**5. Computations.**—Temperatures are calculated from the pressure by use of the formula

$$t = 444.60° + 0.0910\ (p - 760) - 0.000049\ (p - 760)^2.$$

If necessary, account should be taken of any difference in pressure between the levels at which the thermometer bulb and the open end of the barometer, respectively, are located. Pressures are to be expressed in the equivalent millimeters of mercury at 0° and under standard gravity ($g = 980.665$).

WASHINGTON, D. C

## NOTE.

**Jellies by Slow Neutralization.**—In a research with R. E. Rindfusz[1] we found that jellies of excellent texture and clearness could be obtained by peptizing ferric arsenate with ferric chloride and dialyzing the resulting colloid. Although at first some ferric chloride was found in the dialysates later only hydrochloric acid passed through the membrane. It was evident that gel formation depended on the slow removal of the acid derived from the hydrolysis of ferric chloride. In fact, when the ferric arsenate precipitate was peptized by barely enough ferric chloride rather than by a decided excess the gel formed more quickly and was not as clear nor of so good a texture. The small amount of hydrochloric acid developed was dialyzed out too rapidly to insure the best gel structure. Without question the time element is of prime importance.

We believed that dialysis disturbed the equilibrium indicated below.

$$Fe_2(HAsO_4)_3 + 6HCl \rightleftarrows 2FeCl_3 + 3H_3AsO_4.$$

The ferric hydroxide resulting from hydrolysis of the ferric chloride is adsorbed in the gel structure by the ferric arsenate. Addition of any base would, of course, neutralize the hydrochloric acid and thus remove the hydrogen ion as effectually as is done by dialysis. But if this is attempted, a lumpy precipitate results. It occurred to us that if the hydrochloric acid could be neutralized slowly enough a gel of good texture must result. To test this we filled a bottle to the top with colloidal ferric arsenate (peptized by ferric chloride) and tied a membrane of goldbeater's skin over the mouth of the bottle, taking care that the membrane was in contact with the liquid.

On top of the membrane we attached a glass tube by a wide rubber band. In this upper vessel we poured about 2 cc. of $N$ ammonium hydroxide. After 6 or 8 days a beautiful, clear gel resulted, red by transmitted light and smoky gray by reflected light. The ammonium hydroxide slowly dialyzed into the colloid neutralizing the hydrochloric acid at a rate permitting the formation and hydration of the ferric arsenate into

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[1] THIS JOURNAL, 38, 1970 (1916).

a good gel structure. The reactions of this base with ferric chloride and arsenic acid do not interfere. It may be objected that 2 cc. of water on the upper side of the membrane would allow hydrochloric acid to dialyze out in the usual manner even in the absence of a base. Evidently this is not a factor as in our experiment the volume of the colloid below the membrane was 10 cc.

A similar experiment was performed with a colloid volume of 15 cc. below and 2 cc. of water above the membrane, the upper vessel containing some solid calcium hydroxide as the base. A good gel formed in a week.

Finally we tried an experiment with 50 cc. of the same colloid below and 2 cc. of a saturated solution of sodium acetate above the membrane. Some solid sodium acetate was added to replace what dialyzed down through the goldbeater's skin. A good gel resulted in one week. Here the sodium acetate slowly repressed the ionization of the hydrochloric acid and, for gel-forming purposes, did the same work as the ammonium hydroxide or the calcium hydroxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

# THE ADDITION OF NITROMETHANE TO UNSATURATED ESTERS.

BY E. P. KOHLER AND H. ENGELBRECHT.[1]

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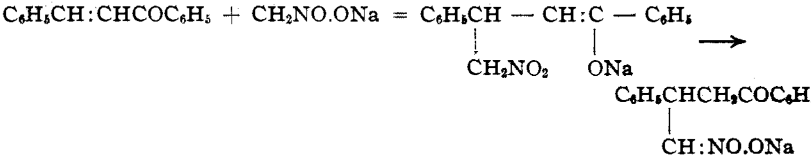
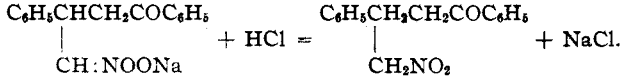
In an earlier paper[2] it was shown that sodium nitro-paraffins combine with $\alpha,\beta$-unsaturated ketones and form metallic derivatives from which acids liberate $\gamma$-nitro ketones:



$$C_6H_5CH{:}CHCOC_6H_5 + CH_2NO.ONa = \underset{\displaystyle CH_2NO_2}{C_6H_5CH} - \underset{\displaystyle ONa}{CH{:}C} - C_6H_5 \longrightarrow \underset{\displaystyle CH{:}NO.ONa}{C_6H_5CHCH_2COC_6H_5} \quad (I).$$



$$\underset{\displaystyle CH{:}NOONa}{C_6H_5CHCH_2COC_6H_5} + HCl = \underset{\displaystyle CH_2NO_2}{C_6H_5CH_2CH_2COC_6H_5} + NaCl. \quad (II).$$

The reaction takes place so readily and smoothly that we anticipated little difficulty in extending it to $\alpha,\beta$-unsaturated esters. We soon found,

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[1] This work was started with the intention of making cyclopropane derivatives containing nitro and carboxyl groups attached to the ring. It was interrupted when Mr. Engelbrecht joined the army and it is published in the present incomplete form because he died in the service.—E. P. K.

[2] THIS JOURNAL, 38, 889 (1916).