ON THE ABSORPTION OF HYDROGEN CHLORIDE INTO VARIOUS ORGANIC LIQUIDS AND CALCULATION OF THE HEAT OF ABSORPTION. II.

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In a previous paper,[1] we published the results of the absorption of hydrogen chloride into various organic liquids such as 1,1,2,2-tetrachlorethane, ethylene chloride, carbon tetrachloride, and ethylene bromide, and also presented the purpose of this investigation along with necessary discussions in connection with it in detail. The present paper is a further report of similar measurements of the absorption of hydrogen chloride into several other organic liquids of the same series as the previous ones.

Experimental Procedure. The method of measuring the absorption of hydrogen chloride into these liquids is exactly the same as before and the apparatus remains essentially the same as that described previously except that the water-jacketed gas burette has been used with constant temperature water flowing in the jacket, and the measurements of the absorption have been carried out at 20°, 15°, and 12°C. and at various pressures.

Materials. Hydrogen chloride was prepared similarly as described in the previous report by dropping concentrated hydrochloric acid into pure concentrated sulphuric acid, passing the generated gas through two sulphuric acid bubblers, and condensing it twice by liquid nitrogen. Only the middle portion of it was used, after passed finally through a calcium chloride tube before it was allowed to fill the burette and reservoir.

1,1,2-Trichlorethane, b. p. 112.5°–113°C.[2] Eastman's product was distilled twice and once under reduced pressure.

Pentachlorethane, b.p. 158.5°–159.5°C.[2] Eastman's product was distilled twice and the constant boiling part was again distilled under reduced pressure.

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(1) S. Hamai, this Bulletin, **10** (1935), 5.

(2) The boiling points of both liquids are somewhat lower than those given in the literature but they are distilled at essentially constant temperature.

Results. The results of the absorption measurements with these organic liquids—the volume of hydrogen chloride absorbed per 20 c.c. of each liquid is reduced to the corresponding volume at 25°C.—are tabulated in Tables 1 and 2 with their corresponding molal fractions and mole percent.

The treatment of these results is exactly similar to that already published, namely the volume of hydrogen chloride absorbed is plotted against respective pressure at which the system finally reached an equilibrium, as shown, for an example, in Fig. 1 for 1,1,2-trichlorethane. The volume of hydrogen chloride to be absorbed at one atmosphere is obtained by extrapolation and this is converted into mole fraction and then the solubility of hydrogen chloride in respective liquids, i.e. N_{HCl} when P_{HCl} equals 760 mm., is obtained by assuming Henry's law is obeyed. In calculating the mole fractions for both liquids, the densities of the liquids at 20°, 15°, and 12°C. are obtained by interpolating those data given in Beilstein's Handbook. Table 3 shows N (20°, 15°, and 12°C.), log N, and $(1/T) \times 10^{-3}$ and these are plotted in Fig. 2 and 3. ΔH for the heat of absorption can be calculated from

$$d \log N / d(1/T) = -\Delta H / (2.303 \times R).$$

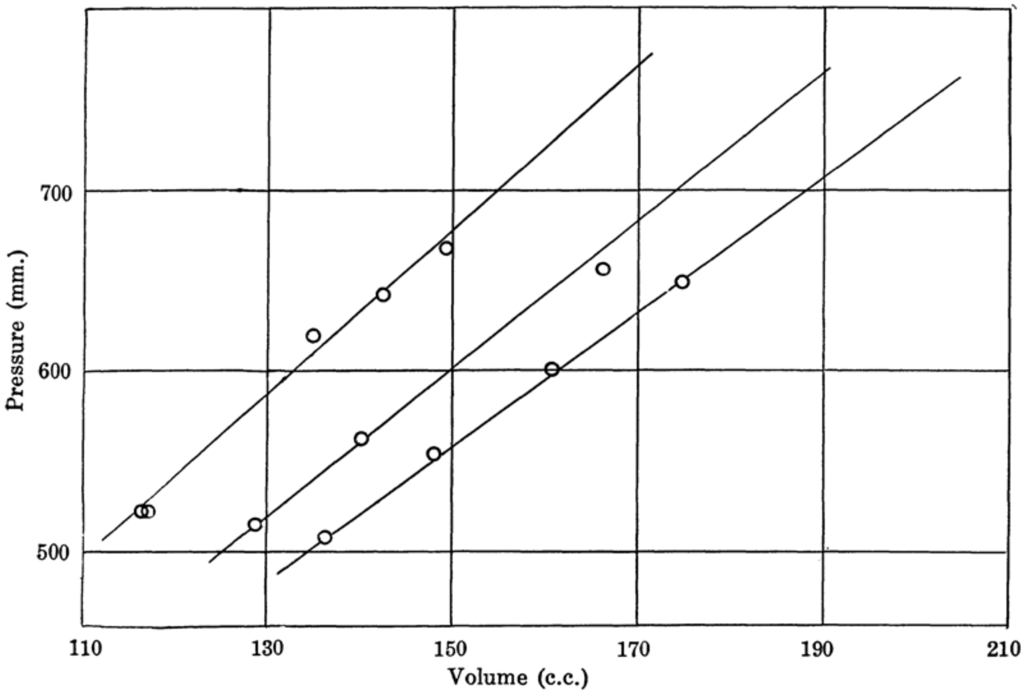
The values of ΔH thus found are also listed in Table 3.

Table 1. Absorption of Hydrogen chloride per 20 c.c. of 1,1,2,-Trichlorethane at 20°, 15°, and 12°C.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mole fraction N	Mole per cent.
		20°C.		
1	620.0	134.33	0.02489	2.49
2	523.5	116.81	0.02171	2.17
3	667.0	149.57	0.02781	2.78
4	640.5	142.33	0.02633	2.63
5	620.0	134.24	0.02488	2.49
6	523.5	116.48	0.02166	2.17
		15°C.		
7	562.0	140.33	0.02588	2.59
8	516.0	128.70	0.02378	2.38
9	655.0	166.50	0.03056	3.06
		12°C.		
10	556.5	147.23	0.02705	2.71
11	649.0	174.77	0.03195	3.195
12	508.5	136.59	0.02514	2.51
13	601.5	160.11	0.02935	2.94

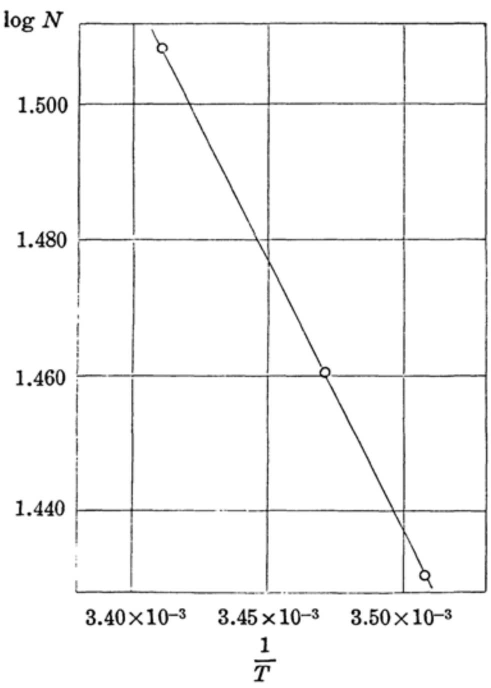
Table 2. Absorption of Hydrogen Chloride per 20 c.c. of Pentachlorethane at 20°, 15°, and 12°C.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mole fraction N	Mole per cent.
		20°C.		
1	718.0	87.44	0.02125	2.13
2	565.5	68.25	0.01666	1.67
3	614.0	75.43	0.01838	1.84
4	666.0	79.58	0.01937	1.94
5	339.5	40.33	0.009946	0.995
		15°C.		
6	661.5	86.60	0.02096	2.10
7	611.5	79.76	0.01934	1.93
8	562.0	73.74	0.01790	1.79
9	661.5	86.60	0.02096	2.10
		12°C.		
10	712.5	98.90	0.02381	2.38
11	611.5	83.50	0.02018	2.02
12	560.5	76.86	0.01865	1.87
13	657.5	91.20	0.02199	2.20



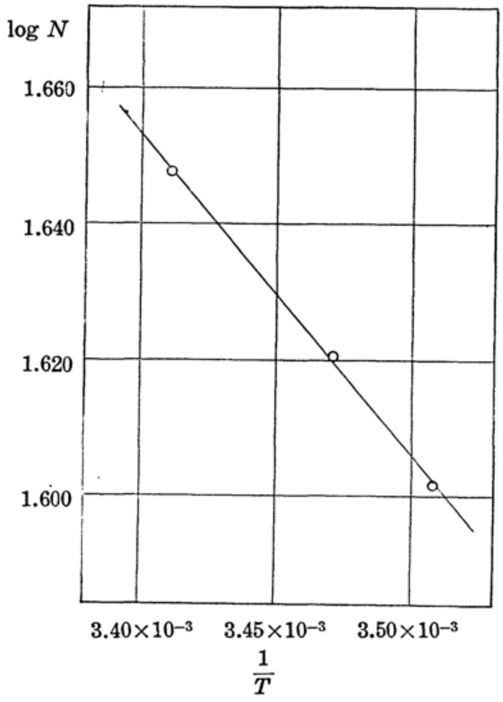
Volume of Hydrogen Chloride Absorbed per 20 c.c. of 1,1,2,-Trichlorethane at 20°, 15°, and 12°C, and at Various Pressures.

Fig. 1.



Variation of the Absorption of Hydrogen Chloride into 1,1,2-Trichlorethane with Respect to Temperature.

Fig. 2.



Variation of the Absorption of Hydrogen Chloride into Pentachlorethane with Respect to Temperature.

Fig. 3.

Table 3.

Substance	N(HCl)	log N	$(1/T)\times10^{-3}$
20°C.			
1,1,2-Trichlorethane	0.03101	1.5085	3.411×10^{-3}
Pentachlorethane	0.02250	1.6478	,,
15°C.			
1,1,2-Trichlorethane	0.03463	1.46055	3.471×10^{-3}
Pentachlorethane	0.02396	1.6205	,,
12°C.			
1,1,2-Trichlorethane	0.03715	1.43004	3.508×10^{-3}
Pentachlorethane	0.02502	1.6017	,,
The Heat of Absorption ΔH/mole in cal.			
	ΔH		
1,1,2-Trichlorethane	3600 cal./mole		
Pentachlorethane	2200 ,,		

Table 5.

Bond	Bond energy	Sub-stance	Total bond energy
C–Cl	3.22*v.e.	$C_2H_4Cl_2$	27.40 v.e.
C–Br	2.89*	$C_2H_4Br_2$	26.74 ,,
C–H	4.34	$C_2H_3Cl_3$	26.28 ,,
C–C	3.60	$C_2H_2Cl_4$	25.16 ,,
		C_2HCl_5	24.04 ,,
		CCl_4	12.88 ,,

Total Bond Energy
$C_2H_4Cl_2 > C_2H_4Br_2 > C_2H_3Cl_3 > C_2H_2Cl_4 > C_2HCl_5 > CCl_4$

Solubility (N 20°C.)
$C_2H_4Cl_2 > C_2H_4Br_2 > C_2H_3Cl_3 > C_2H_2Cl_4 > C_2HCl_5 > CCl_4$

* Average values of the various authors are used (A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56** (1934), 1096).

Table 4.

Substance	N(20°C.)	D.C.(20°)	$\mu\times10^{18}$	Mol. volume	Eötvös K	$T\frac{\alpha}{\beta}$	$E/V^{\frac{1}{3}}$
$ClCH_2{\cdot}CH_2Cl$	0.03993	10.8	1.8	78.90	2.15	4158	17.0
$BrCH_2{\cdot}CH_2Br$	0.03441	6.3	1.4	86.20	2.19	{4455, 4760}	17.2
$Cl_2CH{\cdot}CH_2Cl$	0.03101	—	1.15*	92.31	2.21	—	—
$Cl_2CH{\cdot}CHCl_2$	0.02744	8.2	1.6	105.30	2.26	{3362, 3690}	15.58
C_2HCl_5	0.02250	—	1.0*	120.59	2.32	—	—
CCl_4	0.01550	2.24	0.0	97.10	2.20	—	14.3

	Total bond energy	$(n-1)L/V$	$\frac{5200+30t_b}{V}$	Van Laar's a	$\gamma/V^{\frac{1}{3}}$	Suther-land	Ma-thews
$ClCH_2{\cdot}CH_2Cl$	27.40 v.e.	406	97.45	475	7.5	—	—
$BrCH_2{\cdot}CH_2Br$	26.74 ,,	422	105.23	549	8.7	710	3900
$Cl_2CH{\cdot}CH_2Cl$	26.28 ,,	—	93.05	335	—	—	—
$Cl_2CH{\cdot}CHCl_2$	25.16 ,,	368	90.72	555	7.71	—	—
C_2HCl_5	24.04 ,,	—	82.8	503	—	—	—
CCl_4	12.88 ,,	308	77.06	496	5.78	490	2660

* Van Arkel and Snock (unpublished) (C. P. Smyth, " Dielectric Constant and Molecular Structure ").

Discussion of Results. As we expected, the absorption of hydrogen chloride into 1,1,2-trichlorethane is much greater than into pentachlorethane as obvious from the tables; furthermore, by comparison with the data already published,(1) we find that the order of the solubilities in these various substances are not quite concordant with the order expected either from internal pressures as measured by various different methods or from polarities as indicated by several different ways, e.g. dielectric constant, electric moment, etc., as shown in Table 4, where the various quantities listed have significances as explained in our previous report. Also as already pointed out, we can hardly find any regularity with respect to molal volumes as well as Eötvös's K but they are well in the order of the total bond energies, as illustrated in Table 5.

Thus the solubilities of hydrogen chloride in these various halogen derivatives of the aliphatic hydrocarbon are not well accounted for either in the light of various criteria which are already considered elsewhere but they are well taken into account in the term of bond energies which have been more fully discussed in our previous paper.(1)

Summary.

(1) The absorption of hydrogen chloride into 1,1,2-trichlorethane and pentachlorethane at 20°, 15° and 12°C. has been measured.

(2) The heat of absorption of hydrogen chloride into these organic substances has been calculated.

(3) The order of the solubilities of hydrogen chloride into these liquids including those mentioned in our previous paper, is found to be well fitted in a scheme already described, namely they are in the order of the total bond energies of these substances.

In conclusion, the author wishes to express the best thanks to Prof. S. Mitsukuri for his kind advices and criticisms in the course of this investigation also hearty appreciation to generosity that a part of the expenses of this research has been covered by the grant given to Prof. S. Mitsukuri by the Saito Gratitude Foundation.

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Correction to the previous paper (this volume, p. 5):

Read Ethyl bromide *for* Ethylene bromide *in Table 7 on page 13 and in line 2 on page 14.*
