(not weighed). In this experiment it is seen that the benzoic anhydride has the same effect as the other acid anhydrides but gives a considerable yield of benzophenone as well.

Summary.

1. Friedel and Crafts' method of preparing orthobenzoyl-benzoic acid, as used by Heller, was found to give a 97% yield and nearly 1.2 formula weights of hydrogen chloride for each formula weight of aluminium chloride used (Al_2Cl_6).

2. When less aluminium chloride is used the yield of orthobenzoyl-benzoic acid is very much reduced and diphenylphthalide is obtained, and this is found to be due to the action of the phthalic anhydride on the intermediate compound.

3. Succinic anhydride, acetic anhydride, benzoic anhydride and phthalyl chloride also give diphenylphthalide with this intermediate compound.

4. In the preparation of benzophenone from benzoyl chloride, benzene and aluminium chloride, reducing the amount of aluminium chloride reduces the yield almost in the same proportion and the addition of phthalyl chloride gives diphenylphthalide, without materially reducing the yield of benzophenone.

5. Benzophenone may be obtained from benzoic anhydride, benzene and aluminium chloride, but the yield is not good.

6. In the case of the addition of benzoic anhydride to the preparation for orthobenzoyl-benzoic acid, benzophenone is produced in addition to diphenylphthalide.

These experiments were carried out under the direction of F. B. Allan.

UNIVERSITY OF TORONTO.

SOME PHYSICAL PROPERTIES OF ETHANE, ETHYLENE AND ACETYLENE.

BY O. MAASS AND D. MCINTOSH.

Received February 21, 1914.

In the course of an investigation on the physical properties of bodies at low temperatures, we have found it necessary to measure some of the constants of ethane, ethylene and acetylene, which are not given in the chemical literature. A comparison of these three bodies, each containing two carbon atoms, but with different linkages, is not without interest, while a publication of the results may save labor on the part of some chemists. We give them here, therefore, together with a description of the methods employed in their determination.

Ethane.—The ethane was made from methyl iodide, by the action of the zinc-copper couple. It was washed with alkali, dried by phosphorus pentoxide, passed through three spirals cooled to —78°, twice distilled, the middle portions being retained, and was finally introduced into the density and vapor pressure bulbs. In this method of preparation, the ethane must be repeatedly cooled almost to the point at which it condenses, in order to remove the last traces of methyl iodide.

The vapor pressure and density of the liquid were determined in the apparatus shown in Fig. 1. *B* is a constant temperature bath consisting of a large Dewar flask containing anhydrous ether. *H* is the bulb of a hydrogen thermometer and *D* is a calibrated density bulb with a graduated stem. The bath is cooled with liquid air which is dropped in small portions into *A* and is stirred by a stream of dry air from the tube *C*. S is the apparatus for molecular surface energy determinations; it was used only with acetylene. The bath could be maintained constant within 0.1°.

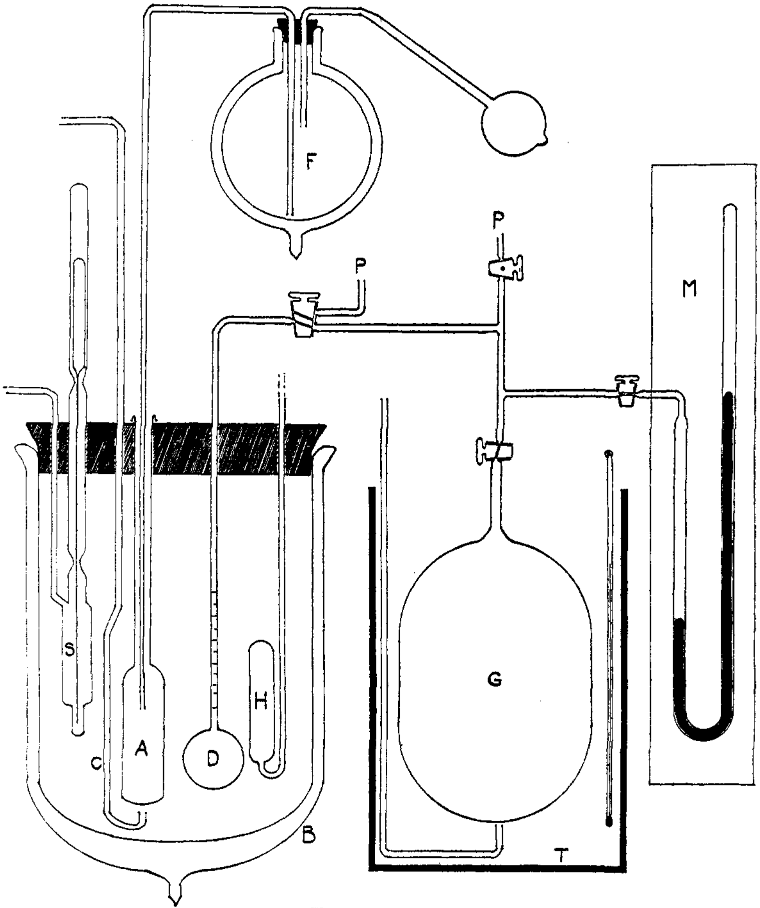

FIG. 1.

The vapor pressures were determined by the manometer *M* connected with the bulb *D*, which was about $^1/_3$ filled with liquid. During the density measurements the bulb was filled to a convenient point on the stem, the variation in volume noted at various temperatures, and the weight found by measuring the gas at a known pressure and temperature in the flask *G*. The volume of *G* was found by weighing it full of water, and that of the various connecting tubes by exhausting the air in them by a Toepler pump and measuring the volume. The apparatus is not drawn to scale.

ETHANE

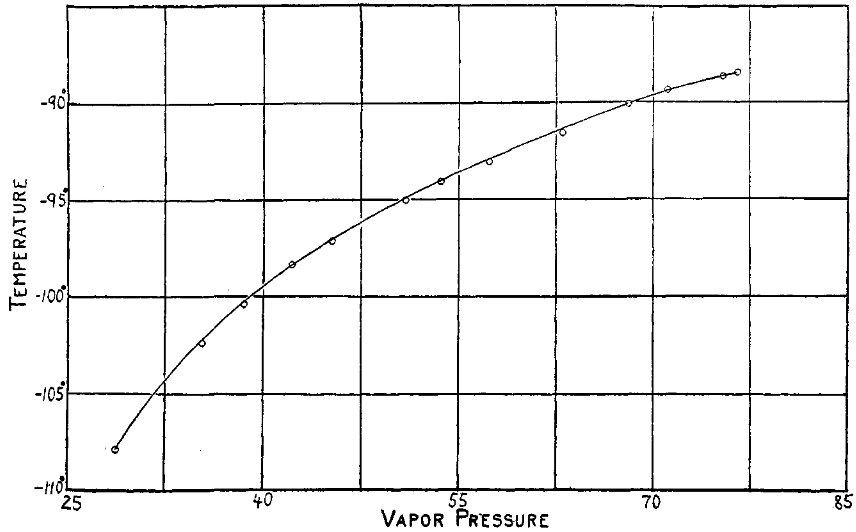

FIG. 2.

The result of the vapor pressure experiments are given in Table I and the density determinations in Table II. These are shown as curves in Figs. 2 and 3. The boiling point at normal pressure is —88.5°, the heat of vaporization calculated by the Clausius equation is 14.6×10^{10} ergs for a gram molecule, and the density at the boiling point is 0.5490.

ETHANE

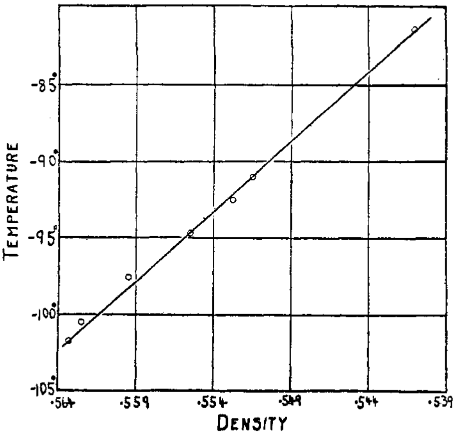

FIG. 3.

TABLE I.

Temperature.	Pressure (mm.).	Temperature.	Pressure (mm.).
—107.9	28.8	93.0	57.5
102.4	35.4	91.5	63.0
...	..	89.9	68.1
100.4	38.5	89.3	71.3
98.2	42.2	88.6	75.4
97.1	45.4	88.4	76.5
95.0	51.0	..	..
94.0	54.6	..	..

TABLE II.

Temperature.	Density.
—101.8°	0.5633
100.6	0.5625
97.6	0.5595
94.8	0.5555
92.6	0.5528
91.1	0.5516
81.7	0.5410

TABLE III.

Temperature.	Density.
—114.2	0.5752
107.7	0.5696
105.9	0.5674
105.0	0.5669
103.3	0.5657
99.4	0.5631

Ethylene.—The vapor pressure of ethylene has been measured by Ramsay and Travers, and the boiling point is given as —102.5°. We have determined, therefore, only the density of the liquid, with the results given in Table III and Fig. 4. The ethylene was made from alcohol by the action of alumina at 450° and was washed, dried and repeatedly distilled as with ethane. Its density, at its boiling point, is 0.5650.

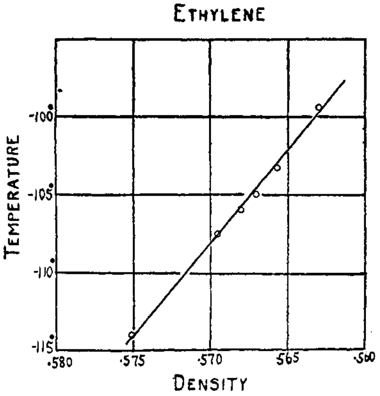

FIG. 4.

Acetylene.—The density and molecular surface energy of this substance were measured at various temperatures. The results of the former agree with the previous determinations of one of us, and need not be given here. The values of the surface energy are shown in Fig. 5 and given in Table IV, where *T* is the

TABLE IV.
Radius of capillary 0.01918 cm.

T.	D.	*h*.	γ.	$\gamma\,(MV)^{2/3}$.
—77.4°	0.6082	3.160	17.993	220.1
75.7	0.6036	3.135	17.718	217.8
70.5	0.5912	2.960	16.370	204.1
69.0	0.5877	2.915	15.992	200.1
67.0	0.5828	2.870	15.605	196.4
64.0	0.5778	2.780	15.005	189.9
62.4	0.5718	2.705	14.444	184.1

temperature, D the density, h the rise in the capillary tube in centimeters, γ the surface tension in dynes, and $\gamma(Mv)^{2/3}$ the molecular surface energy in ergs.

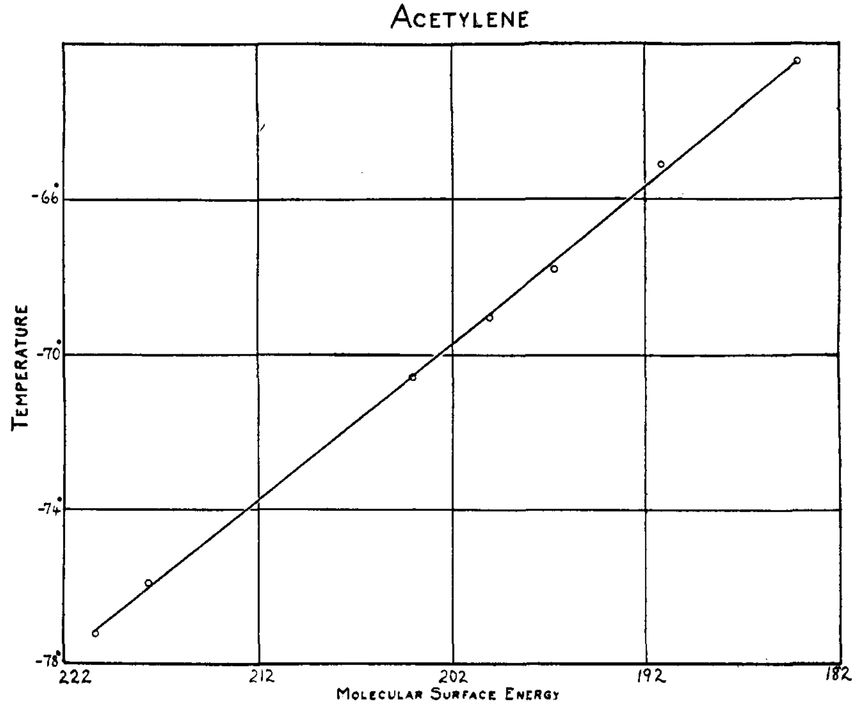

FIG. 5.

The variation of the molecular surface energy with temperature is 2.40 per degree, a result much higher than that ordinarily found for liquids. Some substances, such as diphenylamine and quinoline, exhibit the same anomaly.

The Atomic Volume of Carbon.—The density of ethane, ethylene and acetylene at their boiling points are 0.5490, 0.565 and 0.618, and their molecular volumes are therefore 54.7, 49.6 and 42.1.

If we take 5.5 as the atomic volume of hydrogen, the atomic volumes of carbon for different linkages are:[1]

Single	10.9
Double	13.8
Triple	15.5

In the case of carbon monoxide, its molecular volume is 35.1. When two atoms of chlorine are added, the compound $COCl_2$ has a density of 1.415, at its boiling point, and consequently a molecular volume of 70. Deducting the atomic volumes of C and O, the atomic volume of carbon

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[1] See *Bas. Phil. Mag.*, 27, 355 (1914).

is seen to be 12.2, in good agreement with Kopp's number. The atomic volume of divalent carbon in the carbon monoxide is 23. It is interesting to note that, if acetylene be assumed to have a divalent and a tetravalent carbon atom, *i. e.*, the acetylidene structure, its atomic volume agrees exactly with that found experimentally.

We have endeavored to produce addition compounds of acetylene and hydrobromic at low temperatures. Acetylene is quite soluble in this acid, but solutions containing even 50% of acetylene show no tendency to precipitate compounds at temperatures as low as —115°.

With liquids having high vapor pressures at their freezing points, such as hydrobromic and hydriodic acid, but particularly with acetylene, the phenomenon of freezing and boiling occurring simultaneously is shown in a striking way. Liquid acetylene in a sealed tube can be supercooled about 5°. As crystallization takes place the remaining liquid boils furiously.

McGILL UNIVERSITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE PREPARATION AND PROPERTIES OF THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS.

BY LEROY MCMASTER.

Received January 31, 1914.

As stated in two previous papers,[1] most of the ammonium salts of organic acids described in the literature are the acid salts instead of the neutral salts Many of the "neutral" salts purchased have also been found to be "acid." This is due to the fact that they have been prepared by neutralizing the aqueous solution of the organic acid with ammonia water or ammonium carbonate and the solution allowed to evaporate to crystallization. The salts thus formed are generally hydrolyzed and the acid salt results. Many of these salts also contain water of crystallization. Neutral ammonium salts free from water of crystallization can be obtained by passing dry ammonia gas into an absolute alcohol or ether solution of the organic acids. Most of the organic ammonium salts are insoluble in alcohol or ether and are thus precipitated. Keiser and McMaster prepared, by this method, the neutral ammonium salts of fumaric, maleic, mesaconic and citraconic acids. I prepared also, by this method, the neutral ammonium salts of propionic, isobutyric, benzoic, cinnamic, malonic, succinic, malic, tartaric, *o*-phthalic and *m*-phthalic acids and studied some of their properties. Many of the properties of the salts made by this method were found to be different

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[1] Keiser and McMaster, *Am. Chem. J.*, 49, 84–87 (1913); *Chem. News*, 108, 136–137 (1913); McMaster, *Am. Chem. J.*, 49, 294–301 (1913); *Chem. News*, 108, 182–183, 193–194 (1913).