XXXIII.—*The Influence of Foreign Substances on Transition Temperatures and the Determination of Molecular Weights.*

By HARRY MEDFORTH DAWSON and COLIN GYRTH JACKSON.

THE object of this paper is to record the results of experiments made to determine the depression of certain so-called transition temperatures on the addition of foreign substances soluble in the liquid which is formed at the temperature of transition.

The systems involved in such transition phenomena are more complex than those which are met with in the application of the freezing-point method of determining molecular weights. Whereas, in the case of the freezing point, the temperature constancy is determined by the co-existence in equilibrium of a solid and a liquid phase of the same composition, two or more solid phases are in equilibrium with a liquid phase, the composition of which bears, in general, no simple relationship to that of the solid phases, when a transition phenomenon of the type investigated in this paper is in question. If the change is the dehydration of a hydrated substance, two solid phases participate in the equilibrium corresponding with the transition temperature; if it is the formation of a double salt from two simple salts or the decomposition of a double salt into its component simple salts with loss of water, the number of such solid phases is three. Apart from this difference in the number of the solid phases which participate in the equilibrium and the absence of any simple relationship between the composition of the liquid phase and that of the solid phases, there is, however, no essential distinction between true freezing points and transition points of the type referred to. The practical constancy of such transition temperatures has been clearly demonstrated by Richards and Churchill (*Zeitsch. physikal. Chem.*, 1898, **26**, 690), who found the temperature at which sodium sulphate decahydrate is transformed into the anhydrous salt to be 32.379° (hydrogen scale). Richards and Wells (*Zeitsch. physikal. Chem.*, 1906, **56**, 348) found similarly that the transformation of sodium bromide dihydrate into the anhydrous salt takes place at 50.674° (hydrogen scale). Such temperatures have been suggested as suitable fixed points for thermometric purposes (compare also Meyerhoffer and Saunders, *Zeitsch. physikal. Chem.*, 1898, **27**, 367; Richards and Churchill, *ibid.*, 1898, **28**, 313).

The depression of the temperature, at which sodium sulphate decahydrate is transformed into the anhydrous salt and a solution

saturated with regard to this substance, on the addition of foreign soluble substances, was investigated by Löwenherz (*Zeitsch. physikal. Chem.*, 1895, **18**, 70). A constant representing the molecular lowering of the transition temperature was calculated, and by using various non-electrolytes—carbamide, glycocoll, dextrose, formamide, and glycerol—it was found that molecular weight values in close agreement with theory are obtained when the molecular depression of the transition temperature is taken as 32·6.

This is the numerical value obtained for the constant when the concentration of the foreign substance present is referred to 100 grams of the decahydrate. Since the lowering of the transition temperature is determined solely by the concentration of the foreign substance in the solution formed at this temperature, it may be doubted whether this is the most convenient way of evaluating the constant. In the authors' opinion, the referring of the concentration to 100 grams of the solution in which the foreign substance is contained is a more convenient and correct procedure. The relationship between the two constants, calculated in these different ways, is determined by the equation which expresses the change taking place at the transition temperature in terms of the composition of the solution formed. Since 100 parts of this solution contain 33·34 parts of Na_2SO_4 , this equation may be written: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 0\cdot367\text{Na}_2\text{SO}_4 + 0\cdot100(100\text{H}_2\text{O}, 6\cdot33\text{NaSO}_4)$.

From this, it follows that 100 parts of the decahydrate yield 87·3 parts of solution, and the molecular lowering of the transition temperature, when the concentration of the dissolved substance is referred to 100 grams of the saturated solution, is $32\cdot6 \times \frac{87\cdot3}{100} = 28\cdot5$.

Van't Hoff and Dawson (*Zeitsch. physikal. Chem.*, 1897, **22**, 598) examined the influence of foreign substances on the temperature (116·67°, according to van't Hoff and Meyerhoffer, *ibid.*, 1898, **27**, 81) at which magnesium chloride hexahydrate is converted into the tetrahydrate according to the equation :

and found similar regularities, the value of the molecular lowering of the transition temperature referred to 100 grams of the solution being 76.

The temperature (40·41°), at which rubidium racemate,

is converted into a mixture of the anhydrous *d*- and *l*-tartrates, was found by van't Hoff and Müller (*Ber.*, 1898, **31**, 2206) to be depressed on the addition of rubidium carbonate. The molecular lowering, referred to 100 grams of rubidium racemate, was calculated to be 100. Since the saturated solution at the transition temperature

contains 13.48 molecules of tartrate per 100 molecules of water, the change taking place may be written :

According to this, 100 parts of racemate yield 34.4 parts of solution, and the molecular lowering of the transition temperature referred to 100 grams of the solution is therefore $108 \times \frac{34.4}{100} = 37.1$.

So far as the authors are aware, these isolated observations are the only ones relating to the depression of transition temperatures by foreign substances, which can be utilised for the evaluation of constants for the purpose of molecular weight determinations.

In the experiments recorded in this paper, three further changes have been investigated and constants which represent the molecular lowering of the temperature of transition have been calculated.

The apparatus used was similar to that described by Meyerhoffer (*Zeitsch. physikal. Chem.*, 1897, **22**, 619), effective mixing of the reacting phases being achieved by means of a rapidly rotating perforated cylindrical stirrer surrounding the Beckmann thermometer on which the temperature readings were made. By means of a small electric motor with an easily adjustable resistance in circuit, the stirrer could be made to revolve with any desired rapidity and the rate of rotation maintained practically constant throughout each experiment. During the period of supercooling and subsequent rise of temperature, the tube containing the reaction mixture was surrounded by a wider glass tube, which was immersed in a regulated water thermostat having a temperature a few degrees below the transition temperature under investigation. As a readily soluble foreign substance, carbamide was used to depress the investigated transition temperatures.

Transformation of Sodium Thiosulphate Primary Pentahydrate into Primary Dihydrate.—At about 48°, sodium thiosulphate primary pentahydrate loses 3 molecules of water and yields the corresponding dihydrate (compare Young and Burke, *J. Amer. Chem. Soc.*, 1906, **28**, 315) together with a solution which at the transition temperature contains 159.8 parts of sodium thiosulphate per 100 parts of water. Corresponding with this, the change taking place may be represented by the equation : $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 0.14\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 0.0472(100\text{H}_2\text{O}, 18.20\text{Na}_2\text{S}_2\text{O}_3)$.

From this equation, the quantity of solution yielded by a given weight of sodium thiosulphate of determined composition can be readily calculated.

From 65 to 100 grams of recrystallised thiosulphate were used in each experiment, the temperature being maintained at 55—60° until the

primary pentahydrate had completely disappeared. When the system had been supercooled to the extent of about 0.5° , a crystal of the primary pentahydrate was added. In order to prevent surface evaporation, the partly fused mass was in some cases covered with a layer of heavy petroleum, but this was not found to have any definite influence on the results obtained. Table I contains the recorded experimental data, the composition of the thiosulphate used being indicated in the first column :

TABLE I.

Composition of thiosulphate.	Weight of thiosulphate in grams.	Weight of carbamide in grams.	Observed lowering of temperature.	Molecular lowering.
$\text{Na}_2\text{S}_2\text{O}_3, 5.007 \text{ H}_2\text{O}$	65.4	0.4425	0.554°	43.7
$\text{Na}_2\text{S}_2\text{O}_3, 5.03 \text{ H}_2\text{O}$	90.06	0.7195	0.640	43.1
$\text{Na}_2\text{S}_2\text{O}_3, 5.007 \text{ H}_2\text{O}$	65.6	0.6940	0.857	43.3
$\text{Na}_2\text{S}_2\text{O}_3, 5.03 \text{ H}_2\text{O}$	102.5	1.4055	1.072	42.1
$\text{Na}_2\text{S}_2\text{O}_3, 5.03 \text{ H}_2\text{O}$	90.06	1.2605	1.095	42.1
Mean.....				42.9

Referred to 100 grams of the saturated transition solution, the depression of the transition temperature is therefore 43° per gram-molecule of foreign substance present.

Transformation of Sodium Bromide Dihydrate into Anhydrous Sodium Bromide.—The saturated solution at the temperature of transition (50.7°) contains 117.4 parts of sodium bromide per 100 parts of water. The change which occurs at this temperature may therefore be represented by the equation : $\text{NaBr} \cdot 2\text{H}_2\text{O} = 0.589\text{NaBr} +$

according to which 100 grams of the dihydrate yield 56.36 grams of the saturated solution.

About 100 grams of sodium bromide ($\text{NaBr} \cdot 0.035\text{H}_2\text{O}$) and 35 grams of water were heated at about 60° with vigorous stirring of the contents of the tube until a saturated solution of the anhydrous salt was obtained. The system was then allowed to cool in the air until the transition temperature was approximately reached, when the tube was placed in its outer jacket immersed in a thermostat at a temperature of $43-45^{\circ}$. Table II contains the experimental data :

TABLE II.

Weight of bromide in grams.	Weight of water in grams.	Weight of carbamide in grams.	Observed lowering of temperature.	Molecular lowering.
101.7	34.66	0.4905	0.370°	34.7
103.0	36.20	0.5685	0.415	35.1
101.7	34.66	0.908	0.680	34.5
103.0	36.20	1.0535	0.738	33.7
Mean.....				34.5

Referred to 100 grams of the transition solution, one gram-molecule of foreign substance depresses the transition temperature 34.5° .

Formation of Tachhydrite from Calcium and Magnesium Chloride Hexahydrates.—When the hexahydrates of calcium and magnesium chloride are intimately mixed and gently warmed, the two simple salts react to form the double salt tachhydrite, $\text{CaCl}_2, 2\text{MgCl}_2, 12\text{H}_2\text{O}$. Taking into account the composition of the saturated solution which is formed at the transition temperature by the water set free in the reaction, the change may be represented (van't Hoff and Kenrick, *Sitzungsber. K. Akad. Wiss. Berlin*, 1897, 508) by the equation :

The temperature at which this change takes place under atmospheric pressure can be determined with great precision, and has been given by one of us (Dawson, *Zeitsch. physikal. Chem.*, 1902, **39**, 27) as 22.40° . At this temperature, the solution ($100\text{H}_2\text{O}, 9.27\text{CaCl}_2, 4.92\text{MgCl}_2$) is in equilibrium with three solid phases: tachhydrite, calcium chloride hexahydrate, and magnesium chloride hexahydrate.

In the experiments recorded here, about 50 grams of crystallised magnesium chloride and 60 grams of crystallised calcium chloride, corresponding approximately with the proportions of the two substances on the left side of the above equation, were heated at a temperature not exceeding 30° until the formation of tachhydrite was complete. The mixture was then allowed to cool slowly in the air until the temperature had fallen to nearly 22° , when the tube containing it was placed in its outer jacket immersed in a thermostat at $19-20^{\circ}$. When the desired amount of supercooling, 0.3° to 0.4° , had been obtained, minute crystals of the two simple chlorides were added to start the reaction represented by the equation in the direction from right to left.

The calcium chloride used had the composition $\text{CaCl}_2, 6.07\text{H}_2\text{O}$; the magnesium chloride corresponded with the formula $\text{MgCl}_2, 6.11\text{H}_2\text{O}$. The small amounts of water, in excess of that required for the pure hexahydrates, give rise to the formation of a considerable amount of solution, but this can be calculated from the known composition of the solution. This may be illustrated in reference to the first experiment in table III. The 52.9 grams of $\text{MgCl}_2, 6.11\text{H}_2\text{O} + 61.6$ grams of $\text{CaCl}_2, 6.07\text{H}_2\text{O}$ correspond with 0.2576 molecule of $\text{MgCl}_2, 6\text{H}_2\text{O} + 0.2795$ molecule of $\text{CaCl}_2, 6\text{H}_2\text{O} + 0.0480$ molecule of water. If x and y denote the number of molecules of $\text{MgCl}_2, 6\text{H}_2\text{O}$ and $\text{CaCl}_2, 6\text{H}_2\text{O}$ dissolved by 0.048 molecule of water, and if z similarly denotes the number of formula weights of the solution

$$(100\text{H}_2\text{O}, 9.27\text{CaCl}_2, 4.92\text{MgCl}_2)$$

which are thereby formed at the transition temperature, we obtain the equation :

from which, by equating corresponding terms, we have :

$$x = 4.92z, y = 9.27z, 100z = 6x + 6y + 0.048$$

$$\text{or } x = 0.0299, y = 0.0159, z = 0.00323.$$

The weight of saturated solution which results from the excess of water in the crystallised magnesium and calcium chlorides amounts therefore to $z \times$ formula weight of solution :

$$(100\text{H}_2\text{O}, 9.27\text{CaCl}_2, 4.92\text{MgCl}_2) = z \times 3300 = 10.66 \text{ grams,}$$

which is about one-eighth of the total weight of solution yielded by the formation of tachhydrite. From this, it is evident that a careful estimation of the water content of the substances employed in the experiments is necessary before the weight of the solution in which the foreign substance is dissolved can be ascertained. Table III contains the data for three experiments :

TABLE III.

Weight of magnesium chloride in grams.	Weight of calcium chloride in grams.	Weight of solution in grams.	Weight of carbamide in grams.	Observed lowering of temperature.	Molecular lowering.
52.9	61.6	80.8	0.3812	0.410°	52.4
49.75	61.45	80.4	0.4274	0.430	48.6
49.48	64.45	84.2	0.4562	0.455	50.5
Mean.....					50.5

When the complex nature of the change involved in the tachhydrite formation is considered, the concordance of the values obtained in the three independent experiments must be considered very satisfactory.

Some further experiments, made to determine the depression of the temperature at which sodium carbonate decahydrate is transformed into a lower hydrate, have not given sufficiently concordant results to justify their inclusion in the present paper, and these experiments are being continued.

The changes in multi-component systems, for which the depression of the characteristic transition temperatures on the addition of small quantities of foreign substances has been quantitatively determined, are summarised in the following table. The equations representing the changes in terms of the various transition solutions, and the values of the molar depressions, referred to 100 grams of these solutions, are given. By means of these constants, determinations of the molecular weights of substances in aqueous solutions may be made at

a series of temperatures between 0° and 100° . Between the values of the constants, the heat changes associated with the chemical processes, and the temperatures at which the transitions occur, a similar relationship exists as is well known to hold between molar freezing-point depressions, latent heats of liquefaction, and absolute freezing temperatures in the case of pure liquids.

Chemical change.	Molar depression.
$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} = 0.367\text{Na}_2\text{SO}_4 + 0.10(100\text{H}_2\text{O}, 6.33\text{Na}_2\text{SO}_4)$	28.5
$\text{MgCl}_2, 6\text{H}_2\text{O} = 0.0795\text{MgCl}_2, 4\text{H}_2\text{O} + 0.0568(100\text{H}_2\text{O}, 16.2\text{MgCl}_2)$	76
$(\text{Rb}_2\text{C}_4\text{H}_4\text{O}_6)_2, 4\text{H}_2\text{O} = 0.73d\text{-Rb}_2\text{C}_4\text{H}_4\text{O}_6 + 0.73t\text{-Rb}_2\text{C}_4\text{H}_4\text{O}_6 +$ $0.04(100\text{H}_2\text{O}, 13.48\text{Rb}_2\text{C}_4\text{H}_4\text{O}_6)$	37
$\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O} = 0.14\text{Na}_2\text{S}_2\text{O}_3, 2\text{H}_2\text{O} + 0.0472(100\text{H}_2\text{O}, 18.20\text{Na}_2\text{S}_2\text{O}_3)$...	43
$\text{NaBr}, 2\text{H}_2\text{O} = 0.589\text{NaBr} + 0.02(100\text{H}_2\text{O}, 20.54\text{NaBr})$	34.5
$\text{MgCl}_2, 6\text{H}_2\text{O} + 1.188\text{CaCl}_2, 6\text{H}_2\text{O} = 0.252\text{CaCl}_2, 2\text{MgCl}_2, 12\text{H}_2\text{O} +$ $0.101(100\text{H}_2\text{O}, 9.27\text{CaCl}_2, 4.92\text{MgCl}_2)$	50.5

ADDENDUM.

Since the above experiments were completed, two papers have appeared bearing the title "Molten Hydrated Salts as Solvents for the Freezing-Point Method." In the first (*J. Amer. Chem. Soc.*, 1907, 29, 1168), J. L. R. Morgan and H. K. Benson have examined the influence of foreign substances on the freezing points of $\text{CaCl}_2, 6\text{H}_2\text{O}$, $\text{LiNO}_3, 3\text{H}_2\text{O}$, and $\text{Na}_2\text{CrO}_4, 10\text{H}_2\text{O}$, and in the second (*ibid.*, p. 1439), Morgan and F. T. Owen have determined the molar freezing-point depressions of $\text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2, 3\text{H}_2\text{O}$, and of $\text{Mn}(\text{NO}_3)_2, 3\text{H}_2\text{O}$. The invariant points involved in these cases appear to be true freezing points, although in the case of sodium chromate it is not quite clear whether the temperature investigated is the melting point of the decahydrate or the temperature at which this is converted into the hexahydrate. The authors, however, appear to regard their work as a continuation of that of Löwenherz (*loc. cit.*) on sodium sulphate, but this is not the case, for the change which $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ undergoes at 32.4° is accompanied by the appearance of a new solid phase.

PHYSICAL CHEMISTRY LABORATORY,
THE UNIVERSITY, LEEDS.