XCIV.—*The System Water–Chloroform.*

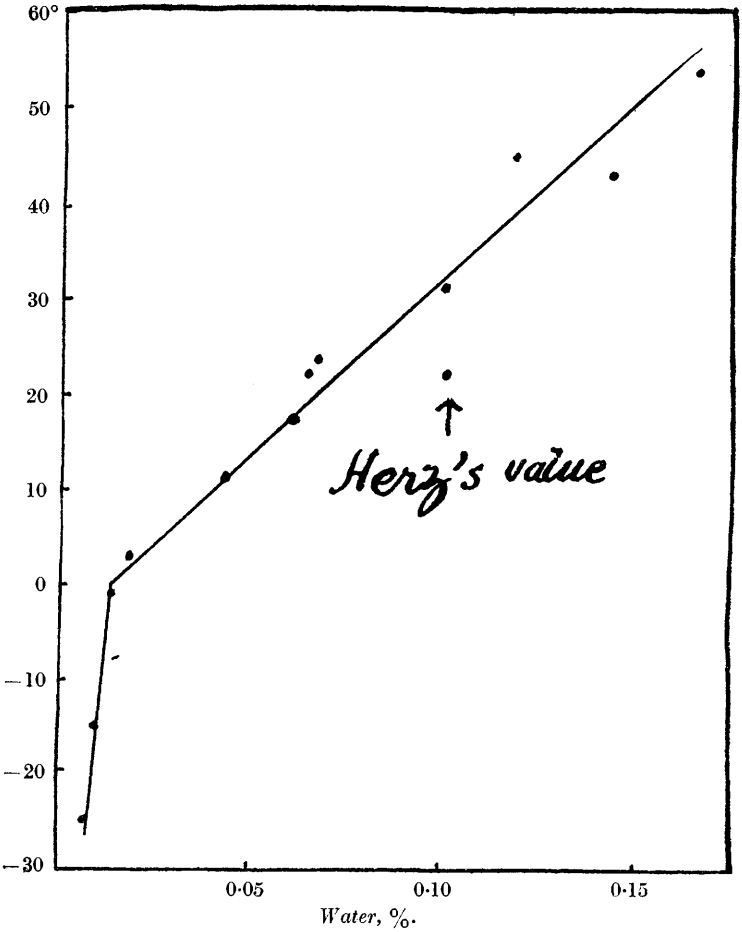
By Clifton William Gibby and John Hall.

In the course of an investigation of the system acetone–chloroform–water, it became necessary to know the mutual solubilities of the last two solvents. The data for the solubility of chloroform in water are summarised in the International Critical Tables, but for the solubility of water in chloroform the only available datum appears to be that of Herz (*Ber.*, 1898, **31**, 2669), who states that at 22° 1000 c.c. of chloroform and 1·52 c.c. of water give 996·2 c.c. of solution.

Dry chloroform was prepared as follows. "Chloroform Pure, B.P." was shaken twice with concentrated sulphuric acid, and then successively with dilute aqueous sodium hydroxide and with water; after being separated, it gave no iodoform reaction. It was dried by standing over anhydrous sodium carbonate, and finally by refluxing for ½ hour with magnesium nitride (prepared in the laboratory), being distilled off after standing over-night. Chloroform so dried was without action on bright metallic calcium; it reacted slightly with sodium, but the quantity of gas liberated was too small to be measured.

Mixtures of known weights of chloroform and water were then prepared. A small quantity of water was weighed in a glass tube, sealed at one end and constricted at the other, in which was first placed a thermometer of the Anschütz type; chloroform was introduced, and the tube sealed at the constriction and weighed again. For measurements at low temperatures, the thermometer used was of such a length that the tube could not be weighed on the accurate balance available; in such cases water was weighed out (to 0·0001 g.) from a pyknometer, by difference, and the chloroform in the tube weighed on a larger balance sensitive to 0·01 g.

The tube was heated until all the water had dissolved, and, while cooling, was observed from the side in a beam of light from a projection lantern. The first appearance of turbidity could easily be detected, and the temperature noted. Stirring was ensured by gentle rocking of the tube. When the clearing temperature of the solution was below that of the room, the liquid was cooled until distinctly opalescent, and then allowed to become warm, with constant stirring, until clear. To reduce the rate of heating at the lowest temperatures, the tube was surrounded by a glass jacket containing alcohol.



By this method, the solubility of water in chloroform was determined between −25° and 54°. The clearing temperatures could be observed more easily by this method than by heating and cooling in a large bath of water, and noting the temperature of the latter.

The results are given in the following table. On account of the steepness of the curve it was not considered justifiable to record temperatures to less than 1°.

Water, g.	$CHCl_3$, g.	Water, %.	Temperatures. Observed.	Temperatures. Mean.
0·0825	50·00	0·165	54, 53, 54, 53, 54°	54°
0·0704	48·86	0·144	43, 44, 42, 43	43
0·0564	47·79	0·118	43, 44, 46, 46, 47, 46	45
0·0583	58·37	0·100	30, 32, 31, 31	31
0·0338	47·19	0·072	23, 23	23
0·0388	59·91	0·065	21, 22, 22, 22	22
0·0370	60·84	0·061	16, 16, 18, 18	17
0·0208	48·88	0·043	12, 11, 11	11
0·0216	110·89	0·019	3, 3, 3, 4, 3	3
0·0067	48·61	0·014	– 1, – 1	– 1
0·0074	86·99	0·009	– 15, – 15	– 15
0·0097	136·09	0·006	– 25, – 25	– 25

The results are represented in the accompanying graph by two lines drawn to intersect at 0°, this temperature corresponding to the change from the solubility of ice to that of water.

Chancel and Parmentier (*Compt. rend.*, 1885, **100**, 25) describe a hydrate of chloroform, prepared by keeping it with water in melting ice for an unspecified time. We have made 36 unsuccessful attempts to repeat this preparation, with chloroform freed from alcohol as described above, and also with a sample prepared from chloral hydrate and potassium hydroxide.

UNIVERSITY SCIENCE LABORATORIES,
DURHAM.

[*Received, January 29th,* 1931.]