"	"	201	3	90.9 at 18°	" "
	Cu- "	"	126	1	" "	" "
	"	"	156	2	" "	" "
$C_{11}H_7BrO_2$	Ca- α -bromnaphthoate	$C_{10}H_6Br \cdot CO_2H \dots$	142	1	65.5 at 20°	Hausemann, <i>Ber.</i> , 9 , 1521
	" β - "	"	256	2	5000 "	" "
	Ba- α - "	"	142	1	59 at 21°	" "
	" β - "	"	256	2	4300 "	" "
	K- α - "	"	142	1	—	" "
	" β - "	"	256	2	—	" "
$C_7H_3IO_3 \dots$	Ba-iodosalicylate	$CO_2H : OH : I = 1:2:5 \dots$	197	1	120 at 8°	Miller, <i>Ber.</i> , 16 , 81.
	"	"	198	2	190 "	" "

Formula of acid.	Salt.	Constitution.	M. p.	Order of solubility.	One part of salt dissolved by parts water.	Authority.
$C_6H_6O_6S_2$	K-benzenedisulphonate	$(SO_3H)_2 = 1:3$	of chloride 63° 131	1	—	<i>Watts' Dict.</i> , 8, 251.
	" "	" = 1:4		2	—	" "
	Ba- " "	" = 1:3	63	1	2·2 at 100°	Körner, <i>Ber.</i> , 9, 583.
	" "	" = 1:4	131	2	13·9 "	" "
	Pb- " "	" = 1:3	63	1	1·2 at 26°	" "
	" "	" = 1:4	131	2	4·0 "	" "
$C_7H_6O_3S$	K-toluenesulphonate	$Me:SO_3H = 1:3$	of amide 108° 136 154	1 } 2 } 3 }	—	Claessen, <i>Ber.</i> , 12, 1851.
	" "	" = 1:2			—	" "
	" "	" = 1:4			—	" "
	Ba- " "	" = 1:3	108	1	4·4 at 12°	" "
	" "	" = 1:2	136	2	4·8 "	" "
	" "	" = 1:4	154	3	26·0 "	" "
	Na-Ag-Ca or Pb-salt	" = 1:3	108	1	—	" "
	" "	" = 1:2	136	2	—	" "
	" "	" = 1:4	154	3	—	" "
	Na-Ag-Ca or Pb-salt	" = 1:3	108	1	—	" "
$C_{10}H_8O_3S$	Ba-β-naphthalenesulphinic acid	$C_{10}H_7SO_3H$	of acid 105°	1	21·5 at 15°	Gessner, <i>Ber.</i> , 9, 1500.
	" "	" "	high temp.	2	201·0 at 14°	" "
	" "	" "				" "

Formula of acid.	Salt.	Constitution.	M. p.	Order of solubility.	One part of salt dissolved by parts water.	Authority.
$C_{10}H_8O_3S$	K-naphthalenesulphonate	α	of amide 150° 217	1	13 at 13°	<i>Watts' Dict.</i> , 6, 860.
	"	β		2	15 at 10°	"
	Ba-	α	150° 217	1	87 at 10°	"
	"	β		2	290 "	"
Ca-	"	α	150° 217	1	16.5 at 10°	"
	"	β		2	76.0 "	"
	Pb-	α	150° 217	1	27.0 at 10°	"
	"	β		2	115 "	"
$C_{10}H_8O_6S_2$	K-naphthalenedisulphonate	α	158 229	1	1.4 at 14°	<i>Watts' Dict.</i> , 8, 1356.
	"	β		2	19.2 at 18°	"
	Na-	α	158 229	1	2.2 at 18°	"
	"	β		2	8.4 at 19°	"
Ca-	"	α	158 229	1	6.2 at 18°	"
	"	β		2	16.2 at 19°	"
	Ba- or Pb-salt	α	158 229	1	—	"
	"	β		2	—	"
$C_{10}H_{11}O_3S$	Ba-cymenesulphonate	Me : Pra : $SO_3H = 1:4:2$	of acid 51° 87	1	40 at 12.5°	Spica, <i>Ber.</i> , 14, 653.
	"	" = 1:4:3		2	214 "	"
$C_9H_{11}O_4SN$	Ba-sulphamine mesitylenate	Me ₂ : ($SO_2 \cdot NH_2$) : $CO_2H = 1:3:4:5$	263 276	1	30.6 at 0°	Jacobsen, <i>Ber.</i> , 12, 606.
	"	" = 1:3:2:5		2	48.8 "	"

Published on 01 January 1888. Downloaded by University of Michigan Library on 30/10/2014 07:56:01.

No.	Formula.	Name.	Constitution.	M. p.	Order of solubility.	1 part dissolved by parts solvent.	Authority.	Remarks.
1, 2, & 3.	C ₄ H ₆ O ₅	Glycollic anhydride..... Diglycollic acid	HO·CH ₂ ·CO·O·CH ₂ ·CO ₂ H ..... O(CH ₂ ·CO·OH) ₂	129° 148	2 1	insoluble in alcohol, ether, and water easily soluble in alcohol, water, and sparingly in ether	Watts' Dict., 7, 570 ..... ,, 2, 913	{ Three exceptions, since they are exceptions as regards all three solvents. The symmetry accords with the m. p. but not with the solubility. Diglycollic acid crystallises with 1 mol. H ₂ O. Would this affect the solubility?
4 & 5.	C ₃ H ₈ O ₄	Dimethyl malonate..... Ethylmalonic acid..... Dimethylmalonic acid	CH ₂ (CO ₂ Me) ₂ ..... CHEt(CO ₂ H) ₂ ..... CM ₂ (CO ₂ H) ₂	liquid 112° 170	3 1 2	insoluble in water ..... easily soluble..... sparingly soluble	Osterland, Ber., 7, 1286 ..... Markownikoff, Annalen, 182, 62 ,, ,, ,,	— — —
6 & 7.	C ₁₁ H ₁₂ O ₃	β-Ethoxyphenylacrylic acid .... β-Methoxyphenylcrotonic acid... Butyrocoumaric acid.....	OEt : (C ₂ H ₅ ·CO ₂ H) = 1 : 2 ..... OMe : (C ₃ H ₄ ·CO ₂ H) = 1 : 4 ..... (C ₄ H ₇ O) : CO ₂ H = 1 : 2	135 154 174 p.d.	2 2 1	not very soluble in alcohol .... moderately soluble..... extremely soluble.....	Perkin, Ch. Soc. Jour., 39, 414 ,, ,, 31, 412 ,, ,, 21, 476	{ Does the butyrocoumaric acid form a compound with alcohol?
8.	C ₂₁ H ₁₄ O	ββ-Dinaphthylketone ..... αα- " " ..... ββ- " "	CO(C ₁₀ H ₇) ₂ ..... " ..... "	125 135 165	2 1 3	267 alcohol at 19° ..... 77 " 14 ..... 1256 " 19	Watts' Dict., 8, 1157 ..... " " ..... " "	{ The modification melting at 125° is said to be a physical isomeride of that melting at 165°.
9.	C ₁₀ H ₆ N ₂	γ-Dicyanonaphthalene..... δ- " "	C ₁₀ H ₆ (CN) ₂ ..... "	204 236	2 1	slightly soluble in alcohol.... easily " "	Watts' Dict., 6, 848 ..... " "	{ cf. Zeitsch. f. Chem. [2], 5, 571.
10.	C ₆ H ₅ IO	Iodophenol ..... "	OH : I = 1 : 3 (?) ..... = 1 : 4 (?) View Article Online	65 89	2 1	sparingly soluble in water.... readily " "	Lobanoff, Ber., 6, 1251. .... " "	{ The symmetry accords with the m. p. but not with the solubility.
11.	C ₇ H ₅ IO ₃	Iodosalicylic acid ..... " "	CO ₂ H : OH : I = 1 : 2 : 5 ..... = 1 : 2 : 3	197 198	2 1	more difficultly soluble in water " easily " "	Miller, Ch. Soc. Jour., 41, 404. " " ..	{ M. ps. very close. The Ba-salts obey the rule.
12, 13, & 14.	C ₈ H ₁₁ O ₂ N	γ-Hydroxyvaleramide ..... Ethylactamide ..... α-Methoxybutyramide..... α-Hydroxyisovaleramide	CH ₃ ·CH(OH)·(CH ₂) ₂ ·CO·NH ₂ ..... CH ₃ ·CH(OEt)·CO·NH ₂ ..... CH ₃ ·CH ₂ ·CH(OMe)·CO·NH ₂ ..... CHMe ₂ ·CH(OH)·CO·NH ₂	50 63 78 104	3 1 1 2	insoluble in ether..... soluble in ether ..... " " ..... sparingly soluble in ether....	Neugebauer, Annalen, 227, 97 Watts' Dict., 3, 452 ..... Duvillier, Compt. rend., 88, 598 Lipp, Annalen, 205, 1.....	— — — —
15.	C ₇ H ₄ O ₆ N ₂	Dinitrobenzoic acid	CO ₂ H : (NO ₂) ₂ = 1 : 3 : 4 ..... " = 1 : 2 : 4	161 u.c. 181	2 1	148 water at 25°..... 54 " "	Claus, Ber., 13, 816..... " "	— —
16.	C ₈ H ₇ O ₄ N	Aldoxime salicylic acid	CO ₂ H : OH : (CH ₂ ·NOH) = 1 : 2 : 5 .. " = 1 : 2 : 3 ..	179 193	2 1	pretty easily soluble in hot water distinctly less soluble in hot water	Fürth, Ber., 16, 2182 ..... " "	{ The 1.2.5-compound crystallises with 1 mol. H ₂ O, whereas the other is anhydrous. Was the m. p. determined with the former in the anhydrous state?
17.	C ₉ H ₇ O ₆ N	α-Nitrouvic acid..... β- " "	(CO ₂ H) ₂ : Me : NO ₂ = 1 : 3 : 5 : 2 .... " = 1 : 3 : 5 : 4	227 250	2 1	crystallises first from water ... " second " ...	Böttiger, Ber., 9, 806 ..... " "	{ The symmetry accords with the solubility but not with the m. p. The α-compound contains 2H ₂ O, and the β-compound ½H ₂ O. Were the m. ps. determined in the anhydrous state?
18.	C ₁₀ H ₆ O ₃ N ₂	Dinitro-α-naphthol..... " -β- "	OH : (NO ₂) ₂ = α ₁ α ₂ β ₁ ; ..... " = β ₁ ² ; β ₁	138 197	2 1	slightly soluble in ether ..... very " "	Watts' Dict., 6, 856 ..... Wallach, Ber., 3, 846	{ The salts obey the rule.
19.	C ₁₁ H ₁₄ O ₂ N ₂	Tolusuccinamide ..... " "	Me : (NH·CO·C ₂ H ₄ ·CO·NH ₂) = 1 : 4. " = 1 : 2.	148 160	2 1	less soluble } solvent not..... more " } stated	Bechi, Ber., 12, 321..... " "	{ The symmetry accords with the solubility but not with the m. p. The corresponding imides agree with the rule both as to symmetry and solubility. Have not the m. ps. got transposed in the original paper?
20 & 21.	C ₁₆ H ₁₅ O ₃ N	α-Ethylidibenzhydroxamate..... β- " "	NBz ₂ EtO..... "	58 63	2 1	easily soluble in alcohol and ether more easily soluble in alcohol and ether	Gürke, Annalen, 205, 279 .... " " " ..	{ (cf. Annalen, 175, 326). M. ps. very close. These are physical isomerides.
22.	C ₃ HClBr ₂ O ₂	β-Chloridibromacrylic acid..... α- " "	CBr ₂ ·CCl·CO ₂ H ..... CBrCl·CBr·CO ₂ H	99 104	2 1	37·1 water at 20° ..... 18·4 " "	Mabery, Am. Ch. J., 6, 157 ... " " " ...	{ Ba-salts obey the rule, Ca-salts do not (see No. 28) ; m. ps. very close. The symmetry accords with the solubility but not with the m. p.
23.	C ₉ H ₁₁ O ₄ SN	Sulphaminemesitylenic acid .... " " "	Me ₂ : CO ₂ H : (SO ₂ ·NH ₂) = 1 : 3 : 5 : 6. " = 1 : 3 : 5 : 2.	263 276 d.	2 1	[hot water] much more easily soluble in	Jacobsen { Ber., 12, 604 ..... Annalen, 206, 167	{ Ba- and Ca-salts obey the rule. The symmetry accords with the m. p. but not with the solubility.
24.	From C ₁₂ H ₁₂ O ₄	Ammonium α-hydropiperate.... " β- "	— —	of acid 78° 131	2 1	less soluble } solvent not..... more " } stated	Buri, Annalen, 216, 172..... " " "	{ The acids obey the rule.</

The above 28 exceptions may be classified thus :—

(1.) Five are only barely exceptions, the melting points being very close, viz., Nos. 11, 20, 21, 22, and 28. The information given in respect to these is not sufficient to allow one to say whether the solubilities are correspondingly close, except in No. 22 (*q.v.*).

(2.) In No. 25 the solubilities of the compounds compared are very nearly equal, whilst the melting points are not very different.

(3.) In No. 27 the two Pb salts referred to were not analysed, and one or other of them might have been a basic salt, and therefore not really isomeric and comparable with the other one.

(4.) Seven, though exceptions themselves, yield salts which obey the rule (viz., Nos. 11, 18, 19, 22, 23, 25, 28).

(5.) Three salts, which are exceptions, are derived from acids which obey the rule (viz., Nos. 24, 25, 26).

(6.) Three (viz., Nos. 8, 20, 21) are physical and not chemical isomerides in the ordinary sense, and our knowledge of the so-called physical isomerides is at present very limited.

(7.) In five (viz., Nos. 1, 2, 3, 10, and 23) the solubilities are exceptional, not only as regards the melting points, but also as regards the symmetry. (The more symmetrical of two isomerides is usually less soluble than the one in which the atomic arrangement is less symmetrical.)

(8.) In five (viz., Nos. 4, 17, 12, 22, 28) the melting points are not only exceptional as regards the solubilities, but also as regards the symmetry. (The more symmetrical of two isomerides usually has the higher melting point.)

(9.) In two (Nos. 16 and 17) one or other of the isomerides contains water of crystallisation, and it is not stated whether the melting point was determined with the anhydrous compound. If made with the hydrated compound, the water would be driven off on heating, and collect in the upper part of the melting point tube, and might run down and lower the melting point of the substance, if proper care were not taken.

(10.) Eight (viz., Nos. 5, 6, 7, 9, 12, 13, 14, 15) are not included in any of the above classes, and so far as one can learn from the statements published in reference to these compounds, there is nothing to lead one to suppose but that they are real exceptions to the rule. We may say, therefore, that out of the 1921 cases in which the rule can be applied, there are only from 9 to 12 exceptions ($= \frac{2}{3}$ per cent.) against which, so far as one can see at present, no objection can be raised. It is possible, however, that most, if not all, of these exceptions may on further investigation turn out to be due to errors either in the determination of the melting points or of the solubilities, or possibly to clerical errors.

The relation between fusibility and solubility may also be illustrated by a great number of cases other than those of isomeric compounds. Among these the following are noteworthy:—

(a.) *Allotropic Modifications of the same Element*.—(1.) *Phosphorus*. Common or yellow phosphorus melts at 44° , and is readily soluble in carbon disulphide, chloride of sulphur, phosphorus trichloride, and phosphorus pentasulphide, and slightly soluble in ether, turpentine, and the essential oils; whereas red phosphorus, which does not melt below 255° , is insoluble in all these solvents. (2.) *Sulphur*. Common or octahedral sulphur melts at 114.5° (Brodie), and is readily soluble in carbon disulphide; whereas plastic sulphur does not melt at 120° (? Brodie), and is insoluble in carbon disulphide. (3.) *Selenium*. Amorphous selenium melts at a little above 100° (Berzelius), and is soluble in carbon disulphide and in benzene; whereas crystalline selenium melts at 217° (Hittorf), and is quite insoluble in carbon disulphide or in benzene.

(b.) *Paraffin Wax*.—The solubility of paraffin wax in benzene is less the higher its melting point, as may be seen from the following table (*Watts' Dict.*, 7, 893):—

M. p.	Quantity of paraffin wax deposited at 18° by 100 c.c. of refined benzene.
35.0°	133 grams.
49.6	6 „
52.8	4.7 „
65.5	1.4 „
80.0	0.1 „

(c.) *Mixtures of Sodium and Potassium Nitrates*.—Table VII (p. 799), which embodies the results of the determinations already given in detail, will show the relations which subsist between the fusibility and solubility of mixtures of sodium and potassium nitrates:—

These results are also shown graphically in Diagrams I and II. Diagram I gives the curves of fusibility and two curves of solubility; in one of the latter, the solubility is referred to the percentage composition of the mixed nitrates *before* solution, and in the other to the composition of the mixed nitrates *after* solution and evaporation to dryness. Diagram II gives the curves, showing the actual weights of sodium and potassium nitrates respectively, dissolved from various mixtures of the two salts, and compares these with the curves of total solubility of the mixed salts.

An inspection of the above table and accompanying diagrams shows:—

(α.) As regards the fusibility and total solubility of the mixed nitrates (see Diagram I):—

TABLE VII.

Per cent. of NaNO_3 in original mixture <i>before</i> solution.	Melting point (cor.) of mixture <i>before</i> solution.	Total weight of mixed salts dissolved by 100 parts of water at 20° } =	Weight of NaNO_3 dissolved. } +	Weight of KNO_3 dissolved. }	Per cent. of NaNO_3 in the mixture <i>after</i> solution and evaporation to dryness.	Melting point (cor.) of the mixed nitrates <i>after</i> solution.
100	316°	86.8	86.8	0	100	316°
90	298	109.6	96.4	13.2	88	294
80	283	136.5	98.0	38.5	71.8	267
70	268	136.3	—	—	—	—
60	242	137.6	90.0	47.6	65.4	256
50	231	106.1	66.0	40.1	62.2	247
45.7*	231	88.0	53.3	34.7	60.6	242
40	231	81.1	45.6	35.5	56.2	238
30	242	73.5	—	—	—	—
20	284	54.1	20.8	33.3	38.5	231
10	306	40.9	9.4	31.5	22.9	278
0	339	33.6	0	33.6	0	339

* = $\text{NaNO}_3 + \text{KNO}_3$.

(1.) That the *fusibility* gradually increases from pure NaNO_3 (m. p. 316°), until the mixture contains about 50 per cent. NaNO_3 , and melts at 231° ; the melting point then remains constant until the sodium nitrate falls to 40 per cent., after which the fusibility gradually diminishes until pure KNO_3 (m. p. 339°) is reached. A mixture having the molecular composition ($\text{NaNO}_3 + \text{KNO}_3$) contains 45.7 per cent. NaNO_3 . According to Schaffgotsch (*Pogg. Ann.*, **102**, 293) the salts when mixed in molecular proportion melt at a lower temperature than when present in any other.

(2.) That, starting with pure sodium nitrate, the total solubility quickly increases until the proportion of the NaNO_3 in the mixture before solution falls to 80 per cent., after this it remains constant until the $\text{NaNO}_3 = 60$ per cent., beyond which the solubility rapidly diminishes until pure potassium nitrate is reached. A mixture containing about 45.7 per cent. NaNO_3 ($= \text{NaNO}_3 + \text{KNO}_3$) dissolves to about the same extent at 20° as pure sodium nitrate, whereas all mixtures containing a smaller proportion of sodium nitrate are less soluble than the pure salt. The above refers to the proportion in which the salts are mixed *before* solution; if, however, the solubilities be referred to the proportion between the two salts in the residue obtained by evaporation of the saturated solution, we find that though the general form of the curve is very similar to that in the first case, yet the solubility is constant over a much smaller range of variation in the composition of the mixed salts. Thus the maximum of solubility is

obtained when the sodium nitrate falls to 72 per cent., and continues constant at this until the sodium nitrate falls to 65 per cent., after which it rapidly diminishes to pure potassium nitrate. It will thus be seen that the depression of the curve, based on the composition of the mixture *after* solution and evaporation, lies throughout its whole course within that of the curve, based on the composition of the mixture *before* solution. This shows that before the maximum of solubility is reached the proportion of sodium nitrate in the dissolved portion is less than in the mixture before solution, whilst beyond that point it is greater. In other words, starting with pure sodium nitrate, there is a smaller proportion of sodium nitrate in solution than in the original mixture until the point of maximum solubility is reached, after which the proportion of sodium nitrate in solution is greater than in the original mixture before solution.

(3.) That the general form of the four curves (two of fusibility and the other two of solubility) in Diagram I is very similar, showing an intimate connection between them. The two curves of solubility, however, differ from those of fusibility in one important particular, in that, starting from the pure sodium nitrate end, the maxima of the two solubility curves occur earlier than those of the curves of fusibility. Thus, whereas the middle of the maximum of fusibility occurs when the composition of the mixture corresponds with the formula ($\text{NaNO}_3 + \text{KNO}_3$), that of the two solubility curves corresponds approximately with the composition ($3\text{NaNO}_3 + \text{KNO}_3$). That is to say, the addition of potassium nitrate to the pure sodium salt affects the solubility more quickly than it does the fusibility, whereas the addition of sodium nitrate to pure potassium nitrate increases the fusibility more rapidly than it does the solubility.

(β .) As regards the solubilities of the sodium and potassium nitrates respectively in the presence of one another (see Diagram II) :—

(4.) That the solubility of pure potassium nitrate at 20° (Curves B_1 and B_2) is scarcely, if at all, affected by the addition thereto of the sodium salt, unless the amount of the latter present in the mixture reaches about 45 per cent. before solution, or 60 per cent. in the dissolved portion. Thus a solution of pure potassium nitrate, saturated at 20° , contained 33.6 parts by weight of the pure salt in 100 parts of water, while a saturated solution obtained by treating a mixture consisting of 20 per cent. NaNO_3 , and 80 per cent. KNO_3 , contained 33.3 parts of potassium nitrate, and one obtained by treating a mixture consisting of 45.7 per cent. NaNO_3 , and 54.3 per cent. KNO_3 , contained 34.7 parts of potassium nitrate. The residues obtained by evaporating the several saturated solutions to dryness weighed 33.6, 54.1, and 88.0 grams respectively, and contained 0, 38.5, and 60.6 per cent. of sodium nitrate. When the mixture contains more than

I. DIAGRAM OF THE SOLUBILITY AND FUSIBILITY OF MIXTURES OF SODIUM AND POTASSIUM NITRATES.

REFERENCE.

Curve of Total Solubility and % composition of mixture before solution .....
 Ditto ..... ditto ..... after solution and evaporation .....
 Curves of Melting Points of mixed Nitrates .....
 Curves of Solidifying Points of ditto .....

II. DIAGRAM OF SOLUBILITY FOR MIXTURES OF SODIUM AND POTASSIUM NITRATES

- A_1 = Curve of Total Solubility of Mixture and % composition of mixture before solution —————
 A_2 = ——— Ditto ————— ditto ————— after solution - - - - -
 B_1 = Curve of Solubility of KNO_3 and % composition of mixture before solution - - - - -
 B_2 = ——— Ditto ————— ditto ————— after solution .....
 C_1 = Curve of Solubility of NaNO_3 and % composition of mixture before solution .....
 C_2 = ——— Ditto ————— ditto ————— after solution - - - - -

45 per cent. of sodium nitrate, the weight of the potassium salt dissolved increases, until the former salt reaches about 60 per cent., after which it rapidly diminishes, until the salt consists of pure sodium nitrate. The weight of potassium nitrate dissolved by a given weight of water at 20° from a mixture containing 82 per cent. of sodium nitrate, is also the same as that dissolved from pure potassium nitrate by the same weight of water at the same temperature.

(5.) That the solubility of pure sodium nitrate at 20° (Curves C₁ and C₂) is at first somewhat increased by admixture with potassium nitrate; this continues until the latter reaches about 20 per cent., after which the solubility of the sodium salt, at first slowly, and then rapidly, diminishes, until the salt consists of pure potassium nitrate.

III. *Influence of the Nature of the Solvent.*

If it be true that the more fusible compound is also the more soluble, it follows that:—

Rule (3). *For any series of isomeric compounds the order of solubility is the same, no matter what may be the nature of the solvent.*

We have been able to apply this rule in 666 cases, and find that the whole of these, without a single exception, accord with the rule. A few examples in illustration of this rule are given in Table II. It holds good not only with acids but also with their salts, so far, at least, as the solubilities of such salts have been tested in solvents other than water (cf. Rule 2). It further holds in many other cases, *e.g.*, the two allotropic modifications of phosphorus, of sulphur, and of selenium (see above, p. 798).

With the view of submitting this rule to a very stringent test we have determined the solubility of meta- and para-nitraniline in 13 different solvents, with the results given in Table VIII, p. 802.*

This table shows, therefore, that no matter what the nature of the solvent, the meta-nitraniline is always more soluble than the para-compound.

The table further shows that:—

Rule (4). *The ratio of the solubilities of the two isomerides in any given solvent is very nearly constant, and is therefore independent of the nature of the solvent.*

This ratio varies from the extreme limits of 1.15 in the case of methyl alcohol, in which the nitranilines are most soluble, to 1.48 in water, in which they are least soluble. The ratios for the other solvents, however, lie very much nearer to the mean value 1.29, the greatest deviation from it, in their case, being confined to the second decimal place.

* For details of these determinations see Table I.

TABLE VIII.

Solvent.	Weight of substance dissolved by 100 parts by weight of solvent.		Ratio. $\frac{\text{meta-}}{\text{para-}}$
	Meta-.	Para-.	
Water, H_2O	0·114	0·077	1·48 highest
Methyl alcohol, CH_4O	11·06	9·59	1·15 lowest
Ethyl alcohol, $\text{C}_2\text{H}_5\text{O}$	7·05	5·84	1·21
Propyl alcohol, $\text{C}_3\text{H}_8\text{O}$	5·65	4·35	1·30
Isobutyl alcohol, $\text{C}_4\text{H}_{10}\text{O}$	2·64	1·91	1·38
Isoamyl alcohol, $\text{C}_5\text{H}_{12}\text{O}$	8·51	6·29	1·35
Ethyl ether, $\text{C}_4\text{H}_{10}\text{O}$	7·89	6·10	1·29
Benzene, C_6H_6	2·45	1·98	1·24
Toluene, C_7H_8	1·71	1·31	1·31
Cumene, C_9H_{12}	1·15	0·90	1·28
Chloroform, CHCl_3	3·01	2·31	1·30
Carbon tetrachloride, CCl_4	0·21	0·17	1·24
Carbon disulphide, CS_2	0·33	0·26	1·27
	—	Mean =	1·29

It will be noted that the solvents employed are numerous and very varied in character, whilst at the same time the range in solubility is very great, varying in the case of the para-compound from 0·077 in water to 9·59 in methyl alcohol, in the latter of which, therefore, it is 124 times more soluble than in water. This forms a very crucial test, at least so far as regards the order of solubility.

Up to the present we have only completed experiments with this single pair of compounds, but we are extending the work to other series of isomerides. If this further work confirms the above results, then the solubility of any pair of isomerides A and B will be represented by the following expression, which is independent of the nature of the solvent:—

$$\frac{\text{Solubility of A in any solvent}}{\text{Solubility of B in the same solvent}} = \text{constant (for any given temperature).}$$

So that if the solubility of A in any solvent at a given temperature be known, that of B at the same temperature may be calculated. The influence of temperature on the above ratio is at present under investigation, and we are also engaged with the determination of the solubility of isomerides at temperatures equidistant from their melting points.

The bearing of the above results on the general question of the nature of solution will be discussed later in connection with other data obtained on entirely independent lines, but all leading to the same point.