

## CHEMICAL STATICS OF THE METHYL HALIDES IN WATER

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The distribution of the methyl halides between water and the vapour state has been measured at various temperatures and pressures, and their heats of dissolution as gases, liquids and crystalline hydrates have been evaluated. The data have been discussed in kinetic and thermodynamic terms, and certain inferences are drawn concerning the nature and number of the water molecules which surround a polar solute molecule in aqueous solution.

Water is such a general solvent that the noun "solution", unless qualified by an adjective, has come to mean an aqueous solution—at least to an experimental chemist. Though physical chemistry, since its origin, has continued the study of aqueous solutions, it is still far from being able to provide an answer to the question of what happens when a simple solute dissolves in water. We shall here attempt to gain, on experimental grounds, a clearer view of what takes place when the methyl halides, as gases, vapours or liquids, dissolve in water. Our approach to the problem has been along the route of chemical kinetics, which regards the methyl halides as compounds which can dissolve in, escape from, and react with liquid water. Experimental conditions can be so chosen as to allow an evaluation of the velocity of each process. All three changes are unimolecular with respect to the methyl halide, or, if we prefer the phrase, are reactions of the first kinetic order. From the rates at which the dissolved halides

\* The results of three preliminary calorimetric measurements of the heat of mixing at 45° C of this system are shown as circles in fig. 3. They are just within the estimated uncertainty of the values derived from free energy measurements, but are uniformly lower than these values. It therefore seems probable that part of the apparent difference in interaction energies between the methanol and ethanol systems is due to experimental error in the heat of mixing values derived from the free energy measurements.

react with liquid water at various temperatures, one can estimate the energy of activation  $\epsilon$ , which is the difference between the critical energy  $\epsilon_c$  of the reacting molecules and their average energy,

$$\epsilon = \epsilon_c - \bar{\epsilon}. \quad (1)$$

Experiments show that  $\epsilon$  decreases as the temperature is raised. This fact is best interpreted by supposing the energy of the solute to be the sum of  $2s$  quadratic terms. The average energy is then  $s\bar{k}T$  and eqn. (1) becomes

$$\epsilon = \epsilon_c - s\bar{k}T,$$

or, in molar rather than molecular notation,

$$E = E_c - sRT. \quad (2)$$

It is the magnitude of  $s$  which is of interest. With methyl bromide, for example, hydrolyzing in liquid water,  $s$  is  $34 \pm 4$ . If all the energy components of the reacting molecules, such as those responsible for their translation, rotation, stretching and bending, took part in the reaction,  $s$  would be 12 for the halide molecule and 6 for the water molecule. The experimental result can thus only be understood by assuming that a number  $n$  of molecules of water take part in the reaction.

$$\text{Since} \quad s = s_{\text{CH}_3\text{Br}} + n s_{\text{H}_2\text{O}}, \quad (3)$$

it follows that  $n$  is 3 or 4. Spectroscopic particulars concerning the internal motions of both reactants make it fairly certain, however, that not all the energy plays a part, and that more likely values of  $s$  are 6 for the methyl halide molecule, and 4 for the water molecule. On this more probable basis,  $n$  becomes 6 or 8 and the hydrolysis is accordingly a reaction of the kinetic order 7-10. A totally different line of argument has led Scatchard<sup>2</sup> to a similar conclusion; in the inversion of cane sugar, one molecule of the sugar reacts with from 5 to 7 molecules of water.

The hydrolysis of even simple molecules, therefore, means a concerted effect between a solute molecule and quite a number of the solvent molecules that surround it. It is with the object of learning something of the nature of the interaction between the dissolved solute molecule and its solvent sheath that this work has been undertaken. The distribution of the halide vapour or liquid between the pure and the aqueous phases has been measured as accurately as possible over a temperature range limited on the low side by the freezing point of the solvent and on the high side by the rapidity of interaction with it. In certain cases we have also measured the distribution of solute between the vapour phase and an aqueous solution saturated with the crystalline hydrate. A consideration of the energy which the methyl halide molecules require before they can escape from the aqueous solution or from the crystalline hydrate, taken in conjunction with recent crystallographic work on the structure of these hydrates, leads to some clarification of the nature of aqueous solutions which are formed under ordinary conditions.

#### EXPERIMENTAL

**MATERIALS AND METHOD.**—Distilled water was freed from ions by percolation in a resin exchange column, and from dissolved gases by vigorous boiling at room temperature, before being transferred to a weighed solubility pipette, which was of the double surface type. Methyl fluoride was prepared as in our earlier work.<sup>3</sup> Methyl chloride, made as described by Shamshurin,<sup>4</sup> was condensed at the temperature of liquid nitrogen, washed in a closed system with dilute KOH and then with concentrated KOH to remove  $\text{Cl}_2$ ,  $\text{I}_2$  and HCl, and finally with concentrated  $\text{H}_2\text{SO}_4$  to remove alkali spray. It was purified by fractionation at  $194.7^\circ \text{K}$ , contained 99.8% of the theoretical amount of chlorine by analysis and possessed a vapour density in complete agreement with that given by Moles and Batuecas.<sup>5</sup> Methyl bromide was made by dropping methyl sulphate on to anhydrous aluminium bromide at room temperatures, and was freed from bromine by washing in the same system of bubblers. Its vapour pressure at  $0^\circ \text{C}$  was 660.0 mm Hg, in agreement with the value given by Egan and Kemp.<sup>6</sup> Methyl iodide was purified by Gand's method,<sup>7</sup> using metallic calcium. The gas burette and absorption pipette

were kept at constant temperature by rapid circulation of thermostat water between the double surfaces, and were connected by flexible copper capillary tubing, with machined metal joints. The glass taps were grease-free and mercury-sealed. The quantity of gas or vapour absorbed by a known weight of water was determined by measuring the volume of the gas absorbed at a definite temperature and pressure. Partial pressures  $p_2$  of the halide are given in mm Hg at 25° C, and concentrations  $c_2$  of the halide are given in moles of solute per litre of solution at the temperature  $T$ .

TABLE 1.—HENRY'S CONSTANTS FOR THE DISSOLUTION OF THE METHYL HALIDES IN WATER

( $p_2$  in mm Hg at 25° C;  $c_2$  in moles/l. solution at  $T^\circ$  K)

methyl fluoride at 303.18°K			methyl chloride at 298.16°K		
$p_2$	$c_2 \times 10^3$	$(p_2/c_2) \times 10^{-3}$	$p_2$	$c_2 \times 10^3$	$(p_2/c_2) \times 10^{-3}$
372.3	25.43	14.64	205.2	28.72	7.15
389.5	26.61	14.64	217.2	30.43	7.14
406.7	27.75	14.66	234.0	32.79	7.14
425.9	29.00	14.69	255.1	35.65	7.16
445.0	30.27	14.70	277.9	38.67	7.19
539.6	36.79	14.67	302.7	42.32	7.15
553.3	37.81	14.63	332.8	46.21	7.20
569.2	38.87	14.64	363.2	50.75	7.16
603.2	41.18	14.65	373.2	80.13	7.15
640.6	43.66	14.67	612.7	85.95	7.13
681.0	46.48	14.65	670.4	93.83	7.15
702.0	47.95	14.64	711.4	99.50	7.15
723.2	49.42	14.63	756.1	105.9	7.15
745.2	51.00	14.61	805.2	112.7	7.15
766.8	52.50	14.61	856.4	119.6	7.15
790.8	54.00	14.64	908.0	126.8	7.16
—	—	—	935.9	130.8	7.16

methyl bromide at 293.16°K			methyl iodide at 298.16°K		
$p_2$	$c_2 \times 10^3$	$(p_2/c_2) \times 10^{-3}$	$p_2$	$c_2 \times 10^3$	$(p_2/c_2) \times 10^{-3}$
295.0	73.31	4.024	86.7	20.85	4.158
311.0	77.71	4.003	91.1	22.30	4.085
334.2	83.30	4.012	97.2	23.72	4.098
502.2	124.31	4.040	103.2	25.32	4.076
524.2	129.98	4.033	110.1	27.18	4.062
552.6	137.12	4.030	118.4	29.27	4.045
583.4	144.84	4.028	125.6	31.02	4.049
618.5	153.28	4.035	133.2	33.01	4.035
653.0	161.99	4.031	140.3	34.73	4.040
690.6	171.76	4.021	147.8	36.67	4.031
731.8	182.36	4.013	155.3	38.74	4.009
774.3	193.33	4.005	162.2	40.46	4.009
791.4	197.89	3.999	—	—	—
828.9	206.94	4.006	—	—	—
870.1	217.25	4.005	—	—	—
981.3	245.87	3.991	—	—	—

HENRY'S CONSTANTS FOR THE METHYL HALIDES IN WATER.—It is already known that Henry's law is obeyed by solutions of methyl chloride and methyl bromide<sup>1</sup> in water at 20° C, and at pressures from 24 to 500 mm Hg. For this reason, and because the plot of  $p_2$  against  $c_2$  must pass through the origin, we have not been concerned with the distribution of the solute vapour at very low pressures. Specimens of our results are given in table 1. During the course of the work, a method was devised, which we do not propose to describe here, which enabled us to measure, from the rate of dissolution of a reacting vapour, both the distribution constant,  $p_2/c_2$ , and the velocity constant governing the hydrolysis. The latter was found to be in exact agreement with that determined more directly in the absence of the vapour phase. The variation of Henry's constant

with respect to temperature is found to be adequately reproduced by the equation (cf. Valentiner<sup>8</sup>):

$$\log_{10} (p_2/c_2) = a - b \log_{10} T - c/T, \quad (4)$$

the three empirical constants of which have been evaluated by the method of least squares (see tables 2 and 3). The figures for methyl alcohol given in table 3 are based on the distribution coefficient determined by Butler, Thomson and McLennan<sup>9</sup> at 25° C, and the calorimetrically measured heats of mixing of the liquids given by Bose.<sup>10</sup> In the last column,  $p_2^0$  stands for the vapour pressure of the pure liquid and  $x_2$  for its mole fraction in solution. It will be observed that only with methyl alcohol does Raoult's law lead to a result which is correct in regard to order of magnitude. The logarithm of  $(p_2/x_2)$  can also be expressed by an equation of the same form as (4): it is found that  $b$  is greater by 1.025 and  $c$  by 123.

TABLE 2.—A COMPARISON OF OBSERVED VALUES OF  $p_2/c_2$  WITH THOSE BY EQN. (4)

methyl fluoride			methyl chloride		
T°K	$(p_2/c_2) \times 10^{-3}$		T°K	$(p_2/c_2) \times 10^{-3}$	
	(obs.)	(calc.)		(obs.)	(calc.)
273.21	6.13	6.12	277.24	3.28	3.29
283.88	8.83	8.72	283.32	4.26	4.23
293.34	11.41	11.43	288.21	5.11	5.09
298.21	12.92	12.96	293.18	6.12	6.08
303.18	14.65	14.61	298.16	7.18	7.18
313.05	17.94	18.07	313.06	11.06	11.04
322.64	21.6	21.6	322.93	13.95	13.99
333.23	25.4	25.5	333.14	16.95	17.25
353.40	32.5	32.5	343.21	20.6	20.6
—	—	—	353.23	23.8	23.8

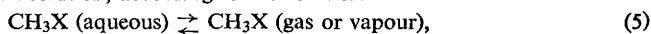
  

methyl bromide			methyl iodide		
T°K	$(p_2/c_2) \times 10^{-3}$		T°K	$(p_2/c_2) \times 10^{-3}$	
	(obs.)	(calc.)		(obs.)	(calc.)
278.16	2.07	2.06	273.16	1.274	1.273
283.16	2.55	2.58	278.19	1.686	1.678
288.14	3.20	3.19	283.35	2.16	2.17
293.16	3.99	3.88	288.27	2.73	2.72
298.13	4.73	4.66	293.10	3.38	3.33
303.16	5.58	5.54	298.08	4.06	4.02
313.21	7.54	7.56	303.08	4.73	4.78
323.18	9.76	9.89	313.02	5.54	5.57
333.19	12.4	12.5	318.03	6.38	6.39
343.16	14.9	15.2	322.91	8.04	8.05
353.16	18.0	18.0	—	—	—

TABLE 3.—CONSTANTS OF EQN. (4) ( $p_2$  IN MM Hg;  $c_2$  IN MOLES/L. OF SOLUTION)

solute	$a$	$b$	$c$	$(p_2/c_2)$ at 298.16° K	$p_2/p_2^0 x_2$ at 298.16° K
CH <sub>3</sub> F	59.096	17.781	3265.7	13,280	31.3
CH <sub>3</sub> Cl	71.005	21.656	4043.9	7,169	100.6
CH <sub>3</sub> Br	73.022	22.261	4254.8	4,664	157.0
CH <sub>3</sub> I	133.252	42.967	6955.2	4,024	572.4
CH <sub>3</sub> OH	55.791	16.163	4552.6	3.447	1.507

THE HEAT OF ESCAPE OF THE METHYL HALIDES FROM WATER.—If we regard the constant  $p_2/c_2$  as governing an equilibrium between methyl halide molecules in solution and in the vapour phase, we may derive the increase in heat content attending the escape of one mole of solute from solution, according to the reaction



by applying the van't Hoff isochore:

$$\Delta H = RT^2 \left[ \frac{d \ln (p_2/c_2)}{dT} \right]_P = -R \left[ \frac{d \ln (p_2/c_2)}{d(1/T)} \right]_P. \quad (6)$$

In terms of the constants of eqn. (4), we have

$$\Delta H = 2.303Rc - bRT \quad (7)$$

and

$$\Delta C_p = C_p(\text{gas}) - C_p(\text{aqueous}) = -bR. \quad (8)$$

These relations are by no means exact. The formal thermodynamics of the escape process requires a knowledge of the partial molar volumes of the solute and solvent and their dependence on pressure, temperature and composition. None of these properties is known. Moreover, were we in full possession of them, a rigorous thermodynamic treatment would still be denied us, because the systems considered are not at equilibrium, but are, like aqueous solutions of sucrose, so often treated in textbooks on thermodynamics, undergoing chemical change at known rates to a true equilibrium state. The present estimates of  $\Delta H$  and  $\Delta C_p$  are merely accepted because there are no others. They may be used to find the specific heats and standard entropies of these solutes in water. The  $\Delta$  terms in table 4 refer to reaction (5). Thus  $\Delta S^\circ$ , for example, means the excess molar entropy of the gas, at a pressure of 1 mm Hg over the molar entropy of the solute at a concentration of 1 mole/l. The specific heats and standard entropies of gaseous methyl fluoride, methyl chloride, methyl bromide and methyl alcohol are experimental values due, respectively, to Michels,<sup>11</sup> Eucken and Hauk,<sup>12</sup> Egan and Kemp,<sup>6</sup> and Weltner and Pitzer.<sup>13</sup> That for gaseous methyl iodide is a calculated value due to Edgell and Glockler.<sup>14</sup>

TABLE 4.—SPECIFIC HEATS AND STANDARD ENTROPIES OF METHYL HALIDES IN WATER AT 298.16° C (CAL/MOLE DEG.)

solute	$\Delta c_p$	$c_p$ (gas)	$c_p$ (solute)	$\Delta S^\circ$	$S^\circ$ (gas, 1 mm)	$S^\circ$ (solute)
CH <sub>3</sub> F	- 35.22	8.95	44.23	33.64	66.49	32.91
CH <sub>3</sub> Cl	- 43.02	8.82	51.84	36.66	69.18	32.52
CH <sub>3</sub> Br	- 44.22	9.33	53.55	37.83	71.80	33.97
CH <sub>3</sub> I	- 85.55	10.55	96.10	37.85	74.04	36.19
CH <sub>3</sub> OH	- 28.19	10.60	38.79	40.21	70.40	30.29

Taken in conjunction with thermochemical data for gas reactions and with standard entropies of ions in water, the results given in the last column are valuable in determining the extent of reactions such as hydrolysis, etherification and ionic substitution in aqueous solutions.

THE HEATS OF DISSOLUTION OF THE LIQUID METHYL HALIDES IN WATER.—An indirect method of obtaining the increase in heat content attending the dissolution of a liquid in water is to subtract the heat of escape,  $\Delta H$ , from the latent heat of vaporization. The latter may be obtained from the vapour pressure of the pure liquid, expressed, for example, in the form

$$\log_{10} p_2^\circ (\text{mm}) = a^\circ - b^\circ \log_{10} T - c^\circ/T, \quad (9)$$

for, when the vapour obeys the ideal gas laws, we have

$$L = 2.303 R c^\circ - b^\circ RT. \quad (10)$$

The data of table 5 show that, with the possible exception of methyl iodide, heat is evolved during the dissolution of the liquid methyl halides in water. It is of interest to note that the calorimetrically measured heat of dissolution of liquid methyl alcohol should lie so near to the indirectly estimated heat of dissolution of liquid methyl fluoride.

TABLE 5.—CONSTANTS OF EQN. (9) (mm Hg) AND HEATS OF ESCAPE AND VAPORIZATION (cal/mole) AT 298.16° K

liquid	$a^\circ$	$b^\circ$	$c^\circ$	$L$	$\Delta H$	$\Delta H - L$
CH <sub>3</sub> F	21.794	5.238	1,328	2,974	4,404	1,430
CH <sub>3</sub> Cl	22.011	5.133	1,701	4,738	5,670	932
CH <sub>3</sub> Br	21.532	4.875	1,865	5,644	6,275	631
CH <sub>3</sub> I	22.974	5.346	2,132	6,533	6,365	- 188
CH <sub>3</sub> OH	22.430	4.634	2,661	9,427	11,251	+1,824

THE SOLUBILITY OF THE METHYL HALIDES IN WATER.—The maximum concentration of halide in solution is found by substituting  $p_2^\circ$  for  $p_2$  in eqn. (4). By making use of eqn. (9), we thus obtain for the saturation concentration at various temperatures, the equation:

$$\log_{10} c_2^\circ = (a^\circ - a) - (b^\circ - b) \log_{10} T - (c^\circ - c)/T, \quad (11)$$

according to which the solubility passes through a minimum value as the temperature is raised. Thus, for example, with our data for methyl iodide, the equation becomes

$$\log_{10} c_2^\circ = -110.278 + 37.621 \log_{10} T + 4823/T,$$

which indicates a minimum solubility of 0.0973 mole, or 13.8 g/l. at a temperature of 295.2° K. Rex<sup>14</sup> found a solubility minimum of 14.2 g/l,000 g of water, and estimated the temperature corresponding to the minimum to lie between 20° and 30° C. Our results thus agree with his, and resemble those found for other alkyl halides (van Arkel and Vles<sup>16</sup>) and for certain hydrocarbons in water (Bohon and Claussen<sup>17</sup>). As  $b$  is always greater than  $b^\circ$ , the saturation solubility of all gases and vapours in water at first diminishes as the temperature is raised, passes through a minimum value when

$$T = 2.303 (c - c^\circ)/(b - b^\circ),$$

and thereafter increases with an increase in temperature (see Wiebe and Gaddy<sup>18</sup>).

**THE HEAT OF ESCAPE OF THE METHYL HALIDE FROM THE CRYSTALLINE HYDRATES.**—When the system halide vapour + aqueous solution + liquid halide is cooled, a point is reached at which a crystalline hydrate appears. In accordance with the phase rule, the

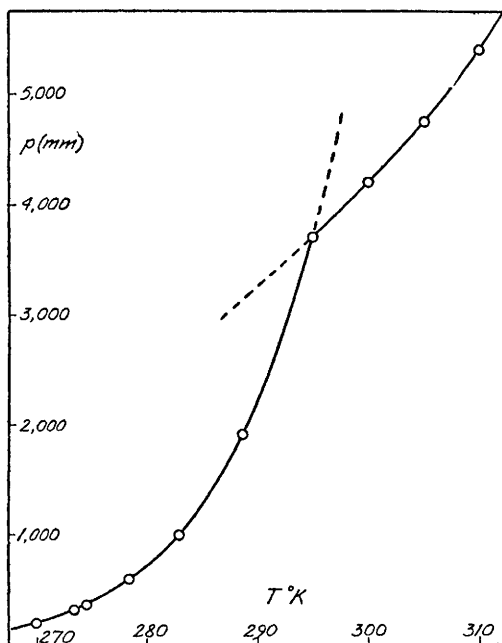
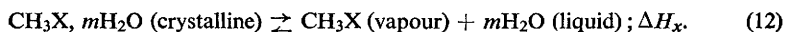


FIG. 1.—The critical point of methyl chloride hydrate.

point is a fixed one, characterized by a definite temperature and a definite pressure. It is usually referred to as the critical point of the solution. The equilibrium pressure  $p_x$  of the system at lower temperatures may be utilized, by means of the Clausius-Clapeyron equation, to determine the increase in heat content attending the change:

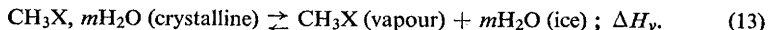


With methyl chloride, for example, the equilibrium pressure in the temperature range 270.05-288.66° K is found to be adequately reproduced by the equation

$$\ln p_x (\text{mm}) = 39.24 - 18,250/RT$$

so that  $\Delta H_x$  for this reaction is 18,250 cal. We have, unfortunately, been unable to measure the pressures with sufficient accuracy to decide on the temperature variation of  $\Delta H_x$ ; and our experiments in this field are confirmatory rather than original. The point of intersection of the  $p$  against  $T$  curves for the two systems discussed in this paragraph give a critical temperature of 293.55° K and a critical pressure of 3,640 mm for aqueous methyl chloride (fig. 1). Another break occurs in the lower curve when ice

separates out, and the pressures  $p_y$  of the system ice + crystalline hydrate + vapour enables one to determine the increase in heat content attending the change:



On subtracting this equation from eqn. (12), and denoting the heat of fusion of ice by  $L$ , we obtain one of the equations developed by de Forcrand<sup>19</sup> to determine the composition of hydrates:

$$\Delta H_x - \Delta H_y = mL. \quad (14)$$

Thus, for example,  $\Delta H_y$  for methyl chloride, though not known accurately, is approximately 6,500 cal at 273.16° K. With  $L = 1,435.7$ ,  $m$  becomes 8 to the nearest integer.

THE STRUCTURE OF GAS HYDRATES.—Crystalline hydrates formed from gases, vapours, and liquids are loosely referred to as gas hydrates. The review by Schroeder<sup>19</sup> covers

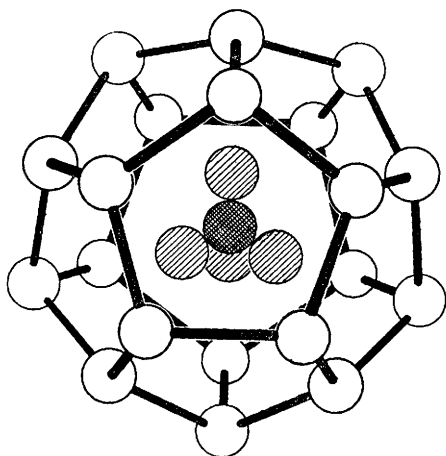


FIG. 2.

the work done upon them during a century from the time of their discovery by Davy, and includes the classical contributions of Faraday, Roozeboom, Tammann, Villard and de Forcrand. Latterly, the gas hydrates have been studied by Claussen<sup>20</sup> who interprets his results on the principle of the molecular model, and by von Stackelberg,<sup>21</sup> who has examined them by the scattering of X-ray and by other methods. From their conclusions, which differ in detail but are in the main mutually confirmatory, it appears that the solute (*Hydratbildner*) occupies holes in a tetrahedral ice structure, each hole being surrounded by a number,  $c$ , of  $\text{H}_2\text{O}$  molecules,\* each of which retains its own co-ordination number of 4. This interesting and unpredictable conclusion is difficult to visualize without seeing the models. The hydrate formed from solutes with a co-ordination number of 20 may be considered as an example. The model (fig. 2) shows how the 20 molecules of  $\text{H}_2\text{O}$  arrange themselves around the solute, each being directly linked to 4 other  $\text{H}_2\text{O}$  molecules, of which 3 are in the co-ordination shell, and the fourth outside it. Without greatly straining the distances or angles which characterize pure ice, the figure formed is a regular dodecahedron, the surface of which consists of equal plane pentagons. von Stackelberg has further shown that the gas hydrates can be classified into groups, with formulae  $M. 6\text{H}_2\text{O}$ ,  $M. 8\text{H}_2\text{O}$  and  $M. 17\text{H}_2\text{O}$ , and values of  $\Delta H_x$  of 15,000, 19,000 and 31,500 cal respectively. Some values of  $\Delta H_x$ , partly calorimetric but chiefly derived from the Clausius-Clapeyron equation, are listed in table 6. With few exceptions, they lie close to our values of  $\Delta H_0$  for the escape process from sub-cooled water (eqn. (7), with  $T = 0$ ). At worst, the coincidence is an accident, due to the compensation of numerous terms. On the other hand, it may be significant, indicating that the minimum energy of the solute + water system, after which eqn. (4) empirically strives, is in fact very near to the actual energy of the crystalline hydrate. These considerations apart, the crystallographic classification of the gas hydrates seems to be supported by the classification based on the magnitude of  $\Delta C_p$ .

Four items call for brief comment.

(i) In computing the lattice energy of hydrates formed in this way, the interaction of a shell molecule with the solute must be regarded as additional to, and not as replacing, its other interactions.

(ii) The 28 water molecules forming the shell in compounds of the formula  $M. 17\text{H}_2\text{O}$  make 4 equal hexagons and 12 equal pentagons. Proceeding to still larger lacunae, we have a plausible structure for the surface of ice, without, as it were, any loose ends.

\* Henceforth in this article,  $c$  denotes the co-ordination number of the solute, and is not to be confused with the empirical constant of eqn. (4) and (7).

(iii) In the smaller crystals, some of the water molecules in the co-ordination shell are attached to 3, and others to 2, water molecules in the shell. Inspection of the models up to  $c = 12$  makes it clear that the number of water-water interactions in the shell is  $(3/2)(c - 2)$ .

(iv) Some of the  $\Delta H_x$  values given in table 6 differ from those previously published. The explanation is that, on plotting  $\log p_x$  for these systems against  $1/T$ , we have found marked breaks in the curves, indicating the existence of at least two different hydrates.

TABLE 6.—CONSTANTS FOR AQUEOUS SOLUTIONS AND CERTAIN HYDRATES

solute	$a$	$-\Delta C_p$	$\Delta H_0$	$\Delta H_x$	$m$	$c$	$\Delta C_p/Rc$	
He	41.71	24.22	7,421	—	—	6	2.05	
Ne	42.61	24.02	9,060	—	—	6		
H <sub>2</sub>	44.27	25.65	8,634	—	—	6		
A	63.00	37.75	14,060	14,885	6	10	1.86	
N <sub>2</sub>	67.88	40.88	14,839	13,300	6	10		
CO	68.39	41.33	15,009	—	6	10		
NO	67.79	41.02	15,131	—	6	10		
O <sub>2</sub>	66.94	40.28	14,970	—	6	10		
CO <sub>2</sub>	55.07	32.25	14,119	14,650	6	10		
N <sub>2</sub> O	57.23	33.39	15,157	15,220	6	10		
H <sub>2</sub> S	59.27	35.74	14,896	15,170	6	10		
C <sub>2</sub> H <sub>2</sub>	58.92	35.53	14,181	15,400	6	10		
CH <sub>3</sub> F	58.97	35.32	14,937	14,480	6	10		
Kr	87.42	54.20	19,820	13,900	8	12	1.93	
Br <sub>2</sub>	68.69	41.12	19,974	19,600	8	12		
CH <sub>4</sub>	80.24	49.20	18,000	17,820	8	12		
CH <sub>3</sub> Cl	71.01	43.02	18,496	18,250	8	12		
CH <sub>3</sub> Br	73.02	44.22	19,461	19,500	8	12		
X	104.38	65.55	23,890	18,266	12	16	2.04	
C <sub>2</sub> H <sub>4</sub>	102.58	64.54	23,150	23,400	12	16		
C <sub>2</sub> H <sub>6</sub>	105.06	65.50	24,330	23,300	12	16		
Rn	124.78	79.33	28,720	—	17	20	2.00	
Cl <sub>2</sub>	130.39	84.30	29,203	17,640	17	20		
CS <sub>2</sub>	146.08	93.25	36,121	—	17	20		
CH <sub>3</sub> I	133.25	85.35	31,812	31,400	17	20		
CH <sub>2</sub> Cl <sub>2</sub>	112.14	70.80	28,900	29,000	17	20		
CHCl <sub>3</sub>	130.52	82.60	33,802	31,000	17	20		
CH <sub>3</sub> CHCl <sub>2</sub>	133.25	81.83	32,179	29,400	17	20		
(CH <sub>2</sub> Cl) <sub>2</sub>	129.79	82.31	32,392	—	17	20		
CCl <sub>4</sub>	178.79	115.22	40,965	—	—	28		2.06

## DISCUSSION

(i) KINETIC.—The order of magnitude of the molar fraction of solute in the solutions which we have examined is  $10^{-4}$ . The surface of the solution is thus effectively free from solute molecules, and we may regard the rate of dissolution of the vapour as being directly proportional to its partial pressure,  $p_2$ . The rate at which solute molecules escape from the solution is, of course, proportional to their concentration  $c_2$ , and to the fraction which can acquire sufficient energy to detach themselves from their solvent envelopes. This fraction can be shown, by means of statistical mechanics, to be  $(\epsilon_c/kT)^s/(s!) \exp(-\epsilon_c/kT)$ , where  $s$  is the number of oscillators among which, under classical conditions, a large number of vibrational quanta of energy are distributed. Since, at equilibrium, the rates of entry into and escape from the solution are equal, it follows that

$$\ln(p_2/c_2) = \text{constant} - s \ln T - (\epsilon_c/kT). \quad (15)$$

This equation has the same form as the experimental eqn. (4), with

$$s = b = -\Delta C_p/R.$$



From table 6, we note a parallelism between the number  $s$  of oscillators and the co-ordination number  $c$ . In fact,  $s = 2c$  very nearly. According to this interpretation, the release of a solute molecule from solution is a difficult process, made possible only by the co-operation of all the solvent molecules which surround it, each solvent molecule contributing two vibrational modes of motion to the ejection process. A similar interpretation has been offered for the processes of the vaporization of liquids (Matthews, Sumner and Moelwyn-Hughes<sup>22</sup>), the ionization of solutes (Moelwyn-Hughes<sup>23</sup>), and hydrolysis.<sup>1</sup> The two major assumptions underlying these treatments are that the energy of the activation step can be expressed as a sum of squared terms, and that a distribution law derived for systems at constant volume may be applied to those examined at constant pressure. It is impossible at present to gauge the soundness of either assumption, of which the latter is the more suspect.

(ii) THERMODYNAMIC.—Provided the molecules comprising a solution and the forces exerted by them are spherically symmetrical, the relative partial pressure of the second component is given by van Laar's equation:<sup>24</sup>

$$\frac{p_2}{p_2^\circ} = \frac{N_2}{N_1 + N_2} \exp \left[ \left( \frac{N_1}{N + N_2} \right)^2 \frac{\Delta u^\circ}{kT} \right]. \quad (16)$$

Here the  $N$ 's stand for the number of molecules, and the interchange energy is defined in terms of the (common) co-ordination number  $c$  and the interaction energies  $\phi$  of the three types of molecular pairs:

$$\Delta u^\circ = c(\phi_{12} - \frac{1}{2}\phi_{11} - \frac{1}{2}\phi_{22}). \quad (17)$$

Applied to the systems under consideration, in which the concentrations of solute are low, van Laar's equation leads to the following expression for Henry's constant:

$$\frac{p_2}{c_2} = \frac{p_2^\circ V_1}{1,000} \exp (\Delta u^\circ / kT), \quad (18)$$

where  $V_1$  is the molar volume of the solvent.

Values of the interchange energy  $\Delta U^\circ$  per mole for the solutions studied in this paper are given in table 7. Except for methyl alcohol, they exceed  $2RT$ , as one would have anticipated, and increase as the temperature is raised.

TABLE 7.—INTERCHANGE ENERGIES  $\Delta U^\circ$  (cal/mole) FOR METHYL HALIDES IN WATER

solute	0°C	$\Delta$	25°C	$\Delta$	50°C
CH <sub>3</sub> F	1,823	(235)	2,058	261	2,319
CH <sub>3</sub> Cl	2,380	339	2,719	267	2,986
CH <sub>3</sub> Br	2,623	374	2,997	263	3,260
CH <sub>3</sub> I	3,378	375	3,753	(214)	3,967
CH <sub>3</sub> OH	114	204	318	149	467
CCl <sub>4</sub>	6,145	1,931	8,076	- 1,016	7,060

This lack of constancy in  $\Delta u^\circ$ , which was dealt with by van Laar, arises in part from the falsity of accepting an average value of  $c$  in eqn. (17) and from the neglect of interactions other than those of the first shell. Although changes of specific heat on dissolving in organic solvents are found in the carbon disulphide + chloroform system,<sup>25</sup> for which

$$\Delta U^\circ = 1,268 - 3.16 T,$$

and in the ether + chloroform system,<sup>26</sup> for which

$$\Delta U^\circ = - 1,761 + 3.70 T,$$

they are small in comparison with the changes of specific heat found on dissolving in water. By applying eqn. (16) to our experimental data, we obtain values  $\Delta u^\circ$  which are found to vary, though not linearly with respect to  $T$ . By omitting

the bracketed increments in table 7, it is found that the interchange energy can be adequately reproduced by the empirical equation:

$$\Delta U^\circ = \Delta U_0^\circ + 59.555T - 0.07888T^2, \quad (19)$$

according to which  $\Delta U^\circ$  has a maximum value at  $377.5^\circ$  K.

Hildebrand<sup>28</sup> and Scatchard<sup>22</sup> have shown how van Laar's treatment may be extended to solutions made from molecules of different sizes. In what may be regarded as a variant of their theory (Moelwyn-Hughes<sup>29</sup>), the interaction energy of the system is obtained by considering positional exchanges between solute molecules, of partial molecular volume  $v_2$ , with groups of solvent molecules (partial molecular volume  $v_1$ ), each group being equal in volume to one solute molecule. The interchange energy  $\Delta u^\circ$  has now a different meaning, and the relative partial pressure of component 2 is given in terms of the volume fractions as follows:

$$\frac{p_2}{p_2^\circ} = \frac{N_2v_2}{N_1v_1 + N_2v_2} \exp\left(\frac{N_1v_1}{N_1v_1 + N_2v_2}\right)^2 \frac{\Delta u^\circ}{kT}. \quad (20)$$

Applied to dilute solutions, we have

$$\frac{p_2}{c_2} = \frac{p_2^\circ V_2}{1000} \exp(\Delta u^\circ/kT). \quad (21)$$

Without a knowledge of the partial molar volume  $V_2$  of the solute, it is impossible to test the relationship. If, however, we use the ordinary molar volumes  $V_2^\circ$  of the pure liquid solute, we obtain for methyl bromide at  $0^\circ$ ,  $25^\circ$  and  $50^\circ$  C, the following volumes of  $\Delta u^\circ$ : 2030, 2316 and 2491 cal. For methyl iodide, we find 2706, 3015 and 2859; for  $\text{CH}_3\text{OH}$ ,  $-312$ ,  $-165$ ,  $-67.5$ ; for  $\text{CCl}_4$ , 5247, 7081, 5965 cal. These quantities are seen to be lower than those obtained on the mole fraction basis, and less sensitive to temperature. One is tempted to ascribe a value of  $\Delta U^\circ = 2860 \pm 155$  cal to the methyl iodide + water system at all temperatures, but the limits thus given exceed the experimental error. This mean value would only reproduce the results to within 28%, which exceeds the combined errors attributable to the vapour pressure, the partial pressure and the molar volume. If, however, the partial molar volume of methyl iodide in the infinitely dilute aqueous system were found to be appreciably different from that of the pure liquid, a constant value of  $\Delta U^\circ$  could emerge, and eqn. (21) fully confirmed. The next step, attempted in various ways by van Laar,<sup>24</sup> Hildebrand,<sup>27</sup> Scatchard,<sup>28</sup> Butler<sup>9</sup> and others, is the determination of  $\Delta U^\circ$  in terms of the properties of the pure components.

According to the theory which leads to eqn. (20), the isothermal gain in entropy on forming a solution from two liquid components is

$$\begin{aligned} \Delta S = & \frac{N_1N_2v_1}{N_1v_1 + N_2v_2} \left[ -\frac{N_2v_2}{N_1v_1 + N_2v_2} (\alpha_1 - \alpha_2) \Delta u^\circ - \frac{d(\Delta u^\circ)}{dT} \right] \\ & + N_1k \left[ \frac{v_1}{v_2} [1 + (\alpha_1 - \alpha_2)] \ln \frac{N_1v_1 + N_2v_2}{N_1v_1} \right] \\ & + N_2k \ln \frac{N_1v_1 + N_2v_2}{N_2v_2}, \end{aligned} \quad (22)$$

in which  $\alpha_1$  and  $\alpha_2$  are the partial coefficients of expansion of the solvent and the solute respectively. For the dilute solutions examined the two final terms are zero and the equation reduces to

$$\Delta S = \frac{N_1N_2v_1}{N_1v_1 + N_2v_2} \left[ -\frac{N_2v_2}{N_1v_1 + N_2v_2} (\alpha_1 - \alpha_2) \Delta u^\circ - \frac{d(\Delta u^\circ)}{dT} \right]. \quad (23)$$

The magnitude of the first term in the square brackets depending on the coefficients of expansion is small in comparison with the final term, so that we

should expect that when  $d(\Delta U^\circ)/dT$  is large and positive,  $\Delta S$  is large and negative, as is in fact found.

(iii) GENERAL.—Solute which react with water to form crystalline hydrates vary from argon to haemoglobin. Concerning them, most chemists have, at one time or another, wondered what happens to the water of hydration when the crystalline hydrate dissolves. No general answer to such a wide question can be given. When, for example, the crystalline dihydrates of the hydrogen halides,  $HX \cdot 2H_2O$ , dissolve in water, it is believed that the ions thus loosened from one another's influence still hang on to their water of hydration. On the other hand, if the heat absorbed during the dissolution of a mole of a crystalline hydrate,  $M \cdot mH_2O$ , lies near to the heat  $mL$  required to melt  $m$  moles of ice, it is fair to assume that the water of crystallization changes its character, on dissolution, from that of ice to that of water. Such is approximately the case with methyl halide hydrates. There is no room to doubt that the  $c$  molecules of solvent which still surround one molecule of solute are liquid in character, and can change places with more distant water molecules. Nevertheless, under all those conditions when the stable form of the solute which separates from the solution is the hydrate, we must regard the solute in solution as exerting some degree of coordination on its solvent neighbours. In many cases, calorimetric and crystallographic evidences support Langmuir's view that the water molecules surrounding a solute resemble liquid water in its surface phase. In this way it is possible to understand why the heat of dissolution of a solute appears to be determined more by its size than by its chemical character.

The present-day study of aqueous solutions awaits a clarification of the structure of liquid water. In the meantime, it may be helpful to regard it as a fluid which, under ordinary conditions, contains, or has a predisposition to form, holes of various sizes, into which solute molecules can fit with varying degrees of comfort. The fraction of the total number of solute molecules occupying different types of holes is governed by Boltzmann's law, in which the work of transfer from one hole to another is the product of the total pressure of the system and the difference between the volumes of the holes. It would be easy, but also inappropriate here, to amend in this sense the elementary kinetic and thermodynamic ideas in terms of which we have considered the experimental results.

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