

EBULLISCOPIC MEASUREMENTS IN MIXED LIQUIDS

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Ebulliscope Measurements in Mixed Liquids by Gerhard Krohn Rollefson

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EBULLIOSCOPIC MEASUREMENTS IN MIXED LIQUIDS

By

Gerhard Krohn Rollefson

A Thesis

Submitted for the Degree of

MASTER OF SCIENCE

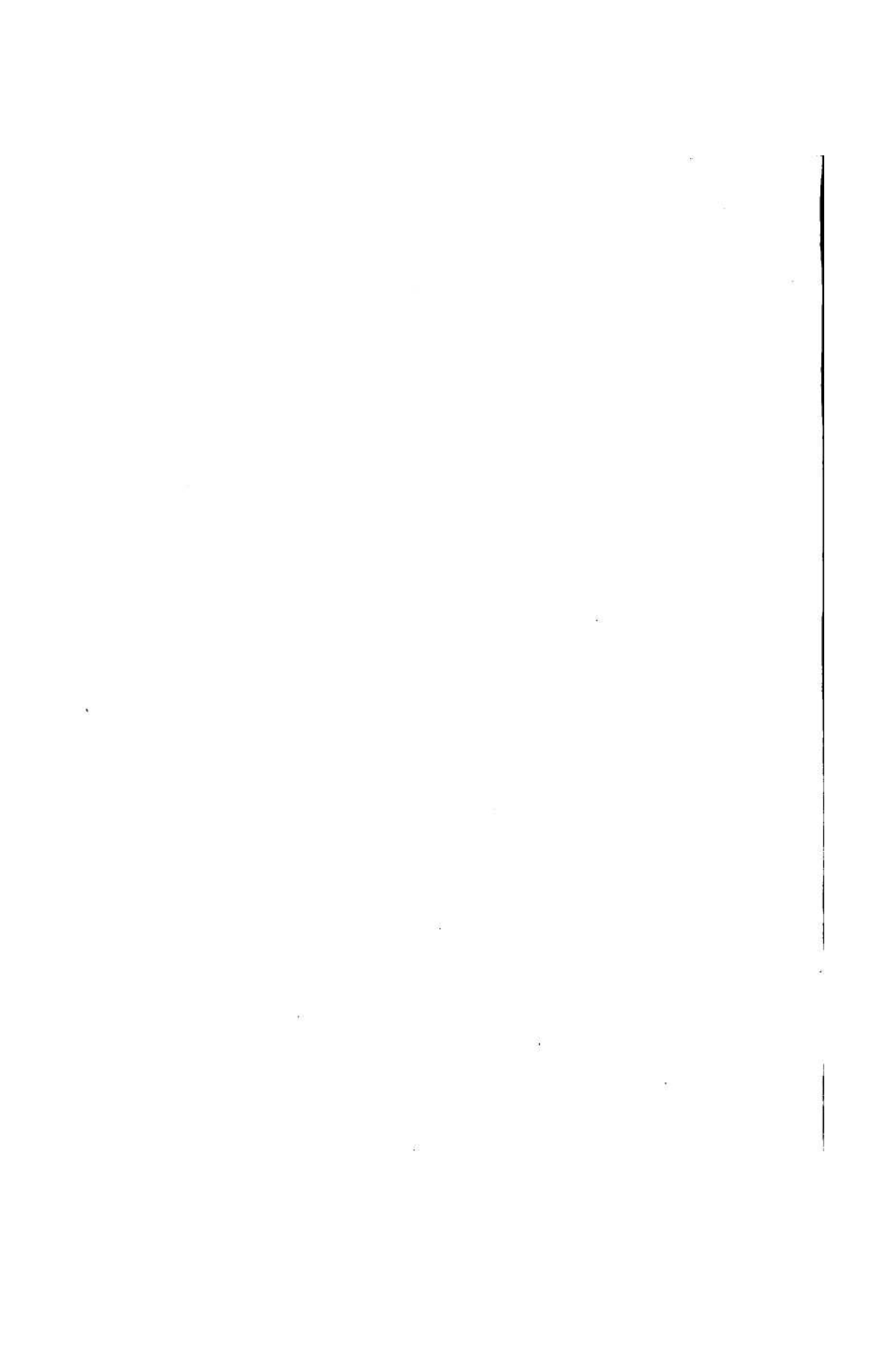
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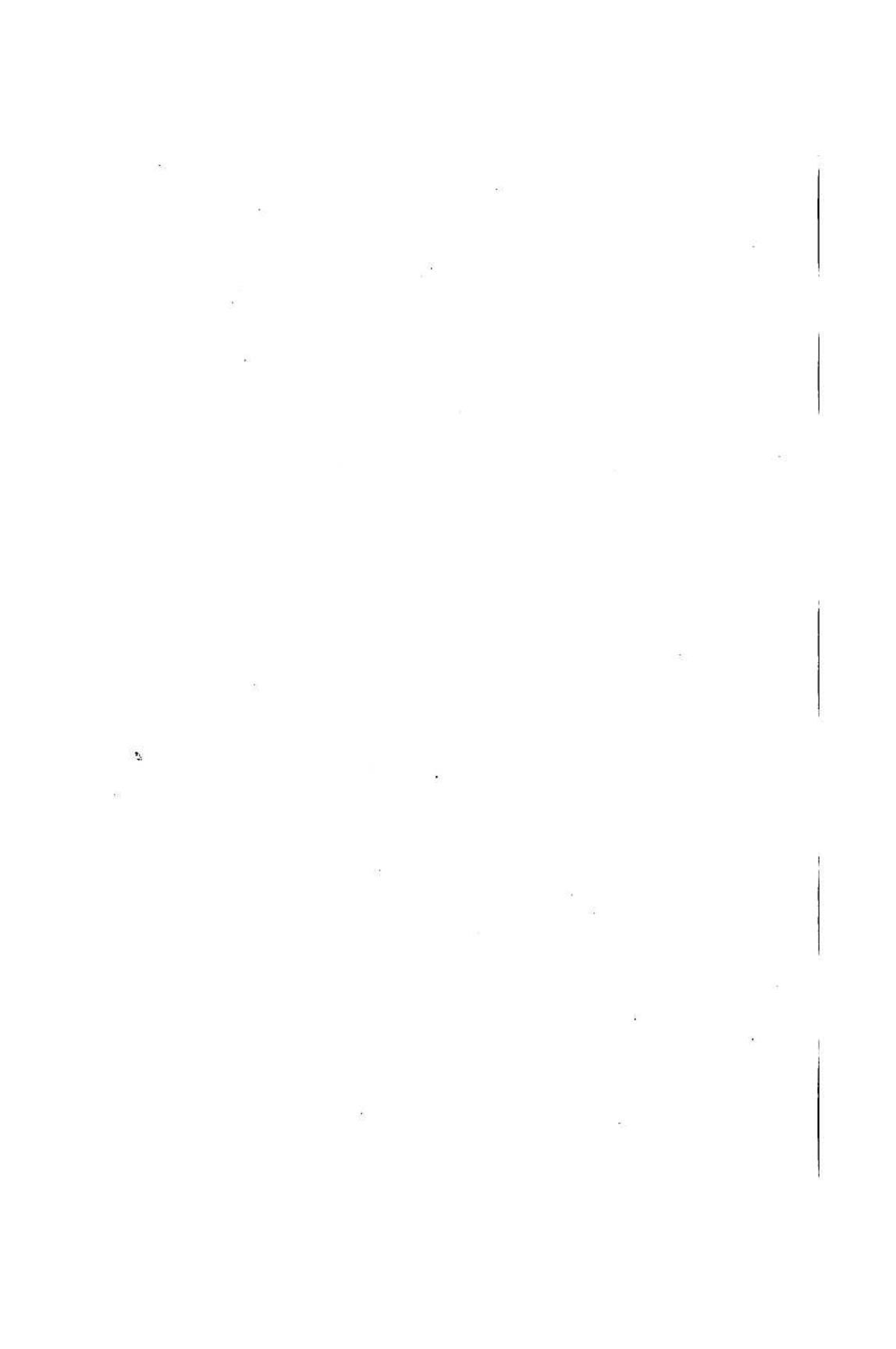
The study of the variation of some physical property with the composition of a binary mixture has been carried on for a long time as a means of securing an experimental basis for a theory of mixtures. The properties which have been studied are numerous including viscosity, boiling points, refractive indices, densities, specific volumes, and various thermal properties. Poisseule in 1843 and 1847 published papers on the viscosity of mixtures particularly those of ethyl alcohol and water. About the same time Bineau found that the constant boiling mixture of hydrochloric acid and water had approximately the composition $\text{HCl} \cdot 8\text{H}_2\text{O}$ and the similar mixture of nitric acid and water was represented as $2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$. This work resulted in the hypothesis that these constant boiling mixtures are definite chemical compounds. That hypothesis has since been shown to be untenable since Roscoe and Dithmar and others have found that the composition of the constant boiling mixture depends on the pressure and in the case of mixtures of ethyl alcohol and water it has been found that at low pressures the minimum in the boiling point curve disappears. Such mixtures are therefore not considered definite compounds any more but the existence of a maximum or minimum in a boiling point curve is taken as evidence of either a certain amount of combination or a change in the association



or dissociation of the liquids composing the mixture. The argument which applies to boiling points has been found to apply also to other properties such as viscosity and heats of mixture.

The thermodynamic treatment of mixtures began with the work of Kirchhoff¹ and Gibbs² on the vapor pressure of liquid mixtures. The theory advanced by Gibbs was worked out independently on an experimental basis by Konowalow³. He distinguished three types of vapor pressure curves for completely miscible liquids and studied the changes occurring in the distillation of mixtures. The work of Kirchhoff was extended by Duhem⁴ who deduced a differential equation for the change of the logarithm of the vapor pressure with the composition of the mixture. This equation was later integrated by Margules⁵ and confirmed quantitatively by v.Zawidzki⁶. Others have studied various special problems in the thermodynamic theory of mixtures and in some cases experimental confirmation has been secured⁷. The general theory of binary systems has been attacked by Gibbs⁸, Planck⁹ and Duhem¹⁰ who

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1. Kirchhoff. Pogg. Ann. 103 104 (1858).
 2. Gibbs. Scientific Papers Vol. I.
 3. Konowalow. Wied. Ann. 4 48 (1881).
 4. Duhem. Traite de Mecanique Chimique IV.
 5. Margules. Sitzungsber. Wien. Akad. 1895.
 6. Zawidzki Z. physikal. chem. 35 129 (1900).
 7. Nernst Theoretische Chemie 6th Ed. P.115. Bose Z.physikal chem. 58 621 (1907), *ibid.* 65 458 (1909) van der Waals Proc. Acad. Amsterdam 10 56,123,183 (1909).
 8. Gibbs Scientific Papers B Vol. I.
 9. Planck Thermodynamik 3 Aufl. Sec. 211.
 10. Duhem. Traite I ch.viii III ch. i,ii.



have derived a general equation for the displacement of equilibrium of a system. This equation has been applied in a few cases and Masing¹¹ has applied it to the calculation of the heats of vaporization of water and ethyl alcohol and mixtures of the two. In general, however, this equation and the others have approximations introduced so as to put them into a form which may be used in calculations so that the calculated results do not agree as well as might be hoped for.

Leaving, for the time being, the purely thermodynamic theory of mixtures we have the work of Dolezalek¹² advocating the chemical theory of mixtures. He started with the assumption that the partial pressure of each component is proportional to its concentration in the liquid phase provided no chemical change occurs on mixing the liquids and that neither one is polymerized in the liquid state. If there is any association of either component the partial pressure curve of that component is concave to the concentration axis indicating dissociation of the polymerized molecules. If the curve is concave the other way, the formation of a compound of the two components is indicated. On this basis Dolezalek discussed the pairs benzene-chloroform, carbon tetrachloride-benzene, and chloroform-acetone. In the case of the chloroform-acetone mixtures by using the assumption

11. Masing Z.physikal. chem. 81 223 (1912).

12. Dolezalek Z.physikal. chem. 54 727 (1908). 71 191 (1910).
83 40,45 (1913).