

Garden has only a half acre experimental field of peppermint, hence, both cultivation and harvest are under rigid control.

(5) This explains satisfactorily the large amount of resin resulting upon rectification but does not account for the unusually high density of the rectified oil.

(6) Gildemeister, "Die aeth. Oele" (3rd ed.), 1, page 560.

THE CHEMISTRY OF HEPTANE AND ITS SOLUTIONS.*¹

No. 6. THE SOLUBILITY OF THE HALOGENS IN HEPTANE.

BY JOSEPH SEMB.

The heptane used was that prepared from some of the by-products obtained in the purification of hydrocarbon from Jeffrey Pine oil placed at the disposal of this laboratory in 1927 by the Ethyl Gas Corporation (1). The material employed (2) was first shaken with concd. sulphuric acid until no more charring occurred (loss 3.0 per cent). Next the oil was shaken with fuming sulphuric acid and allowed to stand over night. After that it was shaken successively with water, also with aqueous solutions of sodium carbonate, sodium hydroxide and potassium permanganate. Finally, it was dried with calcium chloride, refluxed for several hours over metallic sodium and distilled over phosphorus pentoxide. The bulk of the oil distilled within two degrees, *viz.*

550 cc. between 96.8° and 97°.

550 cc. at 97°.

550 cc. between 97° and 97.4°, barometric pressure 743 mm. The "Vorlauf" and residue amounted to 200 cc.

The chlorine (from a cylinder) used was purified by passing it through aqueous copper sulphate, water, concd. sulphuric acid and finally through a calcium chloride tower.

The bromine used was Merck's C.P. article.

Merck's U. S. P. iodine was used without additional purification.

The dissolved halogen was determined directly with standard sodium thio-sulphate (standardized against potassium dichromate) in the case of iodine. In the case of chlorine and that of bromine, the iodine equivalent was set free by the addition of potassium iodide.

Bromine-Heptane Solution.		Iodine-Heptane Solution.	
Temp.	Wt. of 5 Cc. Aliquot.*	Temp.	Wt. of 5 Cc. Aliquot.
-78.0°	3.726 Gm.	-26.5°	3.495 Gm.
-77.0°	3.742 Gm.	0.0°	3.475 Gm.
[-51.0°	3.963 Gm.]	20.0°	3.448 Gm.
-44.5°	4.161 Gm.	34.5°	3.425 Gm.
-34.5°	4.438 Gm.	55.0°	3.395 Gm.
[-32.0°	4.137 Gm.]		
-29.0°	4.724 Gm.		
-28.0°	4.777 Gm.		
-26.5°	5.066 Gm.		

* The accompanying figure shows that the weights determined at -51° and at -32° are off.

The above values are plotted on Fig. 3.

* Scientific Section, A. Ph. A., Madison meeting, 1933.

¹ From the Laboratory of Edward Kremers.

In this work the concentrations are reported in grams of halogen per 100 cc. of solution (not solvent). However, the weights of 5-cc. aliquots of the saturated bromine and iodine solutions were determined at different temperatures. The data are recorded below. These values together with those reported in subsequent tables makes it possible to calculate the solubilities on the gram or mole fraction basis.

Approximately 5 cc. of heptane, placed in a 25-cc. graduated cylinder and kept as remote from light as possible, were saturated with chlorine at the temperature stated, by bubbling the gas through the solvent. When the solution was saturated (15 to 30 minutes, depending on the temperature of experiment) the new volume was recorded. This was then diluted with heptane that was colder than the solution. This tended to cut down the amount of chlorine that might otherwise escape during the subsequent steps of transferring and titrating. It also diminished the losses due to reaction between the chlorine and the heptane.

In experiments Nos. 12, 13, 15, 16, 18, 20, 21, 24 and 25, Table I, all of the diluted solution was dumped into an Erlenmeyer flask and titrated. It is significant to note that in the above series the low temperature experiments gave low results. The other experiments reported in Table I were carried out somewhat differently. Not only was the original volume of the saturated solution recorded but also the volume of the diluted solution. A 5-cc. aliquot of this diluted solution was withdrawn and titrated. From these data the grams of chlorine dissolved in 100 cc. of solution were calculated and recorded in column "C," Table I. The values chosen for plotting on Fig. 1 are found in column "D."

In Table I, it will be observed that numerous experiments gave low results, particularly so for the low-temperature ones. This is probably due to one or both of two possibilities. Firstly, the solution may not have been saturated to start with; or if it had been, too much chlorine was lost in subsequent operations. Naturally, the higher the concentration of chlorine the more acute this danger becomes. In the second place, as chlorine and heptane do react, and as the increased concentration is favorable to secondary reactions, the discrepancy due to thermal secondary reactions, initiated by a photochemical reaction, should be greater at the higher concentrations of the lower temperatures. Several times, without apparent provocation, the reaction between chlorine and heptane became so violent that the experiment was lost. Usually this took place for the higher concentrations, and then when the gas had been bubbled through for a considerable period. This would indicate that the accumulation of HCl or probably heptyl chloride catalyzes this thermal reaction between chlorine and heptane. The data in column "E," Table I seem to verify these assumptions. Take, for instance, in experiments Nos. 5 and 6, the amounts of HCl found were small. Therefore, the low chlorine yield was not due to losses arising from the reaction between the chlorine and heptane, but the solution was probably unsaturated when removed from the saturating chamber.

In experiments Nos. 12 and 13, Table I, it will be noted that the amount of chlorine found is low, but that the amount of HCl found ("E") is very high. This would indicate that the heptane had been saturated with chlorine, and that the subsequent reaction between the chlorine and the heptane, with the formation of HCl and the liberation of heat, decreased the chlorine content.

The HCl was determined as follows: After the chlorine had been titrated as stated above the free HCl was titrated with standard NaOH using a methylene blue-phenolphthalein indicator. To establish whether $\text{Na}_2\text{S}_2\text{O}_3$ ($\text{H}_2\text{S}_2\text{O}_3$) or $\text{Na}_2\text{S}_4\text{O}_6$ ($\text{H}_2\text{S}_4\text{O}_6$) had any effect on this titration the following experiment was conducted. A solution containing I_2 was titrated with $\text{Na}_2\text{S}_2\text{O}_3$. To this was added 1 cc. of HCl solution equivalent to 9.25 cc. of 0.0818N NaOH. Three different titrations gave 9.38, 9.35, 9.05 cc. of 0.0818N NaOH or an average of 9.26 cc. Hence, for this work at least, the presence of the above named compounds does not hinder the titration of HCl with NaOH.

Taylor and Hildebrand (3) reported the solubility of chlorine in grams per 1 Gm. of solution at 0° to be 0.196, 0.205, 0.210 or an average of 0.2036 Gm. These investigators obtained erratic values at 20° and 40°, therefore, they did not report these values. As I have reported my solubilities in grams per 100 cc. of solution, an exact comparison is not possible.

When 10 cc. of bromine were added to 10 cc. of heptane, there was but one liquid phase. It is, therefore, assumed that bromine is miscible with heptane at

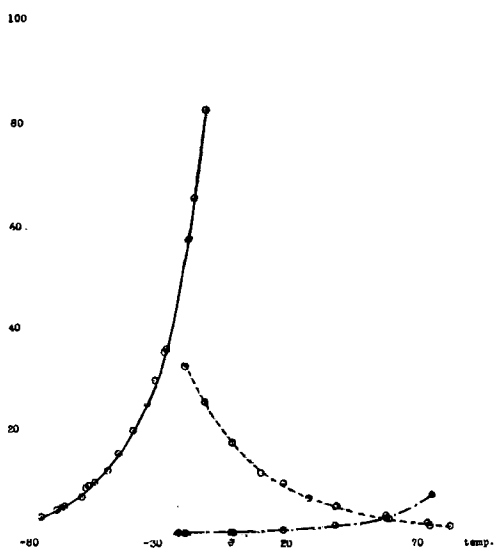


Fig. 1.——— Bromine (unbroken line). ---- Chlorine (broken line). ····· Iodine (dots and dashes).

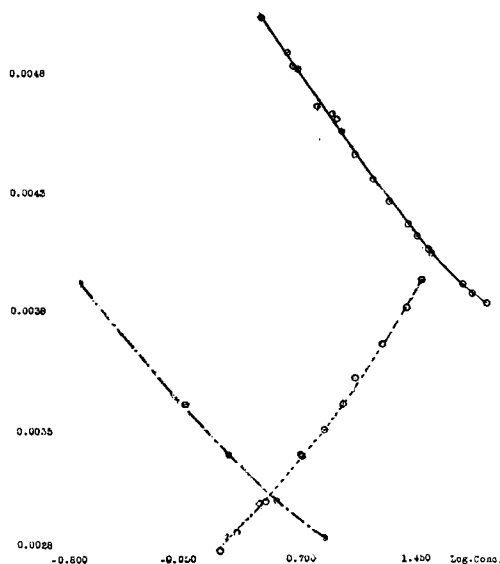


Fig. 2.——— Bromine (unbroken line). ---- Chlorine (broken line). ····· Iodine (dots and dashes).

room temperature. Inasmuch as bromine congeals at low temperatures and melts at -7.3° , the bromine solutions were exposed to low temperatures and the solubility of the halogen in heptane determined. This was done by immersing a solution of bromine in heptane, in a test-tube, into a Dewar flask, cooled to the desired temperature by means of acetone and solid CO_2 . The data obtained are recorded in Table II and plotted on Figs. 1 and 2. 2-Cc. aliquots were used in the determinations. The solubility of iodine was determined in a similar manner except that a Dewar flask was not used. The values obtained for iodine are reported in Table III and plotted on Figs. 1 and 2.

From Fig. 2 it will be noted that for both the bromine and the iodine, plotting $1/T$ against the log of the concentration, gives practically a straight line up to a

certain temperature, whereas in the case of chlorine a distinct curve is obtained. In the case of bromine this temperature is about -40° and for iodine about $+40.0^{\circ}$. This indicates that the heat of solution of bromine and iodine is practically independent of temperature within this temperature range and that, in the case of the chlorine, the heat of solution varies appreciably with the temperature throughout the range studied.

The molecular heats of solution of iodine, and bromine, in the region where the heat of solution is practically independent of temperature, were calculated by means of the formula,

$$\text{Log } C_2 - \text{Log } C_1 = \frac{Q}{4.581} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

C_1 and C_2 are the concentrations, respectively, at temperatures T_1 and T_2 . Q is the heat absorbed, or $-Q$ is equal to the heat of solution. It is assumed that Q remains constant within this temperature range, a condition which is fairly well satisfied in the case of the iodine and bromine.

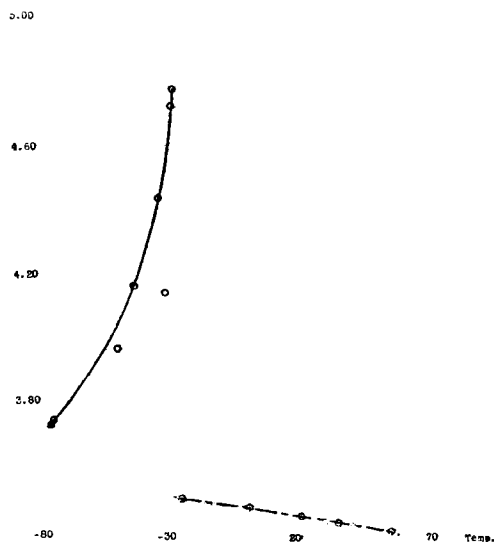


Fig. 3.— — Bromine (unbroken line). - - - Chlorine (broken line). - · - · - Iodine (dots and dashes).

The molecular heat of solution for bromine thus calculated was -4700 calories and for iodine -5940 calories. The molecular heat of solution of chlorine was calculated by the same formula, choosing for T_1 and T_2 20° and 40.5° (Q is not independent of the temperature in this region) and found to be 5200 calories.

The fact that bromine and iodine give a negative heat of solution and chlorine a positive value is accounted for in that heat is required to sublime the iodine and bromine while heat is given off when the chlorine gas is condensed.

Hildebrand and Jenks (4) report the solubilities of iodine in heptane to be 0.6176, 1.702, 2.491 and 4.196 Gm. per 100 Gm. of solution at 0° , 25.0° , 35.0° and 50.0° , respectively. When Figs. 1 and 3 are greatly enlarged, the solubilities of iodine per 100 Gm. of solution were computed by interpolation to be 0.66 Gm. at 0° , 1.71 Gm. at 25° , 2.39 Gm. at 35° and 4.06 Gm. at 50° .

TABLE I.—SOLUBILITY OF CHLORINE IN HEPTANE AT DIFFERENT TEMPERATURES.

No. (A).	Temperature (B).	Gm. Cl Diss. in 100 Cc. Sol. (C).	Average (D).	Gm. HCl Found in 100 Cc. Sol. (E).
1	-23.0	29.50
2	-19.0	32.90	32.9	2.0
3	-12.0	15.50	Omit	..
4	-11.0	25.90	25.9	0.13
5	0.0	11.60	..	0.12
6	0.0	13.61	..	0.44

7	0.0	16.95	..	0.38
8	0.0	19.60	17.9	1.05
9	0.0	17.48	..	0.61
10	0.0	17.39	..	0.99
11	1.0	10.41
12	11.0	4.80	..	2.87
13	11.0	9.74	..	1.66
14	11.0	11.97	12.00	0.77
15	20.0	3.66
16	20.0	3.97
17	20.0	10.11	10.1	0.23
18	30.0	6.14
19	30.0	7.70	7.7	0.18
20	40.0	5.00
21	40.0	5.88	5.4	..
22	40.0	5.26
23	40.5	5.60	5.6	0.15
24	60.0	3.30	..	0.37
25	60.0	2.57	3.17	0.14
26	60.0	3.65	..	0.14
27	61.0	2.95	2.95	..
28	76.0	2.25	2.25	0.03
29	77.0	1.79	1.79	0.15
30	85.0	1.65	1.65	..

SUPPLEMENT TO TABLE I.—CALCULATION BASED ON TABLE NO. I.

Temperature (A).	1/T (Absolute) (B).	Gm. Cl per 100 Cc. of Sol. (C).	Log Conc. (C).
-19.0	0.003937	32.9	1.5172
-11.0	0.003817	25.9	1.4133
0.0	0.003663	17.9	1.2529
11.0	0.003520	12.0	1.0792
20.0	0.003413	10.1	1.0043
30.0	0.003300	7.7	0.8865
40.0	0.003195	5.4	0.7324
40.5	0.003188	5.6	0.7482
60.0	0.003003	3.17	0.5011
61.0	0.002993	2.95	0.4698
76.0	0.002865	2.25	0.3522
77.0	0.002857	1.79	0.2529
85.0	0.002793	1.65	0.2175

TABLE II.—SOLUBILITY OF BROMINE IN HEPTANE AT DIFFERENT TEMPERATURES.

Temperature.	1/T (Absolute).	Gm. Br in 100 Cc. of Sol.	Log of Conc.
-27.0	0.004067	36.12	1.5578
-39.0	0.004272	20.17	1.3046
-44.5	0.004376	16.12	1.2073
-33.5	0.004176	25.89	1.4130
-26.0	0.004049	36.85	1.5663
-30.5	0.004124	30.08	1.4783
-57.5	0.004641	8.88	0.9484
-56.5	0.004619	9.41	0.9736
-54.0	0.004566	10.06	1.0025
-49.0	0.004464	12.22	1.0871
-15.5	0.003874	66.53	1.8230
-12.0	0.003832	83.49	1.9216

-67.0	0.004854	4.84	0.6848
-69.0	0.004902	4.65	0.6675
-66.0	0.004831	5.43	0.7348
-59.0	0.004673	7.05	0.8482
-75.0	0.005050	3.22	0.5079
-17.5	0.003914	57.99	1.7634

TABLE III.—SOLUBILITY OF IODINE IN HEPTANE AT DIFFERENT TEMPERATURES

Temperature.	1/T (Absolute).	Gm. I in 100 Cc. of Solution.	Log of Conc.
-21.0	0.003972	0.16	-0.7959
-18.0	0.003922	0.22	-0.6576
0.0	0.003660	0.46	-0.3372
1.0	0.003650	0.48	-0.3088
20.0	0.003410	1.01	0.0043
40.0	0.003195	1.93	0.2856
60.0	0.003003	3.85	0.5855
78.0	0.002849	7.79	0.8915
20.0	0.003413	1.00	0.0000

While working with these solutions, it seemed desirable to ascertain something of their reactivity with other elements. In making comparisons, it should be borne in mind that the iodine solution, because of the sparing solubility of this halogen, was but one-fifth as strong, as to molecular equivalent, as were the two other solutions. Moreover, it will also become apparent from some of the reactions to be reported, that the solutions of chlorine and bromine contained some of their hydrides as well, resulting from the action of these halogens on heptane in spite of the precautions taken.

Of the elements of the first group, lithium, sodium and copper (foil) were used. The chlorine and bromine solutions yielded bubbles with both lithium and sodium, indicating the presence of hydrogen chloride and of hydrogen bromide in the respective solutions. After standing over night, the halogen had disappeared completely or nearly so. When a freshly prepared solution of chlorine in heptane, saturated at considerably below 0°, was added to finely powdered copper the two elements reacted with the phenomenon of flame. Upon repeating the experiment with the solution which had been kept in an ice bath for several hours, no such phenomenon occurred. The disappearance of the color of the chlorine showed that it had reacted with the solvent.

The phenomenon of flame is produced when chlorine gas is brought in contact with phosphorus, copper, boron and silicon in powder form. As has been shown, chlorine in heptane solution produces like phenomena with red phosphorus and powdered copper.

The effect of chlorine hydrate upon red phosphorus and powdered copper was also tried, but with negative effect so far as the phenomenon of flame was concerned.

Of the elements of the second group, calcium (lumps), magnesium (turnings), cadmium (lumps) and lead (powder) were tried. Calcium yielded bubbles with Cl and Br, indicating the presence of HCl and HBr, respectively. Mg and Cd apparently were affected but little by Cl. The other two elements seemed to have no effect. Pb decolorized the solutions of all three halogens.

Of the elements of Group three, Al (ribbon) only was tried. With Cl bubbles

were produced. Br and I produced a brown, tar-like deposit. The I also produced fumes of HI.

Of the elements of the fifth group, P, Sb and Bi were used. With Cl the P burst into flame immediately as stated in connection with copper. The bromine solution was decolorized the next morning, the I sol. was partly decolorized. Sb decolorized the Cl solution immediately, the Br solution was almost colorless the next morning, the I solution partly decolorized. Bi did not seem to react.

In several instances colorless crystals were obtained (NaCl, NaBr, SbCl₃), in other instances the bright surface of the metallic element was dulled (in the bromine experiment the Cu became black), in still other instances a tar-like product was deposited (AlBr₃).

It may be of interest to note that of the metallic elements sodium appeared more reactive than lithium, and cadmium more than zinc. On the other hand in Group five, P was much more reactive than Sb and Bi. Also, that, with the possible exception of Cu, the order of reactivity of the halogens proved to be Cl, Br, I, as was to be expected.

* For earlier reports see:

No. 1, JOUR. A. PH. A., 9, 857 (1920). No. 2, *Ibid.*, 9, 860 (1920). No. 3, *Ibid.*, 11, 1042, 1153 (1922). No. 4, *Ibid.*, 10, 26 (1921). No. 5, *Ibid.*, 11, 995 (1922).

(1) The principal object was the isolation and identification of the aldehydes. See P. A. Foote, JOUR. A. PH. A., 18, 350 (1929). After shaking out the aldehydes with aqueous sodium acid sulphite from the fractions with a higher boiling point than that of heptane, a complex mixture was obtained. This was fractionated by C. Sondern (*Thesis*, U-W. 1928). Of the fractions thus obtained those marked E. VII and VIII were employed.

(2) Fractions E. VII (b. p. 94.0–94.5°; $d = 0.6800$ at 25°) and E. VIII (b. p. 94.5–95.0°; $d = 0.6815$ at 25.5°) of Sondern, obtained by refractionating the portion of the oil distilling immediately above the boiling point of heptane, were used.

(3) Taylor and Hildebrand, *J. A. C. S.*, 45, 682 (1923).

(4) Hildebrand and Jenks, *Ibid.*, 42, 2180 (1920).

THERAPEUTIC SUBSTANCES DERIVED FROM UNSYMMETRICAL DIPHENYL COMPOUNDS III. SOME ARYL ESTERS OF THE HYDROXY DIPHENYLS.*

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Numerous references have appeared in the literature describing the use of aryl esters of phenol and cresols as urinary and intestinal antiseptics. In extending our survey of diphenyl compounds it was decided to prepare a number of aryl esters of 2-, 3- and 4-hydroxy-diphenyls and some of their substitution products.

The three hydroxy diphenyls, (*o*-, *m*- and *p*-phenyl-phenol) and their alkyl and halogen substitution products are active, non-toxic germicides and it was hoped that by oral administration in the form of an ester they might reach the urine unmetabolized, and there exert the required germicidal action. Fifteen esters were prepared and tested. Results of animal experiments definitely show that they possessed no value as urinary antiseptics.

* Scientific Section, A. PH. A., Washington meeting, 1934.

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