Summary

The total heat of solution of sulfur dioxide has been determined at 25° (very nearly) for a number of concentrations of sulfurous acid produced.

The relation between $-\Delta H$(cals./mole of sulfur dioxide) and **N**(moles of water/mole sulfur dioxide) is given by the equation $-\Delta H = 4911.6 + 1105.26 \log_{10} \mathbf{N}$, which reproduces the experimental data on an average to within 0.2%; the agreement is much closer in most cases, and the relation is considered accurate to better than 1 part in 400 at 25°.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MAINE]

THE SYSTEM: SODIUM IODIDE-ACETONE-WATER

BY RUDOLPH MACY AND EDGAR W. THOMAS[1]

RECEIVED MARCH 23, 1926 PUBLISHED JUNE 5, 1926

The purification of sodium iodide by precipitation of the double compound, $NaI.3CH_3COCH_3$, was first proposed by Shipsey and Werner.[2] This method has since been extensively employed in place of the former practice of precipitating the double compound with sodium bisulfite, $NaHSO_3.CH_3COCH_3$. Purification by means of sodium iodide has also been applied to methylethyl ketone,[3] the double compound having been assigned the formula $NaI.CH_3COC_2H_5$.

Several statements in the original article by Shipsey and Werner in regard to the conditions necessary for obtaining large yields of crystals of the sodium iodide compound made it seem advisable to investigate the solubility relationships of sodium iodide in acetone and in mixtures of acetone and water. The solubility of sodium iodide in acetone has been measured up to the boiling point of the saturated solution, and the ternary system with water has been studied at 25°.

The sodium iodide was recrystallized from the Merck product and kept dry in an oven at 105° until used. Two samples of acetone were employed, one obtained from Merck and the other from the Eastman Kodak Co. They were dried over copper sulfate and redistilled, using a 60 cm. fractionating column and a calibrated Anschütz thermometer. Both samples boiled at 56.3° (765 mm.).

Equilibrium between sodium iodide and solution was obtained by stirring the salt with solvent at constant temperature in a tube fitted with a mercury seal. Samples of the saturated solutions were obtained by pressure through a tube fitted with a muslin filter; the samples were forced over from the solubility apparatus into a weighed bottle with a calibrated stem,

---

[1] Some of the data reported in this paper were originally obtained by E. W. Thomas, and submitted in a thesis for the Bachelor's degree at the University of Maine in June, 1925.

[2] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[3] Lochte, *Ind. Eng. Chem.*, **16**, 956 (1924).

which made it possible to obtain the densities of the solutions. The sodium iodide content was then found by evaporation of the solvent. Equilibria in the ternary system at 25° were obtained by rotating weighed quantities in a stoppered flask in a thermostat. The removal of samples and the determination of salt content were in the same manner as just indicated; the analysis of acetone in the saturated solution was made by the Messinger method with the modifications outlined by Ardagh and others.[4] This consisted of the addition of standard iodine solution in excess to convert the acetone into insoluble iodoform, and titration of the excess of iodine by standard thiosulfate. The iodine solution was standardized directly against pure acetone.

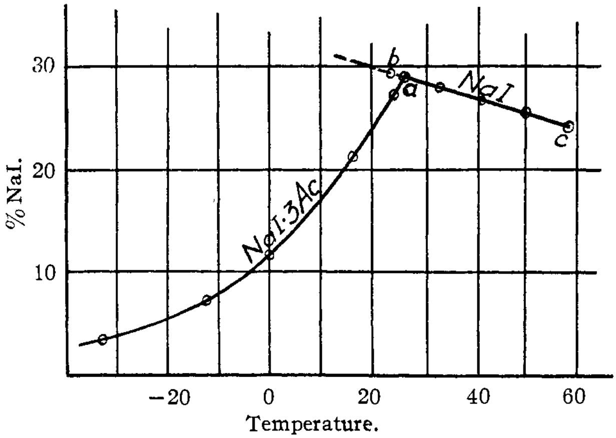

Fig. 1.—Solubility of sodium iodide in acetone.

Binary System: Sodium Iodide-Acetone.—The solubility of sodium iodide in acetone was determined from —34° to the boiling point of the

TABLE I

SODIUM IODIDE AND ACETONE

Solid phase	Temp., °C.	NaI, % by wt.	*Ac*, % by wt.	Density	Point (Fig. 1)
NaI.3 *Ac*	−34	3.2	96.8	...	
	−12.3	7.4	92.6	0.873	
	0.0	11.6	88.4	.899	
	+15.9	21.0	79.0	.984	
	25.0	28.5	71.5	1.062	
NaI.3*Ac* + NaI	25.7	29.2	70.8	1.070	*a*
NaI	25.0	29.4	70.6	1.067	*b*
	32.2	28.2	71.8	1.043	
	40.2	26.8	73.2	...	
	50.0	25.0	75.0	...	
	57.2	23.6	76.4	...	
	59.8	23.0	77.0	...	*c*

---

[4] Ardagh, *Ind. Eng. Chem.*, **16**, 1134 (1924).

saturated solution. The data are given in Table I and Fig. 1 (a molecule of acetone being represented by the symbol *Ac*). Only one double compound was isolated in this range of temperature, and from the character of the solubility curve it is unlikely that other compounds exist at even lower temperatures.

The composition of the double compound was determined by analysis of large crystals obtained by slow evaporation of a saturated solution below 25°. The crystals lose acetone very rapidly, but the error due to this efflorescence can be reduced to a negligible quantity by the analysis of sufficiently large crystals. Four such determinations are given below. The sodium iodide content was obtained by driving off the acetone at 100°, and agrees well with the theoretical value of 45.58% of sodium iodide for the compound $NaI.3CH_3COCH_3$.

	Expt. 1	2	3	4
Sample, g	0.770	1.770	3.879	1.690
NaI, g	.351	0.809	1.779	0.771
NaI, %	45.6	45.7	45.8	45.6

The crystals are clear yellow, but the saturated solution is colorless when removed from the solid phase.

The rapid decrease in solubility of the double compound with decrease in temperature is interesting, and indicates the necessity, when sodium iodide is used in purifying the acetone, of cooling in a freezing mixture to obtain a maximum yield of crystals. Above 25.7°, the solid phase in contact with solution is pure sodium iodide, the solubility curve of the anhydrous salt is practically a straight line, and the solubility decreases with increase in temperature. The saturated solution boils at 59.8°, which is 3.5° higher than the boiling point of pure acetone. This agrees well with the elevation 3.3°, calculated from Raoult's law, using 16.7 as the elevation constant of acetone and 150 as the molecular weight of sodium iodide.

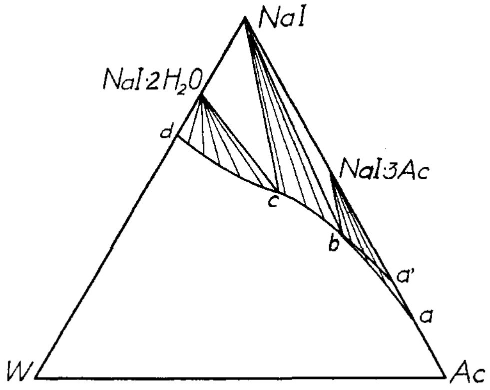

Fig. 2.—Sodium iodide, acetone, water at 25° (not drawn to scale).

Ternary System: Sodium Iodide-Acetone-Water.—The solubility curve at 25° is given in Fig. 2 and the data are contained in Table II.

The curve *ab* is negligibly small, so that no determinations were made on it, the compound $NaI.3CH_3COCH_3$ disappearing from equilibria in the ternary system at 25.7°. The supersaturated solution represented by Point *a'*

TABLE II

SODIUM IODIDE, ACETONE AND WATER AT 25°

Solid phase	NaI, % by wt.	*Ac*, % by wt.	H_2O, % by wt.	Density (Fig. 2)	Point
$NaI.3(CH_3)_2CO$	28.5	71.5	00.0	1.062	*a*
$NaI.3(CH_3)_2CO + NaI$	..	..	..	...	*b*
NaI	29.4	70.6	00.0	1.067	*a'*
	34.7	62.9	2.4	1.144	
	37.7	58.0	4.3	1.192	
	40.5	53.4	6.1	1.240	
$NaI + NaI.2H_2O$	44.5	46.1	9.4	1.320	*c*
$NaI.2H_2O$	46.3	40.3	13.4	1.358	
	49.9	30.1	20.0	1.450	
	54.3	19.4	26.3	1.565	
	60.2	8.2	31.6	1.753	
	64.7	0.0	35.3	1.927	*d*

is that in equilibrium with pure sodium iodide; it is easily obtained and may be kept a long time without depositing crystals of the double compound. The solubility of sodium iodide in acetone is considerably increased by the presence of small amounts of water, as shown by the steep rise of Curve *bc*. The solubility of the dihydrate is represented by Curve *cd*.

Summary

Because of the use of sodium iodide in purifying acetone, the solubility of the salt in acetone has been measured from —34° to the boiling point of the saturated solution, 59.8°. The composition of the compound which is formed has been confirmed as being $NaI.3CH_3COCH_3$. At 25.7° it melts incongruently to sodium iodide. The solubility of the double compound decreases with decrease in temperature, while that of pure sodium iodide decreases with increase in temperature. The 25° isotherm of the system sodium iodide-water-acetone has also been determined.

ORONO, MAINE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

SOME PROPERTIES OF SELENIUM MONOCHLORIDE

BY VICTOR LENHER AND C. H. KAO

RECEIVED MARCH 29, 1926 PUBLISHED JUNE 5, 1926

Selenium monochloride prepared according to the method of Lenher and Kao[1] is a red-brown liquid which cannot be distilled without decomposition. It begins to boil at 127° (733 mm.) but decomposition commences as soon as the vapor phase appears. Distillation in the vapor of hydrogen chloride or carbon dioxide does not prevent this decomposition, nor is it possible to avoid decomposition by boiling under greatly diminished pressure.

---

[1] Lenher and Kao, THIS JOURNAL, **47,** 772 (1925).