TABLE III.—FREE ENERGY OF THE REACTIONS $H_2 + Hg_2SO_4 = H_2SO_4(N = X) + 2Hg$, $2H^+ + SO_4^{--} = H_2SO_4(N = X)$.

N.	Log *N.*	E.	ΔF (Eq. 1).	ΔF (Eq. 4).
0.00009009	—4.0453	0.8160	—37657	—9382
0.0008999	—3.0458	0.7546	—34822	—6547
0.002	—2.6990	0.7343	—33888	—5613
0.005	—2.3010	0.7114	—32830	—4555
0.01	—2.0000	0.6929	—31977	—3702
0.015	—1.8239	0.6812	—31437	—3162
0.02	—1.6990	0.6720	—31010	—2735
0.03	—1.5229	0.6571	—30323	—2048
0.04	—1.3979	0.6442	—29730	—1455
0.05	—1.3010	0.6315	—29140	— 865
0.065	—1.1871	0.6145	—28360	— 85
0.08	—1.0969	0.5975	—27573	702
0.10	—1.0000	0.5770	—26630	1645
0.13	—0.8861	0.5495	—25360	2915
0.20	—0.6990	0.4985	—23003	5272

Lewis and Lacey[1] from a consideration of the data in very dilute solutions found for the cell

$$H_2,\ H^+(M)\ ||\ SO_4^{--}\ (M),\ Hg_2SO_4,\ Hg \qquad (2)$$

corresponding to the reaction

$$H_2 + Hg_2SO_4 = 2H^+(M) + SO_4^{--}(M) + 2Hg; \qquad (3)$$

$E^\circ = 0.6127$, $\Delta F^\circ = —28275$ cal.

By subtracting Equation 1 from Equation 3 we obtain

$$2H^+ + SO_4^{--} = H_2SO_4(N = x);\ \Delta F = y \text{ (Table III, Col. 5).} \qquad (4)$$

These values of the free energy of formation from hypothetical molal hydrogen ion and sulfate ion are given in the last column of Table III.

Since the free energy of formation[2] of H^+ is 0, the valves in the last column also give the free energy of the reaction

$$H_2 + SO_4^{--} + 2 \oplus = H_2SO_4(N = x). \qquad (5)$$

The free energy of formation of sulfate ion from the elements has not as yet been determined.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA.]

TOLANE CHLORIDES FROM CALCIUM CARBIDE, CHLORINE AND BENZENE.

BY CLINTON DAVIDSON.

Received April 11, 1917.

Preparation of α-Tolane Dichloride.[3]—If well-ground calcium carbide

---

[1] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

[2] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

[3] References on tolane dichlorides, *Ber.*, **4**, 289, 379 (1871); **12**, 1973 (1879); **15**, 900 (1882); **17**, 835 (1884); **29**, 2906 (1896); **40**, 2994 (1907).

is added to about four times its weight of benzene saturated with chlorine and cooled in a vessel of water, a reaction will soon set in. Heat is first developed and finally hydrogen chloride is given off. Since the reaction does not start for ten or fifteen minutes, it does not matter whether the chlorine is introduced before or after the calcium carbide. Enough heat is developed to raise the temperature of the benzene to its boiling point if the water used to cool it off is removed.

After the reaction has gone for some time, it will subside of its own accord even though an excess of chlorine still remains. This appears to be due to the formation of a layer of calcium chloride over the calcium carbide, thereby excluding the chlorine. The benzene solution can then be decanted from off the calcium carbide and placed in an ice chest overnight. The next morning a large crop of crystals of a chloro-hydrocarbon will be found on the walls of the vessel. They are a mixture of α- and β-tolane dichloride.

One sample thus obtained melted at 139–140°. After that same sample had been allowed to stand for three months (during the University summer vacation) the melting point had changed to 143°. α-Tolane dichloride melts at 143° and β-tolane dichloride melts at 63°. A mixture of the two isomerides had been produced and had slowly been converted into the more stable α-modification. It was afterward found that the same reaction could be completed in a week by allowing a saturated benzene solution of the two to stand on a steam bath at 100° during that time.

In preparing these compounds certain precautions must be observed. The benzene used must be free from its higher homologs; otherwise a hopeless mixture will be obtained. For the production of pure α-tolane dichloride, the temperature of the reaction should be kept as low as possible to avoid addition of chlorine. But the most important precaution of all is to have the calcium carbide used, free from iron compounds. If much iron is present the benzene solution will become red in color instead of remaining yellow with chlorine and the reaction will not come to an end with an excess of chlorine still present. Instead the iron causes direct substitution of chlorine in the benzene ring so that the product obtained is a mixture of chlorine derivatives of tolane and benzene. If no iron is present, the benzene will remain yellow with chlorine for days without a reaction taking place between them.

Calc. for α-tolane dichloride: Cl: 28.5%. Found: 29.9, 30.0%.

The melting point was correct and not near that of any other compound that might be produced. A molecular-weight determination, obtained from the lowering produced upon the freezing point of benzene, was $230 \pm 4\%$. Theory requires 249. Alcoholic potash removed all of the chlorine from it, thus indicating the absence of any chlorine in the benzene rings. Sodium in alcohol reduced it to dibenzyl. The vapors from it cause the eyes to burn just as does benzal chloride.

Properties of α-Tolane Dichloride.—It is a colorless crystallin solid with a specific gravity of 1.78. If it is slowly crystallized from benzene, crystals of the monoclinic system are obtained. Under atmospheric pressure it boils at 275–278° with slow blackening due to slight decomposition. However, it may be distilled over as white as paraffin if it is cooled quickly after condensation, its boiling point still remaining unchanged.

Preparation of Tolane Tetrachloride.[1]—Referring back to the original reaction; if the decanted benzene, containing chlorine and the two tolane dichlorides, is not cooled at once but is concentrated by boiling on a steam bath for several days until the boiling point reaches 100° and is then cooled, the compound that crystallizes out will have absorbed chlorine and its melting point will have decreased or increased, depending upon the amount of chlorine absorbed. Tolane tetrachloride is the compound produced by this absorption. Under these circumstances its production in the pure state does not seem to be possible. Better results were obtained when the pure α-tolane dichloride was chlorinated at its melting point. A product was obtained that melted at 161°. Tolane tetrachloride melts at 163°.

In the original preparation, if the benzene is replaced with toluene, the reaction goes on with even more ease than before, producing an oil that does not solidify at 0° but that boils at 238–242°. It is probably a mixture of the isomerides having the formula $CH_3.C_6H_4.CCl : CCl.C_6H_4.CH_3$.

The discovery of this reaction resulted from the examination of the action of chlorine upon hot calcium carbide. With great difficulty a small amount of gas was obtained from the latter compound which seemed to be dichloroacetylene. It was spontaneously combustible and decomposable after decomposition had once begun; a thing to be expected considering the properties of dibromo-acetylene.[2] Hoping to obtain a derivative of it, the author decided to try the reaction in the presence of some compound with which it might react. Benzene was chosen for this purpose. The resulting tolane chlorides may therefore be produced as indicated by the following equations:

$$CaC_2 + 2Cl_2 \longrightarrow CaCl_2 + Cl.C \vdots C.Cl$$

$$Cl.C \vdots C.Cl + 2C_6H_6 \longrightarrow C_6H_5.C \vdots C.C_6H_5 + 2HCl$$

$$C_6H_5.C \vdots C.C_6H_5 + Cl_2 \longrightarrow C_6H_5.CCl : CCl.C_6H_5, \text{ and}$$

$$C_6H_5.CCl : CCl.C_6H_5 + Cl_2 \longrightarrow C_6H_5.CCl_2.CCl_2.C_6H_5$$

---

[1] Cf., *Ber.*, **12,** 1971 (1879); **15,** 901 (1882); **17,** 833 (1884); **40,** 2994 (1907); *Chem. Zentr.*, **1907,** 2, 1069.

[2] *Chem. Zentr.*, **1903,** 2, 102, 551; *Compt. rend.*, **136,** 1333 (1903); **137,** 55 (1903).

Thus, although the existence of dichloro-acetylene has not been proven, it existence seems possible.

BERKELEY, CALIF.

THE LIMITS OF ACCURACY OF HOLLEMAN'S METHOD OF DETERMINING THE COMPOSITION OF A MIXTURE OF TWO OR THREE ISOMERS.

BY JOSEPH B. NICHOLS.

Received September 18, 1917.

Holleman[1] gives a method for the quantitative determination of three isomers, depending upon the freezing point. This method is a special application of Bakhuis Roozebooms general method of determing the freezing points of mixed crystals, etc.[2] The purpose of the present experiments is to discover the limits of accuracy of this method, together with the details of the manipulation. While Holleman shows the applications of his method to many compounds, he says nothing of its limit of accuracy. A short résumé of the method will first be given; for a more extended description the reader is referred to Holleman's book, and to the references given therein. It is plain that if the method furnishes accurate enough results, it will save much tedious work formerly required in investigations of isomers of this character, in separating the products to determine the result.

If two isomers are melted together and allowed to cool, unless they form a eutectic mixture, one of the isomers will start to solidify at a definite temperature, depending on the proportion of the substances. This isomer will freeze out until the eutectic point is reached, when the whole mass will solidify together. In this way, after determining a curve for the freezing points of different mixtures of the two substances, the constitution of a binary mixture can be determined from the position on the curve of the freezing point. This curve has two branches, dropping from the freezing point of one pure isomer to the eutectic, and then rising to the freezing point of the second substance. It is always possible, however, to find on what branch of the curve a given point lies, by adding a weighed portion of one of the isomers to the mixture, and observing the position of the freezing point for the resulting mixture.

In most compounds produced by the addition of substituents to the benzene nucleus, two of the isomers occur chiefly, while the third is found in small porportions—from a mere trace to 8 or 10%. In some cases only one isomer is obtained in quantity; this, however, necessitates only changes

---

[1] "Die direkte Einfuhrung von Substituenten in den Benzolkern" (Veit & Co., 1910).

[2] *Z. physik. Chem.*, 30, 386 (1899). Reference may be made to Roozeboom's "Die Heterogene gleichgewichte von Standpunkte der Phasenlehre" Vol. II, 1904 for further information on the general theory.