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sium nitrite and dilute nitric acid. Mix with Plugge's reagent, a solution of mercurous nitrate with a little nitrous acid, and again heat to boiling. A deep red color is developed.

Antipyrin and phenacetin, two other popular antipyretics much used in medicine, may be readily distinguished from acetanilid by the foregoing tests. Antipyrin, for instance, with ferric chloride gives a deep-red coloration and is precipitated from its solutions by mercuric chloride. It has approximately the same melting point as acetanilid, but, unlike the latter, is decomposed by further heating. The characteristic reactions for phenacetin have been given by the writer in a former article.¹

Comparative tests have been made upon various samples of acetanilid of domestic and foreign manufacture. The products of reputable houses seem to be practically identical with the exception of difference in perfection of crystallization and a corresponding difference in appearance.

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HEATS OF SOLUTION OF SOME CARBON COMPOUNDS.

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Received October 14, 1895.

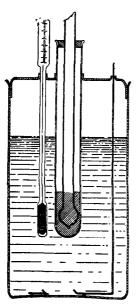
THE following paper contains a few data about the heats of solution of some solid carbon compounds in water, methyl alcohol, ethyl alcohol, propyl alcohol, chloroform, and toluene.

The simple method given by Nernst² was used.

The calorimeter was made of thin glass. The rim was ground to take the cover which fitted fairly well against the inside ground rim of the beaker, not air tight but tight enough to prevent appreciable evaporation of the more volatile solvents during the experiment. The cover had three holes with short tubulures. The center tubulure carried a test tube firmly fastened with a cork, the second tubulure as close to the center one as possible, carried the thermometer, while the third one, somewhat farther from the center, let the handle of the platinum stirrer pass through ; see figure. The calorimeter held com-

2 Ztschr. phys. Chem., 2, 23.

¹ J. Anal. Appl. Chem., 7, 2.



fortably 375 cc., none of the liquid spattering against the cover while stirring. In calculating the water value of the calorimeter, the cover, being some distance from the surface of the solution, was not considered; as the calorimeter without the cover weighed 64.70 grams, its value was 64.70 $\times 0.195 = 12.63$ grams. Later on this calorimeter was broken and replaced by another whose value was 69.44 $\times 0.195 = 13.54$ grams water. The first calorimeter with cover weighed 87.60 grams, the second one, 94.90 grams.

The bottom of the test tube which held the substance to be dissolved was about two inclues below the surface of the solvent. A glass tube closed at both ends and blown out a little at one end, projected above the protecting vessels of the calorimeter and ran down to the bottom of the

test tube. A sharp tap on the top shattered the bottom of the test tube and the solvent entering quickly dissolved the solid when the latter was rubbed off the sides of the test tube by the swelled tube. This was quite necessary, for the finely powdered solids made a pasty mass with the solvent and stuck tenaciously to the test tube.

The test tubes were so near the same size and dipped so equally into the solvent that the water value of this part could be considered constant. In a few exceptional cases the test tubes were of a different size. The same plunger was used throughout.

The platinum stirrer was made of ordinary laboratory foil stiffened with wire. It was disk-shaped and about nine cm. in diameter. From the circumference inward, about one cm., and then parallel with the circumference about two cm., cuts were made. The pieces thus partly cut loose were bent alternately up and down. A stout platinum wire was welded to the disk, and ended in a cork, to serve as a non-conducting handle. A circular hole in the center let the thermometer and test tube pass through. This stirrer has already been described in the chemical literature;¹ it was very effective. Its total weight, without cork, was 12.036 grams, but as only 9.948 grams dipped into the liquid, its value was taken to be 9.948 \times 0.0324 = 0.322 grams of water.

The thermometer was made by Götze some seven years ago. It was divided into hundredths of a degree and thousandths could easily be estimated when observing through a telescope. Its value was determined by cooling in ice and plunging into the calorimeter, as well as by measurement and computation; it was 1.0 gram water. It was carefully calibrated.

The solutions were so dilute, their specific heats could be reasonably considered equal to those of the pure solvents.

The calorimeter stood on three hard wood pins in a bright tin vessel, large enough to leave an air space of an inch all around. The sides and top of the tin vessel were covered with felt. This tin vessel in turn stood on three pins in another bright tin vessel, leaving an air space of two inches all around. The sides and top of this tin vessel were likewise covered with felt. In turn, it stood in a third bright tin vessel, leaving an air space of two inches all around. This last vessel had only a top cover of felt. It was immersed to within an inch of the top in water contained in a large galvanized tank about seventy-five cm. in diameter and thirty cm. deep. The temperature of the water was kept around 25° .

These arrangements were required because the experiments were carried on at night in a small room and the abundant radiation had to be checked. They answered the purpose.

The solvent was contained in a calibrated flask. This stood on a piece of felt in a bright tin vessel, whose sides and top were covered with felt. This vessel in turn stood on three hard wood pins in another bright tin vessel, which had only a top cover of felt because it was immersed to within an inch of the top in the water of the large tank just mentioned. The flask was carefully calibrated for delivery. It had a long neck with a felt wrapping

¹ I cannot recall where.

to protect against the heat of the hand when pouring out the solvent.

Some hours before an experiment was to be made the flask was filled and put in the proper vessel in the tank. The calorimeter, with substance in the test tube, and test tube, thermometer, and stirrer, in place, was also put in the proper vessel in the tank. When the time came, the solvent was carefully poured into the calorimeter and the apparatus put together again. The mercury in the thermometer soon assumed a slow, regular motion. Observations were then made every minute for five minutes, at the same time the liquid was stirred slowly and regularly. At the end of the fifth minute a sharp tap on the projecting glass tube shattered the bottom of the test tube and a few up and down rubs removed the pasty mass from the walls of the tube. The stirring was kept up all the time, slowly and regularly. The solution was generally completed within a minute, but in any case, no more than five minutes were required for complete solution. The mercury then resumed the previous slow and regular movement. The beginning of this regular movement was sharply marked and showed when solution was complete. The mercury was again observed every minute for another five minutes. The change in temperature from the time of adding the solid to the time of slow and regular movement was considered as the change in temperature produced by dissolving the substance.

The corrections were calculated by Regnault's and Pfaundler's method. $^{\scriptscriptstyle 1}$

In the following tables, these abbreviations are used :

m = mass of substance dissolved in grams.

 $\Delta t_i = Average change in temperature for one minute during the first five minutes.$

 $\Delta t_2 = ditto during the second five minutes.$

t = correction.

 $\Delta T =$ corrected change in temperature produced by dissolving the substance.

M = value in grams of water, of liquid, calorimeter, thermometer, test tube, and plunger.

¹ See Berthelot : Calorimetrie chimique, p. 41. (4) q = quantity of heat in small calories connected with the solution of m grams of substance.

Q = quantity of heat in small calories connected with the solution of one gram molecule of substance.

T = temperature of solvent at commencement of experiment.

HEATS OF SOLUTION IN WATER.

The water was carefully distilled, but was not further purified.

Urea.

The urea came from Merck; it was recrystallized from alcohol, powdered, and dried. Melting point = 132.7° cor.; melting point according to Beilstein = 132° .

Thomsen gives 3349 calories ; Ostwald, quoting Berthelot and Petit, gives 36 K, where K may be considered as 100 calories.

Urethane.

The urethane came from Kahlbaum. Melting point $= 48.5^{\circ}$ cor. It was melted, dried, and powdered. Melting point $= 47.33^{\circ}$ cor. Tested for chlorine, but none found.

Chloral Hydrate.

From Kahlbaum. Aqueous solution slightly acid. On adding silver nitrate and nitric acid to an aqueous solution a slight precipitate formed after twenty-four hours. Concentrated sulphuric acid caused the separation of chloral, without any coloration. Melting point = 49.4° cor. Beilstein quotes melting point = 57° ; Fehling gives figures varying from 46° to 58° .

Ostwald quoting Berthelot would make the heat of solution 8.1 K on 810 cals. at 22° , the heat of solution decreasing with rising temperature.

Succinimide.

From Kahlbaum. Recrystallized from water and dried at $85^{\circ}-100^{\circ}$. Small quantity of white fume given off at about 95° . Melting point = 124.5° cor. Beilstein gives $125^{\circ}-126^{\circ}$.

m.	Δt_1 .	Δt ₂ .	t.	ΔΤ.	м.	q.	Q.	т.
5.5606	-0.0040	-0.0080	-0.024	—0.621	389.6	-242.0	-4306	21.5°
2.3592	-0.0026	-0.0024	-0.002	-0.262	389.5	—I02.0	-4282	23.2°
					Av	verage,	-4294 0	cals.

Acetamide.

From Eimer and Amena. Distilled in ammonia and stirred while cooling to get small crystals. Seemed to be slightly moist though carefully protected from the air. Melting point = 73.3° cor. Beilstein gives $82^{\circ}-83^{\circ}$. Fehling gives 78° .

m.	Δt_1 .	Δt_2 .	t.	ΔT.	М.	q.	Q.	т.	
5.1249	0.0000	-0.0006	-0.001	-0.439	389.6	—171.0	—1969	24.0 ⁰	
2.7516	-0.0016	-0.0022	-0.002	-0.241	389.7	-93.90	-2014	23.0°	
							·		
					Average, —1991 cals.				

Ostwald, quoting Berthelot and André, gives 19 K or 1900 cals.

Mannite.

From Kahlbaum. Crystalline white. Was not further purified. Melting point = 165.5° cor. Beilstein gives $164^{\circ}-166^{\circ}$. <u>m. Δt_1 . Δt_2 . t. ΔT . M. q. Q. T. 4.5287 -0.0028 -0.0056 -0.011 -0.335 389.5 -130.5 -5245 22.5° 2.1767 -0.0004 -0.0010 -0.001 -0.162 389.8 -63.14 -5279 23.5° Average, -5262 cals.</u>

Sugar.

Prepared from the purest rock candy obtainable. Only well developed crystals were kept. These were washed with water, dried, and powdered. Only a trace of glucose could be found. ^{m.} Δt_1 . Δt_2 . t. ΔT . M. q. Q. T. 6.3794 -0.0006 -0.0004 -0.001 -0.061 389.8 -23.73 -1275 23.0° 2.6436 +0.0004 +0.0002 -0.000 -0.027 189.4 -10.52 -136 22.7° Average, -1318 cals.

Resorcinol.

From Kahlbaum. Crystallized. Was assumed to be pure. Melting point = 110.6° cor. Decomposed a little on melting. Beilstein gives melting point = 110° and 119°.

HEATS OF SOLUTION IN METHYL ALCOHOL.

Methyl alcohol from Kahlbaum. Labeled "Acetonfrei." Dehydrated with large excess of calcium oxide. After twentyfour hours distilled. Portion coming over at 64.3° cor was used. Sp. gr. $\frac{15^{\circ}}{4^{\circ}} = 0.79619 = 99.9$ per cent. methyl alcohol by Landolt's and Bjornstein's tables. Mass of alcohol delivered between $20^{\circ}-25^{\circ} = 373.9 \times 0.7870 = 294.3$ grams, or in water terms = $294.3 \times 0.62 = 182.4$ grams water.

Urethane.

From Kahlbaum. Recrystallized from alcohol. Air dried. White. Slight, agreeable, aromatic odor. Melting point = 113.5° cor. Beilstein gives 112° ; Fehling gives from $101^{\circ}-113^{\circ}$. m. Δt_1 . Δt_2 . t. ΔT . M. q. Q. T. 2.1823 -0.0020 -0.0072 -0.018 -0.361 198.8 -72.38 -4477 24.5° Acenaphthene.

From Kahlbaum. White. Recrystallized from alcohol. Air dried. Melting point $= 93.5^{\circ}$ cor. Beilstein gives 95° and 101° ; Fehling gives over 100° .

m. Δt_1 . Δt_2 . t. ΔT . M. q. Q. T. 1.4266 -0.0072 -0.0082 -0.008 -0.288 198.8 -57.26 -6180 24^{\odot} Naphthalene.

From Kahlbaum. White. Recrystallized from alcohol. Air dried. Melting point = 80.1° cor. Beilstein gives 79.2° and 80.1° .

HEATS OF SOLUTION IN ETHYL ALCOHOL.

Ethyl alcohol from Eimer and Amend and Chas. Cooper and Co. Marked absolute. Distilled, treated with calcium oxide, and redistilled. Boiling point, 77.6°–78.7° cor. Sp. gr. = 0.7873. Mass of alcohol delivered between 20° and 25° = 373.9 \times 0.7873 = 294.4 grams, or in water terms = 294.4 \times 0.59 = 173.7 grams water.

Urethane.

м. t. ΔΤ. Δt₁. Δt₂. q. Q. Т. m. $3.4826 - 0.0010 - 0.0084 - 0.019 - 0.976 190.3 - 185.7 - 4746 23.5^{\circ}$ 2.5207 -0.0110 -0.0172 -0.017 -0.701 190.3 -133.4 -4710 23.8° Average, -4728 cals. Acetanilid. Δt₂. t. ΔT. M. q. m. Δt₁. Q. Τ. $2.8726 + 0.0014 - 0.0048 - 0.009 - 0.471 190.3 - 89.74 - 4212 23^{\circ}$ Acenaphthene. ΔΤ. t. Δt_2 . М. q. Q. Т. m. Δt₁. $3.8306 + 0.0038 - 0.0046 - 0.009 - 0.772 190.1 - 146.7 - 5899 25.0^{\circ}$ $1.6855 - 0.0014 - 0.0024 - 0.005 - 0.340 190.3 - 64.71 - 5914 23.6^{\circ}$ Average, —5906 cals. Naphthalene. ΔΤ. м. Δt_2 . t. m. Δt₁. q. Q. Т. 2.9976 —0.0036 —0.0104 —0.021 —0.599 190.1 —113.9 —4861 24° Urea. t. ΔT. М. m. Δt₁. Δt_2 . q. Ο. Τ. $1.3715 + 0.0003 - 0.0046 - 0.025 - 0.434 190.1 - 82.6 - 3612 24^{\circ}$ Acetamide. ΔΤ. t. М. m. Δt_1 . Δt_2 . q. Q. Т. 3.4805 +0.0014 -0.0094 -0.019 -1.119 190.1 -212.7 -3606 23.3° Phenanthrene.

From Kahlbaum. Crystallized three times from toluene. Air dried. Melting point = 100.4° . Beilstein gives 99° ; Fehling gives 96° to 100° .

t. ΔT. М. m. Δt_1 . Δt₂. q. Q. $0.8259 - 0.0008 - 0.0022 - 0.004 - 0.105 190.3 - 19.98 - 4306 24^{\circ}$ Chloral Hydrate. Δt_1 . t. ΔT. M. q. Δt₂. m. Q. Т.

Succinimide.

m. Δt₁. Δt₂. t. ΔT. M. q. Q. T. 4.1413 —0.0018 —0.0106 —0.032 —1.199 190.3 —228.2 —5456 21.5° Benzamide.

From Kahlbaum. Recrystallized from water. Air dried, Melting point 126.0°. Beilstein gives 123°; Fehling gives 125°. ^{m.} Δt_1 . Δt_2 . t. ΔT . M. q. Q. T. 1.9457 -0.0018 -0.0052 -0.005 -0.361 190.3 -68.7 -4238 22.5° *Resorcinol.*

m. Δt_1 . Δt_2 . t. ΔT . M. q. Q. T. 4.2003 -0.0016 -0.0016 -0.0024 +0.054 190.3 +10.28 +2692 22.5° *Toluidin* (p).

From Kahlbaum. Very impure. Recrystallized from alcohol three times. Slightly yellowish, turned darker on exposure to air and light while drying. Air dried. Melting point 44.6° . Beilstein gives 45° .

HEATS OF SOLUTION IN PROPYL ALCOHOL.

Propyl alcohol from Kahlbaum. Dehydrated with calcium oxide. Distilled. Distillate collected until an empyrcumatic odor was observed. Sp. gr. $\frac{24^{\circ}}{4^{\circ}} = 0.80128$. Mass of alcohol delivered between 20° and 25° = 373.9 × 0.8013 = 299.5 grams, or in water terms = 299.5 × 0.66 = 197.7 grams water.

Urethane.

m.	Δt_1 .	Δt_2 .	t.	ът.	М.	q.	Q.	т.		
3.3360	-0.0144	-0.0212	-0.021	-1.054	214.3	-225.9	-6045	2 4.7 ⁰		
Acenaphthene.										
m.	Δt_1 .	Δt ₂ .	t.	ΔT .	м.	q.	Q.	т.		

111.		LLC2.	••	-1.	1,1,	4.	¥'	÷.	
3 .07 44	-0.0152	—0.0198	-0.040	-0.634	-214.3	135.9	-6807	130	
Naphthalene.									
m.	Δt ₁ ,	Δt _e ,	t.	ΔΤ.	М.	α.	0.	Т.	

m. Δt_1 , Δt_2 , t. ΔT , M. q. Q. T. 2.6408 -0.0112 -0.0158 -0.032 0.547 214.3 -117.2 -5681 23.0° HEATS OF SOLUTION IN CHLOROFORM.

Chloroform from Eimer and Amend, Powers and Weightman,

and Charles Cooper and Co. Purified by washing with water till it gave no reaction for alcohol, drying with sulphuric acid or calcium chloride and distilling. No reaction for impurities with silver nitrate or potassium hydroxide. Sp. gr. between 20° and $25^{\circ} = 1.479$. Mass of chloroform delivered = $373.9 \times 1.479 =$ 553.0 grams, or in water terms = $553.0 \times 0.2337 = 129.3$ grams water.

Urethane.										
m.	Δt_1 .	Δt_2 .	t.	ΔΤ.	м.	q.	Q.	Т.		
3.2930	+0. 0014	∆t₂. —0.0082	-0.032	—1.161	145.7	—169.2	-4573	23.5°		
Acetanilid.										
m.	Δt_1 .	Δt ₂ .	t.	ΔΤ.	М.	q.	Q.	т.		
2.5859	+0.0026	-0.0038	-0.022	—0.584	145.7	—85.10	-4442	24.5°		
Acenaphthene.										
		Δt_2 .								
2.4138	+0.0008	-0.0072	-0.035	0.482	145.7		4480	21 ⁻		
			-	thalene.						
m.	Δt_1 .	Δt ₂ . 0.0052	t.	ΔΤ.	м.	q٠	Q.	т.		
0.9407	0.0060	0.0052	-0.005	—0.194	145.9	—28.31	3852	23°		
Chloral Hydrate.										
m.	Δt_1 .	Δt_2 .	t.	ΔT .	М.	q.	Q.	т.		
7.0497	-0.0042		-0.137	1.753	145.9	-255.7	5993	21.7 ⁰		
Toluidin (p).										
		Δt_2 .								
1.2787	-0.0028	-0.0034	-0.011	—0.286	145.9	41.74	—3492	2 3 .3°		

HEATS OF SOLUTION IN TOLUENE.

From Kahlbaum, Colorless. Redistilled. Boiling point $110.4^{\circ}-110.7^{\circ}$. Sp. gr. between 20° and 25° = 0.8621. Mass of toluene delivered = 373.9 + 0.8621 = 322.3 grams, or in water terms = $322.3 \times 0.3942 = 127.1$ grams water.

Urethane.

Δt₁. Δt₂. t. ΔТ. M. q. m. Q. т. 1.7615 - 0.0002 - 0.0100 - 0.018 - 0.881 143.7 - 126.6 - 6399230 Acenaphthene. t. ΔΤ. м. m. Δt₁. Δt₂. q. Q. т.

Naphthalene.										
1 11.	Δt_1 .	Δt ₂ .	t.	ΔT.	м.	q.	Q.	Т.		
		0.0074						23°		
0.9916	-0.0034	-0.0064	-0.013	0.232	143.7	33.34	4302	23 ⁰		
					A	verage,	-4267	cals.		
			Chloral	Hydrat	e.					
m.	Δt_1 ,	Δt_2 .	t.	ΔT .	м.	q.	Q.	т.		
2.8739	0.0090	-0.0156	0.056	0.913	143.5	131.0	7537	24 ⁰		
Phenanthrene.										
m.	Δt_1 .	Δt_2 .	t.	ΔT .	м.	\mathbf{q}_{\cdot}	Q.	Τ.		
		0.0076								
1.3179	-0.0084	—0.0108	-0.011	-0.179	143.5	—25.69	—3469	23°		
					A	verage,	3528	cals.		
	Toluidin (p).									
111.	Δt_i .	Δt_2 .	t.	ΔT .	М.	q.	Q.	т.		
3.8683	-0.0080	—0.0186	-0.019	— I.247	143.7	—179.2	—4956	24.7 ^ర		
1.9525	+0.0024	-0.0032	-0.003	—0.636	143.7	—9 1.40	—5011	23 ⁰		
Average, —4983 cals.								cals.		

The quantity of solvent compared with the quantity of substances dissolved is so large that it is safe to conclude that further addition of solvent would produce no appreciable evolution of heat. Besides, it is plain from the above experiments that in many cases a difference of 100 per cent. in the quantity of solvent produced no decided change.

The following table shows the heats of solution in a convenient form for comparison.

Water.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Chloroform	Toluene
Urea — 3628		—3612	• • • • • •	• • • • • •	
Urethane3787	-4345	-4728	6045	-4573	—6399
Chloral hydrate — 929	• • • • •	—1131			-7537
Succinimide ·· —4294	• • • • • •	-5456		• • • • • •	• • • • • • •
Acetamide ···· —1991	• • • • • •	—3606			• • • • • • •
Mannite —5262	• • • • • •				• • • • • •
Resorcin — 3960	• • • • • •	+269.2	• • • • • •	• • • • • •	• • • • • •
Benzamide	••••	-4238	••••	• • • • • •	• • • • • •
Toluidine $(p) \cdot \cdots \cdots$	• • • • • •	—3650		-3492	—4983
Acetanilide	-4477	-4212	• • • • • •	-4442	
Acenaphthene	-6180	—5986	6807	-4480	-4788
Naphthalene	-4233	-4861	—5681	<u> </u>	-4267
Phenanthrene	• • • • • •	-4306		•••••	—3528
Sugar —1318	• • • • • •	• • • • • •	• • • • • •	· • • • • •	• • • • • •

RUTGERS COLLEGE, October 12, 1895.