Summary

The photochemical decomposition of gaseous nitrogen pentoxide in the presence of nitrogen dioxide has been investigated with approximately monochromatic radiations of the wave lengths 4350, 4050 and 3660 Å. From a comparison of the rates of photochemical decomposition of nitrogen pentoxide and nitrogen dioxide, it is concluded that the mechanism of this sensitized photochemical decomposition is essentially that suggested by Norrish, namely, the formation of nitric oxide and oxygen from the photodecomposition of nitrogen dioxide, followed by dark reaction between nitric oxide and nitrogen pentoxide.

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VAPOR PRESSURES OF RELATED COMPOUNDS. THE APPLICATION OF DÜHRING'S RULE

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Several methods have been proposed to show the relation between the vapor-pressure data for various substances. The approximate Clausius-Clapeyron equation states that the slope of the vapor-pressure curve of any substance is proportional to its molal entropy of vaporization. In other words, the slopes of the vapor-pressure curves of non-associated substances at the same pressure should be the same. However, due to deviation from the gas laws and for other reasons, over wide pressure ranges this is not the case. Hildebrand[1] has suggested that this equation would be more nearly correct if the comparisons between various liquids were made at equal vapor concentrations rather than at equal pressures. Wilson and Bahlke[2] found that this method is applicable to the paraffin hydrocarbons.

Another common method, also based on the Clapeyron equation, is to plot the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Over short ranges of temperature the data for related substances give straight lines which are nearly parallel. However, as the temperature range increases, the straight lines are replaced by curves. Still other methods are empirical, such as those proposed by Ashworth[3] and Cox.[4] Calingaert and Davis[5] applied the Cox method to several groups of related substances and found that the lines representing

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[1] Hildebrand, THIS JOURNAL, **37**, 970 (1915).

[2] Wilson and Bahlke, *Ind. Eng. Chem.*, **16**, 115 (1924).

[3] Ashworth, *J. Inst. Petroleum Tech.*, **10**, 787 (1924).

[4] Cox, *Ind. Eng. Chem.*, **15**, 592 (1923).

[5] Calingaert and Davis, *ibid.*, **17**, 1287 (1925).

the vapor-pressure data for each substance in the groups so plotted tend to intersect in a common point.

It is the purpose of this paper to show that the Dühring lines, representing the vapor-pressure data for each one of a family of substances, intersect in a common point. As will be shown, this simplifies the construction of the vapor-pressure curve for each substance in the group. Relatively few experimental determinations are required to obtain these vapor-pressure data, which are sufficiently accurate for many purposes.

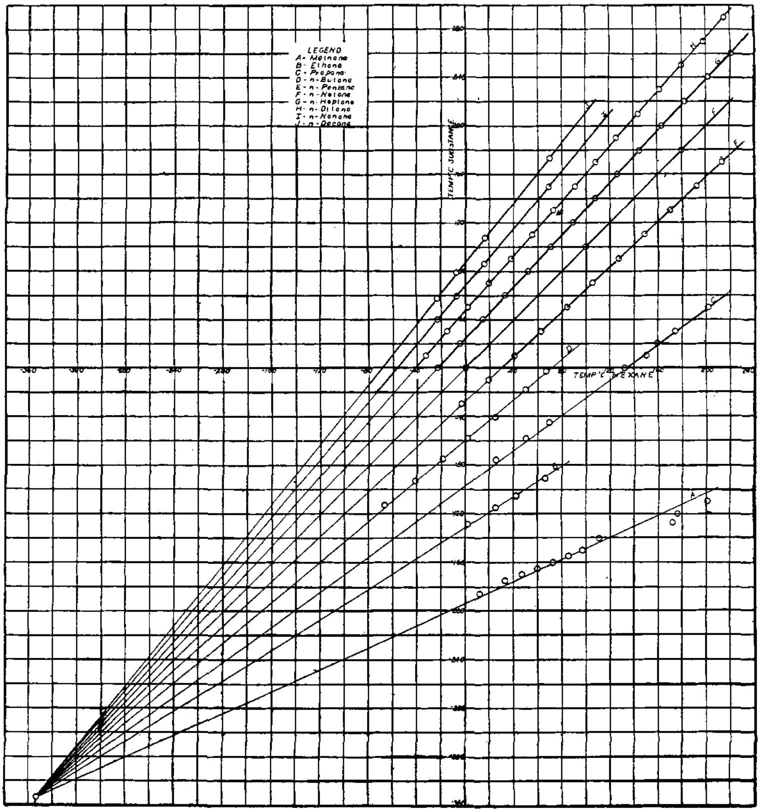

Fig. 1.

In 1878, Dühring[6] discovered a simple relation between the boiling points of pure substances. He plotted the boiling point of one substance at a given pressure as the ordinate against the boiling point of water at the same pressure as the abscissa. Repeating this process for several widely different pressures, he showed that a straight line could be drawn through all the points thus determined. This rule greatly simplifies the

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[6] Dühring, "Neue Grundgesetze zur Rationelle Physik und Chemie," Leipzig, 1878.

construction of vapor-pressure curves. Once the Dühring line for the substance or compound is constructed, the pressure corresponding to any boiling point may be found in the following manner. Through any temperature representing the boiling point of the substance, draw a line parallel to the horizontal axis and intersecting the Dühring line. Through this point of intersection, draw a line parallel to the vertical axis and read the boiling point of the reference substance under the same pressure as that of the substance in question. From the vapor-pressure curve of the reference substance read the pressure corresponding to this temperature. By repeating this process for various temperatures, the vapor-pressure curve for the substance may be determined.

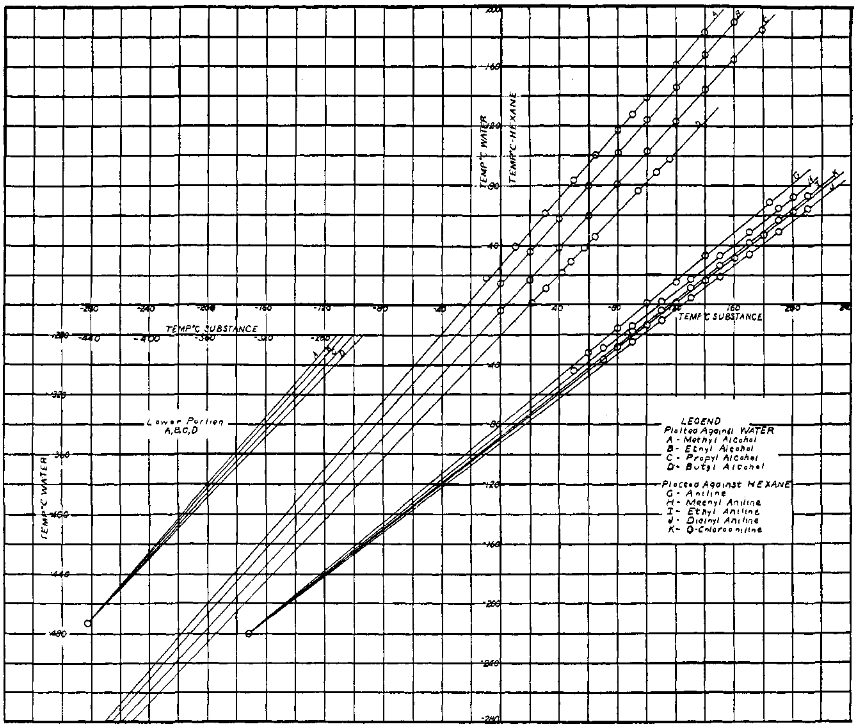

Fig. 2.

Dühring expressed his rule algebraically as follows

$$\frac{T_1 - T_2}{\Theta_1 - \Theta_2} = K$$

in which T_1 and T_2 are the boiling points of one substance at two different pressures, while Θ_1 and Θ_2 are the boiling points of the other substance at the same two pressures and K is a constant which is the slope of the line. Dühring's rule has been shown to hold remarkably well for substances and compounds over pressure ranges of several thousand millimeters when the boiling points of the substance or compound in question are plotted against the known boiling points of a chemically similar substance. In general the broader the pressure range and the less similar the substances, the greater will be the deviation from a straight line.

Furthermore, it may be seen from the charts that the Dühring lines for a family of substances either intersect in a common point or are parallel.

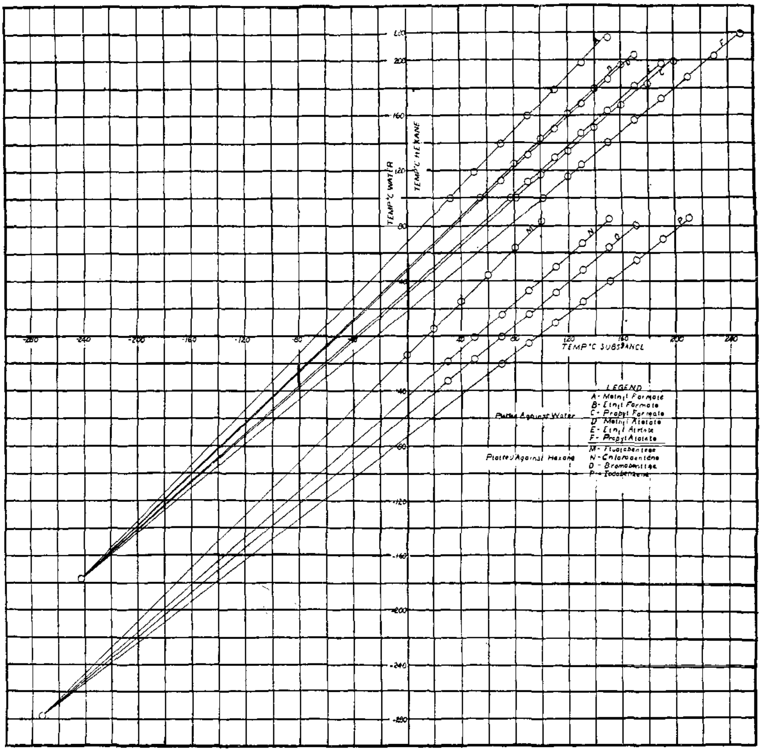

Fig. 3.

The requirements for the construction of a Dühring chart for a family of substances are as follows: (1) the vapor pressure of some reference substance, such as water or hexane, must be accurately known and (2) at least two boiling points at different pressures of two substances in the family should be determined in order to establish the common point of intersection of the Dühring lines for the family. After this point of intersection is established, it is possible to construct the vapor-pressure curve of any member of the family of substances from a single boiling point.

Fig. 1 shows the normal paraffin hydrocarbons from methane through decane. These are plotted against normal hexane as the reference substance. The lines for most of these hydrocarbons fit the data very accurately through wide pressure ranges, but from butane down the data become somewhat discordant, with that of methane deviating most widely from a straight line. The vapor-pressure data of the reference substance, hexane, which we have used were taken from Von Rechenberg.[7] The Dühring lines for the isomers of the normal hydrocarbons, not shown in the figure, intersect in a different point from that of the normal hydrocarbons.

In Fig. 2, A, B, C and D are, respectively, methyl, ethyl, propyl and butyl alcohols plotted against water as the reference substance, while G, H, I, J and K are aniline, methylaniline, ethylaniline, diethylaniline and *o*-chloro-aniline, respectively, plotted against hexane. The anilines when plotted against water showed curves of similar shape, but with hexane as the reference substance they formed straight lines which intersected in a common point.

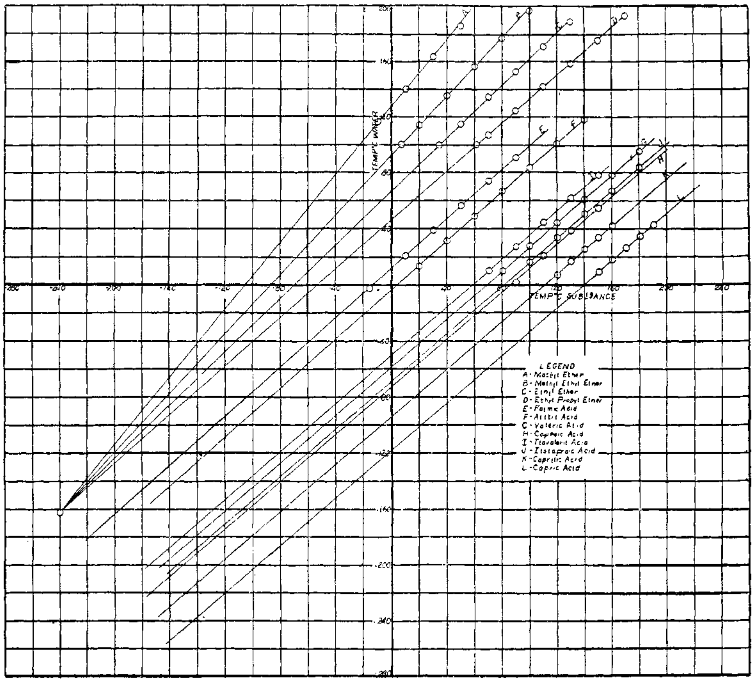

Fig. 4.

In Fig. 3, A to F inclusive are the lines for several organic esters plotted against water, while M to P inclusive are halogen derivatives of benzene plotted against hexane. Fig. 4 gives several ethers and several acids with

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[7] Von Rechenberg, "Einfache und Fraktionierte Destillation in Theorie und Praxis," Von Schimmel and Company, Leipzig, 1923.

water in both cases as the reference substance. It is a curious fact that the Dühring lines for the various organic acids studied are parallel.

The literature does not yield complete vapor-pressure data over wide temperature ranges for many whole families of compounds. Where such data were available and were plotted against a similar substance for reference, the Dühring lines so formed were straight and intersected in a common point.

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