4. A comparison of basic lead carbonate obtained electrolytically, with two samples of dry commercial white lead, indicates that it is possible by the addition of small quantities of gelatin, to obtain a product having particles smaller in average size, and of more uniform distribution, than those of the commercial dry white lead examined.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

HEAT OF VAPORIZATION, A FUNCTION OF THE TEMPERATURE

BY MANUEL M. GREEN

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The similarity in appearance (but difference in position) of the vapor pressure-temperature curves of quite unrelated substances suggests that in view of the Clapeyron equation the heat of vaporization might be the same function for all substances, differing only in the constants involved. Within recent years, several equations of more or less complexity have been suggested[1] in which the heat of vaporization has been expressed as a function of the temperature, volume, pressure, density, etc., but none of these has been generally accepted. The simplest possible expression is of course desirable, and the calculation presented in this paper has been devised to show that if the heat of vaporization (ΔH) is assumed to be a function of the temperature (T) alone, the same function for all substances but differing in the constants involved (such as in the Kirchhoff-Hertz or Nernst equations), a conclusion is arrived at which indicates the approximate limits of accuracy of such a relation [that is, $\Delta H = F(T)$].

Derivation

Let us take two entirely unrelated, non-associated liquids A and B, with boiling points T_{B_1} and T_{B_2}, and critical temperatures T_{C_1} and T_{C_2}. For these substances, $\Delta H = F(T)$, which can also be written $\Delta H = T\,f(aT)$, where a is a constant. That is, $\Delta H_1 = T\,f(kT)$; and $\Delta H_2 = T\,f(KkT)$, where k and K are constants, and the functions are the same in both cases.

At the critical temperature, Mathias[2] has shown that the heat of vaporization is zero, that is, $\Delta H_1 = T_{C_1}f(kT_{C_1}) = \Delta H_2 = T_{C_2}f(KkT_{C_2}) = 0$, or $f(kT_{C_1}) = 0; f(KkT) = 0_{C_2}$, and since the function is the same in both cases, differing only in the constants, $kT_{C_1} = KkT_{C_2}; K = T_{C_1}/T_{C_2}$.

At the boiling points, $\Delta H_1 = T_{B_1}f(kT_{B_1})$; $\Delta H_2 = T_{B_2}f(KkT_{B_2})$, from which $\frac{\Delta H_1}{T_{B_1}} = f(kT_{B_1})$; $\frac{\Delta H_2}{T_{B_2}} = f(KkT_{B_2})$, and since for non-associated

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[1] See THIS JOURNAL, **36,** 1620 (1914) for a review.

[2] Mathias, *Ann. chim. phys.*, [6] **21,** 69 (1890).

liquids at their boiling points Trouton's rule holds,[3] $f(kT_{B_1}) = f(KkT_{B_2}) = f\left(\frac{T_{C_1}}{T_{C_2}} kT_{B_2}\right)$, from which $\frac{T_{C_1}}{T_{C_2}} T_{B_2} = T_{B_1}$, or $\frac{T_{B_1}}{T_{C_1}} = \frac{T_{B_2}}{T_{C_2}}$ that is the ratio of boiling point to critical temperature is a constant.

Guldberg[4] was the first to point out that the ratio of the boiling point to the critical temperature is approximately a constant, the mean being about 0.66. Although the values do vary somewhat, they are nevertheless in the vicinity of that value.

Summary

It has been shown that if the heat of vaporization (ΔH) is assumed to be a function of the temperature alone, the same function for all non-associated liquids, but differing in the constants involved, Guldberg's rule showing the relation of boiling point to critical temperature is derived, indicating that the relation $\Delta H = F(T)$ (for all non-associated liquids) may probably be relied on to approximately the limits of the boiling point critical-temperature ratios.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY AT THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

DEPOLARIZATION OF THE CHLORINE ELECTRODE BY ORGANIC COMPOUNDS[1]

BY MERRILL A. YOUTZ

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The literature upon the subject of electrolytic chlorination of organic substances is not large in comparison with that upon electrolytic oxidation and reduction. Although work has been done upon chlorination of various substances,[2] and upon overvoltage[3] of chlorine, no one has attempted to use the decomposition potential method of determining whether organic

[3] At this point Trouton's rule, rather than the more recent modification of Hildebrand is used because of the fact that the temperatures for which the latter rule holds are known for too few substances to be of any value in checking the relation finally obtained. The derivation would be similar, however, if Hildebrand's modification were used.

[4] Guldberg, *Z. physik. Chem.*, **5**, 374 (1890).

[1] This is an abstract of a portion of a thesis submitted to the faculty of the Massachusetts Institute of Technology in May, 1922, by Merrill A. Youtz in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Haber and Moser, "Die Elektrolytischen Prozesse der organischen Chemie," Knapp, Halle, **1910**, pp. 81–104. Löb, (Lorenz), "The Electrochemistry of Organic Compounds," Wiley and Sons, New York, **1906**.

[3] Müller, *Z. Elektrochem.*, **6**, 573 (1900); **8**, 426 (1902). Sacerdoti, *ibid.*, **17**, 473 (1911). Billiter, "Die Elektrochemischen Verfahren der chemischen Gross-industrie," Knapp, Halle, **1909**, vol. II, p. 140. Newbery, *J. Chem. Soc.*, **119**, 477 (1921). Lewis, THIS JOURNAL, **33**, 299 (1911).