The condensation of methylurea and acetylacetone was also conducted in the presence of only sufficient sulfuric acid to form the calculated amount of sulfate, and at the same time an excess of the urea (2 mol) used. It was hoped that, by this means, a compound of the type described by Evans as a diurimido derivative might be prepared. In all cases the crystalline product obtained was no greater in weight than that where molecule to molecule was used. By analysis, the salt, crystallized from alcohol, accorded with the previous results:

H_2SO_4 calculated for $C_7H_{10}ON_2.H_2SO_4$: 41.53; found: 41.98.

We may conclude, therefore, that the pyrimidine ring is formed at once in this acid reaction-mixture. The free substances obtained by neutralizing the sulfate salt, obtained either by the use of concentrated acid or by this latter method, melted at the same point, 63°, and proved identical. 3,4,6-Trimethyl-2-keto-2,3-dihydropyrimidine is readily soluble in water, alcohol, chloroform, acetone or acetic ester; fairly soluble in ether, benzene, carbon disulfide; and insoluble in ligroin. It crystallizes well from benzene and melts at 63°.

0.2055 gram substance gave 0.4593 gram CO_2 and 0.1387 gram H_2O.
0.1634 gram substance gave 30.9 cc. N_2 (25°, 739.3 mm. over H_2O).

Calculated for $C_7H_{10}ON_2$: C, 60.82; H, 7.30; N, 20.31.
Found: C, 60.95; H, 7.55; N, 20.53.

This product of condensation, as before stated, is identical with the trimethylketopyrimidine obtained by methylation of acetylacetone-urea. It is, however, in a much purer form, requiring but one or two crystallizations for final purification.

The preparation of this trimethylketopyrimidine, by condensation in the presence of hydrochloric acid, was found equally as practical as with sulfuric acid, but with a somewhat longer period of time necessary. The hydrochloride salt crystallizes well from alcohol in colorless prisms.

Calculated for $C_7H_{10}ON_2.HCl$: HCl, 20.88; found: 20.78.

Zeisel's method, for the determination of methoxyl groups, gave negative results with this trimethylketopyrimidine, but at high temperatures, 200–300°, Herzig and Meyer's method succeeded in driving off methyl iodide sufficient to indicate that, at least, one methyl group attached to a nitrogen atom was present in the molecule.

ANN ARBOR, MICHIGAN.

THE RELATION BETWEEN THE BOILING POINT AND COMPOSITION OF A MIXTURE OF ETHYLIODIDE AND ETHYL ALCOHOL.

BY SARAT CHANDRA JANA AND JITENDRA NATH SEN GUPTA.

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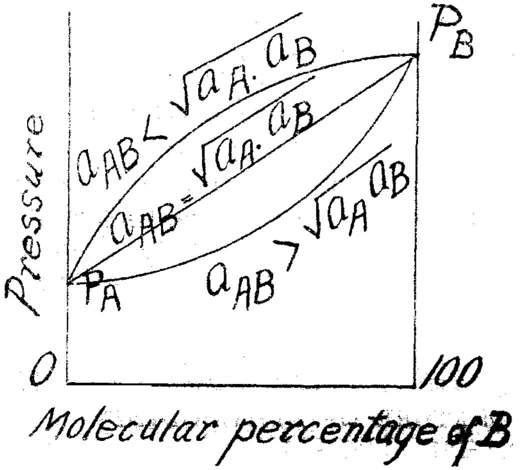
The boiling points, or the vapor pressures, of mixtures of liquids have been determined by many investigators. For non-miscible liquids, such as chlorobenzene and water, this can be accurately calculated by the law of partial pressures. The whole pressure at any given temperature is equal to the sum of the partial pressures of the two components at the given temperature. Thus, one can easily calculate the boiling point of the mixture if he knows the composition of the liquid phase and the pressure under which the distillation is carried on. The relative masses of the vapors in a given volume can also be calculated by means of the formula $D_A \times P_A/D_B \times P_B$, where D_A and D_B are the vapor densities and, P_A and P_B are the vapor pressures at any given temperature.[1] The process of steam distillation in the case of high boiling liquids such as glycerol depends on this principle.

In the case of substances which mix together in any proportion, the above rule cannot, however, be applied. In the case of chemically related substances the vapor pressure can be calculated by means of the formula $100\ P = MP_A\ (100 - M)P_B$, where M is the molecular percentage of A, and P, P_A and P_B are the vapor pressures of the mixture and of A and B, respectively at the given temperature. Van der Waals, however, limits the application of this formula to those substances whose critical pressures are equal.[2] Young has calculated the vapor pressure of a mixture of chlorobenzene and bromobenzene by this formula with fairly accurate results.[3]

The boiling point and the molecular composition of such mixtures of liquids can be calculated easily. In order to do this, the vapor pressures of each substance must be known at all temperatures between their respective boiling points under a given pressure p. The percentage molecular composition which would exert a vapor pressure p is then calculated at a series of temperatures between these limits by means of the formula $M = 100\ P_B - P/P_B - P_A$. Finally the values of M must be plotted against the temperatures and the curve thus obtained will give the relation between the boiling point and molecular composition under the pressure p.



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[1] Naumann, *Ber.*, 10, 1421, 1819, 2015, 2099; Brown, *Trans.*, 547 (1873).

[2] *Proc. Roy. Acad. Amsterdam*, 3, 170 (1900).

[3] *J. Chem. Soc.*, 81, 768 (1902).

In the case of mixtures of substances which are not closely related to one another the preceding formula cannot be applied. As a general rule it may be stated that the relation between the vapor pressure and the composition of such mixtures is represented by a curve. This relation has been expressed graphically by Galitzine and D. Berthelot as shown above, where $a_{A.B}$ denotes attraction of the unlike molecules and a_A and a_B between like molecules. The deviation of the boiling point of mixtures from straightness has been observed in the case of many substances. As instances of mixtures of maximum boiling points, the following pairs of liquids may be cited—propyl and isobutyl alcohol with water,[1] formic, acetic and propionic acids with pyridine (Zawidoski), hydrochloric acid and methyl ether (Friedel) formic, nitric, hydrochloric, hydrobromic and hydriodic acids with water (Roscoe) also chloroform and acetone (Ryland).

As instances of mixtures of minimum boiling points, we may mention carbon bisulfide and acetone, carbon bisulfide and methyl acetate, acetone and methyl acetate, acetone and ethyl iodide (Ryland).

In a mixture of ethyl alcohol and ethyl iodide the boiling point is found to be much lower than that of either of the two. The boiling point of ethyl alcohol is 77.8°, but a mixture of 87% of ethyl iodide and 13% of ethyl alcohol boils at 61.2° under ordinary atmospheric pressure. The boiling point of ethyl alcohol is gradually lowered by the addition of small quantities of ethyl iodide until a minimum is reached, then it rises again. Similarly, the boiling point of ethyl iodide is lowered by the addition of small quantities of ethyl alcohol. The following table gives the relation between the percentage of ethyl iodide in the mixture and the boiling point.

Percentage of ethyl iodide.	Boiling point.	Percentage of ethyl iodide.	Boiling point.
26.69	70.2°	97.63	64.0°
35.69	68.8	94.50	62.0
41.38	67.0	90.5	61.5
52.86	64.8	88.35	61.3
57.28	64.0	84.87	61.4
62.70	63.3	78.36	61.9
...	...	69.42	62.2

A curve drawn from the above data gives the relation between the boiling point of the mixture and the percentage of ethyl iodide. A mixture of 87% of ethyl iodide and 13% of ethyl alcohol boils at 61.2° and the mixture will distil off as a homogeneous liquid.

It has been suggested that such mixtures, of maximum and minimum boiling-point curves, are obtained in the case of associating liquids. Ethyl alcohol is a liquid of great molecular association as can be seen from

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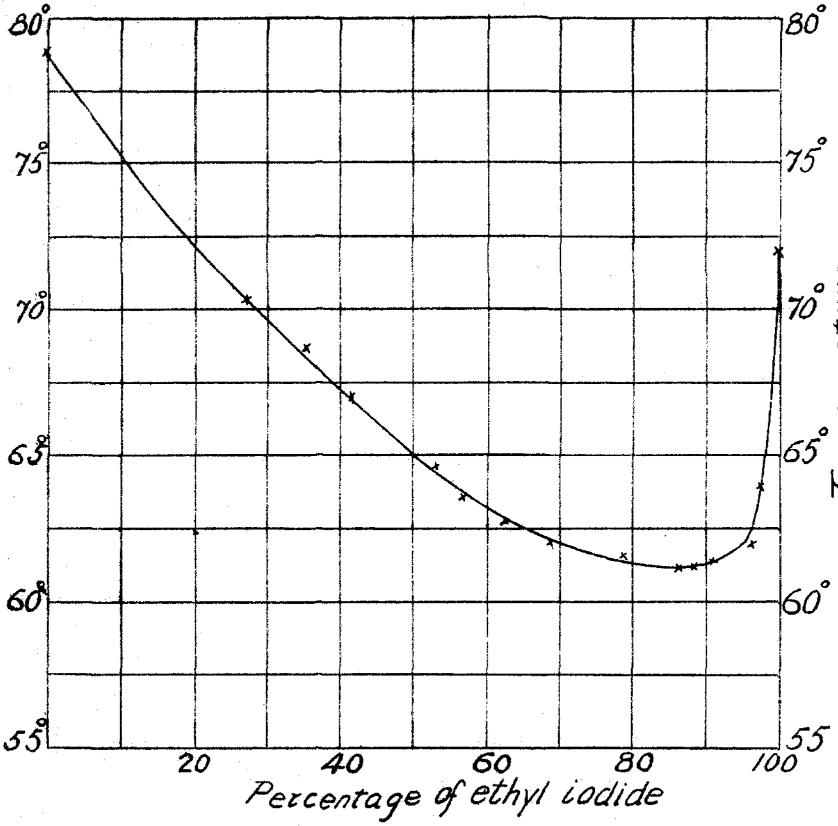
[1] Konowalow, *Wied. Ann.*, 1434 (1881).



capillary measurements, the relation between boiling point and specific cohesion, and also from Traube's volume relations; but ethyl iodide is not an associating liquid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. XII. DERIVATIVES OF ISOCAMPHORIC ACID; DECOMPOSITION PRODUCTS OF ISOAMINODIHYDROCAMPHOLYTIC ACID.[1]

BY WILLIAM A. NOYES AND LLOYD F. NICKELL.

Received November 26, 1913.

Of the four isomeric amino acids derived from *d*-camphoric acid and *l*-isocamphoric acid, the decomposition with nitrous acid of but one,

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[1] Abstract of a thesis presented by Lloyd F. Nickell in partial fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Illinois.