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EQUILIBRIUM IN THE SYSTEM: MERCURIC IODIDE AND ANILIN.

E. J. FRY AND J. N. PEARCE.

Those who have worked with anilin have no doubt observed its extraordinary high solvent power upon many of the inorganic salts.

Like ammonia it also has the power of combining with salts to form stable crystalline compounds containing from one to as high as six molecules of anilin of crystallization.

Among the large number of crystalline compounds which have been prepared are $CoCl_2.2C_6H_7N$, $NiCl_2.2C_6H_7N$,[1] $Cu_2Cl_2.2C_6H_7N$, $Cu_2Br_2.2C_6H_7N$, $Cu_2I_2.2C_6H_7N$[2]. Tombeck[3] produced the corresponding compounds of the chlorides, bromides, iodides, and nitrates of zinc and cadmium and magnesium nitrate. He also prepared similar compounds of zinc, cadmium, magnesium, nickel, cobalt, and copper sulphates, all of which combine with two molecules of anilin, except nickel sulphate, which crystallizes with six molecules, and cobalt sulphate, which crystallizes with four molecules of anilin. Grossman and Hunter[4] prepared the compounds of the thiocyanides of cadmium, cobalt, nickel, iron, manganese, and zinc, each combining with two molecules of the base. Upon further treatment of the addition compounds thus formed with thio-cyanic acid double thio-cyanides corresponding to the formula $Cd\ (Ph.NH_3)_2\ (SCN)_4$ were obtained. The dichromates of cobalt, nickel, copper, cadmium, zinc, and manganese, each with four molecules of anilin, were prepared by Parravaus and Pasta[5]. Franquoise[6] contributed the compound $HgI_2.2C_6H_7N$.

The usual method of preparing these compounds has been to treat alcoholic solutions of anilin with the salt, or vice versa. No reference to compounds made by direct combinations of anilin with the inorganic salts was found.

Only one system containing anilin and an inorganic salt has been studied quantitatively. This was worked out by Menchutkin[7] for the system magnesium bromide and anilin. These two substances react with the liberation of much heat and produce three compounds. The tempera-

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[1] Lippmann and Vortmann, Ber., *12*, 79, 1889.
[2] Saglier, C. r., *106*, 1422-25.
[3] C. r., *124*, 961; *126*, 967.
[4] Z. anorgan. Chem., *46*, 361, 1903.
[5] Gazzetta, *37*, ii, 252-264, 1907.
[6] J. Pharm. Chem. VI, 21-24, 1906.
[7] Gazzetta, *37*, i, 252-264, 1907.

ture-solubility equilibrium curve consists of three branches, viz., $MgBr_2.6C_6H_7N$ in equilibrium with its saturated solution at all temperatures up to 103°C; that of $MgBr_2.4C_6H_7N$ between 103° and 237° C; and probably the compound $MgBr_2.2C_6H_7N$ or $MgBr_2.C_6H_7N$ at still higher temperature, but owing to decomposition the investigation could not be carried higher than 250° C. or 260° C.

OBJECT.

Owing to the relatively high solubility of mercuric iodide in anilin at ordinary temperatures, the dimorphic nature of the solid mercuric iodide and the power of the two to form crystalline compounds, it was thought worth while to make a careful study of this system over the maximum possible range of temperature. For this purpose the regular solubility method was used.

MATERIALS.

Kahlbaum's anilin "I" was dehydrated over fused potassium hydroxide for two weeks and carefully distilled, only that portion passing over at 180°-182° C. (uncor.) being collected for the work, while the first and last portions were rejected.

The mercuric iodide was precipitated from a saturated solution of chemically pure mercuric chloride by means of an equivalent weight of pure potassium iodide. The precipitate was allowed to settle and then washed by decantation, using large volumes of distilled water, until all traces of chlorine were removed. It was then transferred to a large Büchner funnel, washed with distilled water, sucked dry, and finally spread upon porous plates and thoroughly dried.

APPARATUS.

The solubility determinations were made in an apparatus similar to the one used by Pearce and Moore.[8]

For all temperatures between 0° C. and 42.9° C. an electrically heated and electrically controlled water thermostat was used; a cooling coil for running water was added for all temperatures below that of the room. In this way temperatures constant to within a few hundredths of a degree could be kept for any desired period of time. For temperatures above 42.9° C. the saturation tube was immersed in the vapor of a boiling liquid whose boiling point was approximately equal to the temperature desired. The tube containing the motor-driven spiral was inserted through a tightly fitting cork into a large boiling vessel containing the

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[8] Amer. Chem. Jour., *50*, 220, 1913.

liquid and this was fitted with a long vertical condenser to prevent the loss of the boiling liquid by evaporation. The liquid was maintained at the boiling temperature by means of an electrically heated platinum spiral. In order to prevent variation in the temperature, due to radiation, which increases with rise in temperature, the whole apparatus, excepting the condenser, was inclosed in an asbestos case fitted with a glass door through which the temperature readings could be taken. In order to still further prevent loss of heat by radiation, the inside of the case was heated by means of incandescent electric lights. By this means even the highest temperatures could be held constant to within ±.05° C., any variation being due to changes in barometric pressure only. For temperatures below 0° C., the saturation tube and stirrer were transferred to a larger tube, which was surrounded by a freezing mixture of salt and ice. These temperatures could likewise be kept constant for four to six hours by the careful addition of salt and ice. All temperatures were read on a certified mercury thermometer passing through the cork and kept at the same level as the material in the saturation tube. All thermometers used were graduated in 0.1° C., permitting estimations accurate to ±.05° C.

Repeated tests showed saturation to be complete in about one and one-half hours. In most cases, however, a much longer time was allowed for saturation, except at the three highest temperatures, where, owing to decomposition, the time had to be limited somewhat.

After saturation was complete the stirrer was stopped, the solid phase was allowed to settle for a few minutes and a sample of the liquid phase was removed by a small tube covered at one end by a double thickness of muslin. In order to prevent solidification within the tube, the latter was heated to a temperature slightly higher than that of the saturated solution. All samples were run at once into dry glass-stoppered weighing bottles and kept in dry desiccators at room temperatures until analyzed.

The difficulties in the analysis of either phase of the system are readily appreciated by one familiar with the extremely volatile nature of the iodide and its inertness in the ordinary acids. The complications are still further increased by the difficulties of eliminating the easily oxidized anilin and its oxidation products.

Three possible methods for the determination of the mercury seemed available. An attempt was made to dissolve out the anilin with dilute hydrochloric acid and to weigh the mercuric iodide directly, but the iodide was found to be appreciably soluble in the anilin hydrochloride formed. Likewise, the electrolytic method was found to be unsatisfactory, owing to the formation of anilin black at the anode. This was deposited upon the surface of the mercury and exposed platinum and could not be removed. The method finally adopted was to dissolve the sample in a solution of acetic acid containing an excess of potassium iodide and to precipitate the mercury as the sulphide by passing in hydrogen sulphide to complete precipitation. This method proved very satisfactory and was used in all determinations.

Samples taken at the three highest temperatures seemed to be more difficultly soluble, and complete transformation to the sulphide was accomplished by placing the solid mass in the acetic acid-potassium iodide solution and passing in hydrogen sulphide for two or three hours until portions of the filtrate gave no test for mercury on further treatment with hydrogen sulphide. The precipitate was transferred to a weighed Gooch crucible, washed with water and dried. The free sulphur was removed by carbon bisulphide in an electrically heated extraction apparatus of the form recommended by Treadwell and Hall.[9]

The quantities of acetic acid or potassium iodide added did not seem to affect the speed of transformation of mercuric iodide to sulphide, but the physical nature of the precipitate seemed to be a little better, if the solution was heated slightly before being filtered.

However, the nature of the mercuric sulphide precipitated from the anilin solutions made it necessary to do all drying at temperatures below 70° C. to avoid loss due to the volatilization of mercuric sulphide. In order to test the effect of temperature upon the extent of volatilization of the sulphide, weighed Gooch crucibles containing the pure dry sulphides were heated for intervals of one to three hours at 70°, 80° and 110 ° C., the temperature recommended by Treadwell and Hall.[10]

TABLE I.

HgS	One hour at 110° C.	Two hours at 110° C.
1.4352 gr.	1.4201	1.2784
2.3076	2.2321	2.0375
HgS	Two hours at 80° C.	Three hours at 80° C.
.5412	.5378	.5300
.6879	.6765	.6685
HgS	One hour at 70° C.	Three hours at 70° C.
.1311	4311	.4311
.4432	.4432	.4432
.2054	.2054	.2054
.1802	.1801	.1801

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[9] Analytical Chemistry, Vol. II, 3d Ed., 169.
[10] loc. cit.

By observing these precautions, results were obtained which leave little to be desired as to the accuracy of the method. Analyses made on known weights of mercuric iodide in anilin gave results for mercuric iodide averaging to within less than .01 per cent.

TABLE II.

ANALYSIS ON KNOWN WEIGHTS OF HgI_2.

Gr. taken	Gr. found
.4325	.4323
.2936	.2930
.5872	.5872

Results of analyses are found in table III and are graphically represented by the curve, Plate XIX.

TABLE III.

Temp. ° C.	Sample	HgS	HgI_2	Gr. HgI_2 per 100 Gr. of Anilin	Mean
-6.5	4.0110	.3910	.7636	23.52	23.61
-6.5	3.7128	.3667	.7162	23.10	
-6.5	3.8273	.3719	.7264	23.42	
.4	1.6667	.2054	.4012	28.72	28.69
.4	2.8167	.3214	.6277	28.68	
.4	1.5798	.1802	.3519	28.66	
17.8	2.8032	.4311	.8420	42.94	42.83
17.8	2.8818	.4432	.8670	42.80	
17.8	2.8667	.4396	.8586	42.81	
21.10	3.0095	.4937	.9867	47.43	47.55
21.10	2.7408	.4543	.8848	47.67	
26.9	3.7408	.6842	1.3365	55.58	55.47
26.9	2.7353	.4987	.9707	55.35	
30.1	3.5303	.6927	1.3530	62.14	62.05
30.1	3.3077	.6478	1.2650	61.96	
36.2	2.4979	.5512	1.0770	75.76	75.80
36.2	2.9044	.6456	1.2610	76.03	
36.2	3.1347	.6879	1.3435	75.72	
42.9	3.2802	.8204	1.6025	96.60	96.49
42.9	3.4225	.8604	1.6805	96.47	
42.9	3.5057	.8812	1.7210	96.40	
48.8	3.6347	1.0447	2.0480	128.4	128.1
48.8	3.6440	1.0509	2.0530	128.0	
48.8	3.8001	1.0901	2.1290	127.9	

TABLE III—Concluded.

Temp. ° C.	Sample	HgS	HgI_2	Gr. HgI_2 per 100 Gr. of Anilin	Mean
63.6	2.4242	.7680	1.5000	162.9	163.8
63.6	2.0912	.6652	1.2990	164.0	
63.6	2.1322	.6833	1.3350	163.6	
70.82	7.4980	2.4870	4.8580	184.0	184.1
70.82	7.4982	2.4890	4.8600	184.2	
76.2	4.3407	1.4910	2.9120	202.5	201.8
76.2	3.6806	1.2586	2.4590	201.2	
77.35	.7988	.2779	.5428	211.45	211.5
77.35	.7902	.2747	.5365	211.60	
95.9	1.5092	.5500	1.874	246.8	246.7
95.9	1.5092	.5497	1.072	246.5	
97.2	4.1847	1.4658	2.863	216.2	214.9
97.2	4.0332	1.4095	2.7525	214.3	
97.2	3.7170	1.2950	2.5292	213.0	
99.1	4.2948	1.4540	2.8400	220.7	221.0
99.1	3.7840	1.3339	2.6055	221.5	
99.1	4.6574	1.6415	1.4514	221.0	
105.9	1.1751	.4179	.8343	239.5	239.1
105.9	1.5432	.5566	1.0870	238.3	
105.9	2.4114	.8707	1.7010	239.4	
111.0	4.3550	1.6221	3.0960	245.9	245.0
111.0	4.4086	1.6030	3.1310	245.2	
111.0	4.8830	1.7470	3.4120	243.5	
115.7	2.2389	.8456	1.6520	281.8	281.8
115.7	1.3955	.5274	1.0300	281.8	
137.2	.6997	.2648	.5172	284.9	285.2
137.2	.1893	.0720	.1490	286.5	
181.1	.9820	.3763	.7350	297.6	297.9
181.1	2.4612	.9823	1.9180	298.3	

The freezing point of pure anilin has been found to be —8° C.,[11] hence that part of the curve between —8° and —11.8° represents the freezing point curve for solution in equilibrium with solid anilin.

At —11.50° C. solid anilin and the compound $HgI_2.2C_6H_7N$ separate out in the form of a eutectic mixture. This point was determined three times by determining the cooling curve of the saturated solution. In a freezing point tube fitted with a thermometer and stirrer and surrounded

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[11] E. Lucuis, Ber. V, 154-155, 1872.

by an air jacket was placed the saturated solution. The whole was surrounded by a freezing mixture of salt and ice and gently stirred until a slight under-cooling was obtained. The temperature then quickly rose to —11.6° C., where it remained constant until the entire mass solidified and then fell slowly to the temperature of the bath, which was kept at a temperature of —16°. The points obtained were —11.5°, —11.55°, —11.4°, the mean being —11.483°.

Beginning with the eutectic point, the solubility increases gradually to 10°, then more rapidly to 42.9°. The white crystalline solid in equilibrium with the saturated solution has the composition $HgI_2.2C_6H_7N$. These crystals have parallel cleavage and parallel extinction, and melt at 58.6°. They are third or fourth system crystals, but it was impossible to determine exactly which. At 42.9° we have a quadruple point representing an equlibrium between HgI_2, $HgI_2.2C_6H_7N$, saturated solution and anilin vapor.

The solubility curve rises rapidly with the rise in temperature up to approximately 108°, the solid phase in equilibrium being red mercuric iodide. At approximately 108° we have another quadruple point, the solids being the red and yellow mercuric iodides in equlibrium with saturated solution and vapor. The transition point from red mercuric iodide to yellow mercuric iodide is apparently lowered by the influence of the solvent from 126° to 108°. This is in accord with the work done by J. H. Kastle,[12] in which he finds that the transition point of the iodide is affected by the solvent used.

An insoluble greenish yellow solid begins to appear at this point and the solution assumes a violet permanganate color.

From 108° the increase in solubility with rise in temperature is but slight up to approximately 200°, where the substance passes into a state of fusion, and the decomposition of the anilin prevented the investigation being carried further. The entire mass solidified into a sort of pasty solid on being allowed to cool. The solid in equilibrium with the solution above 105° is yellow mercuric iodide.

The insoluble solid coming in at 108° and above was isolated, thoroughly washed with distilled water and alcohol. It is a greenish yellow, flaky, micalike solid having oblique extension angles and no cleavage, belonging to the fifth or sixth system; it is insoluble in water, alcohol, hot anilin, or the ordinary acids, but dissolves in potassium cyanide, liberating metallic mercury. It will precipitate silver iodide from strong acid solution of silver nitrate and was found to contain 35.7

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[12] Am. Chem. Jour., 22-473, 1899.

per cent of iodine and 56.9 per cent mercury, corresponding very closely to a compound of the composition $C_6H_5N.Hg_2I_2$, which would contain 34.02 per cent iodine and 53.77 per cent mercury.

SUMMARY.

A complete curve representing the conditions of equilibrium between mercuric iodide and anilin has been plotted for temperatures between —11.48° and 199.9°.

The region of stability of the three solids $HgI_2.2C_6H_7N$, red mercuric iodide, and yellow mercuric iodide, has been established.

Sixteen solubility measurements of mercuric iodide in anilin are given, all in duplicate and mostly in triplicate.

A new compound corresponding to the formula $C_6H_7N.Hg_2I_2$ has been identified and described.

The compound $HgI_2.2C_6H_7N$ has been made by direct combination of mercuric iodide and anilin.

A method for the determination of mercuric iodide as mercuric sulphide in the presence of an easily oxidized organic solvent has been tested.

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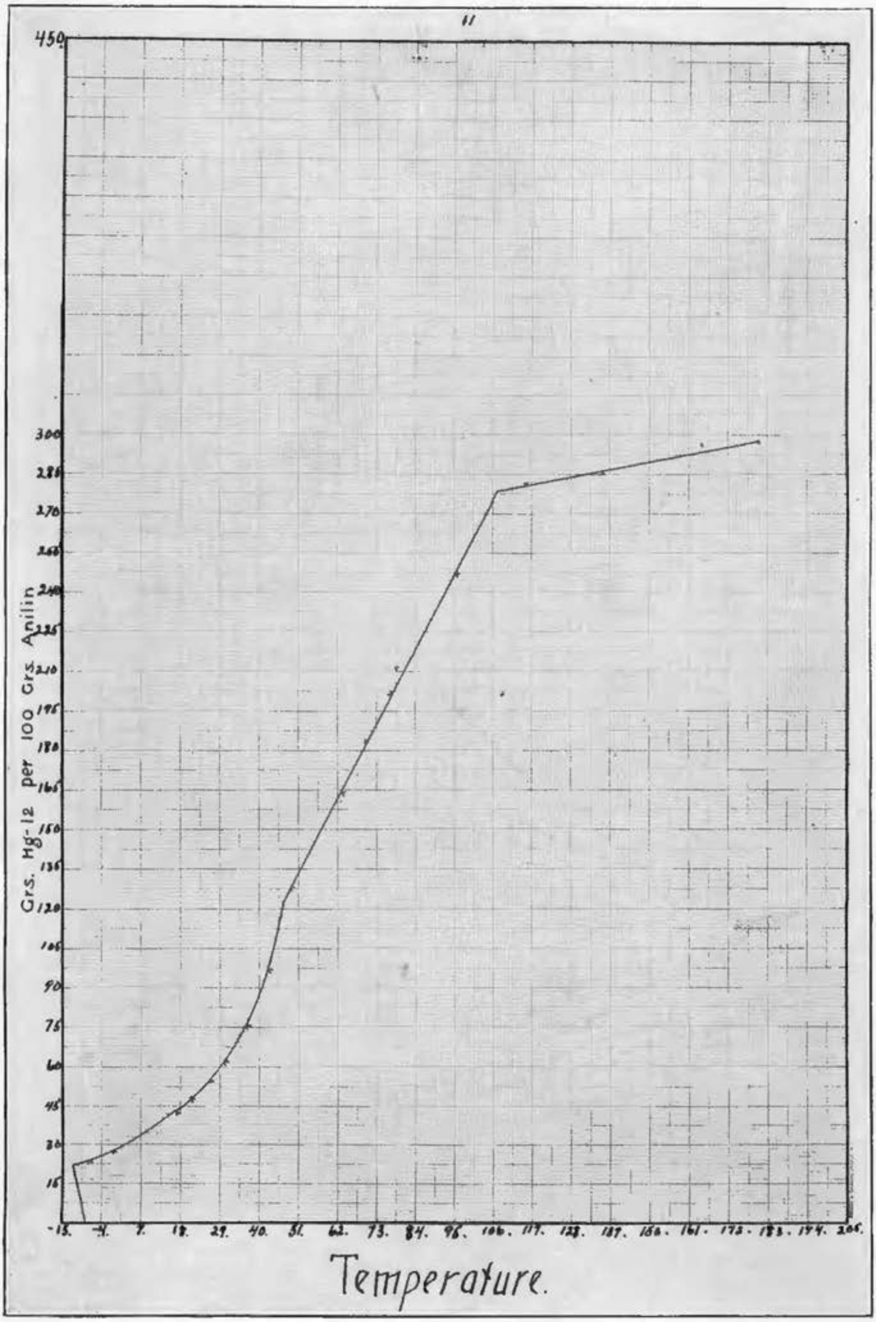

Plate XIX. Curve showing conditions of equilibrium between mercuric iodide and anilin.