

Heavy Water of Crystallisation

IN connexion with the interesting letter by J. Bell¹, we wish to state that we are engaged in measurements of the dissociation pressures of $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$ and other salts containing heavy water of crystallisation, and also intend to study the crystal angles of these compounds. As is well known, measurements of dissociation pressures of salt hydrates, much work on which has been published by one of us, are somewhat difficult, but some preliminary results will shortly be communicated.

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March 31.

¹ NATURE, 137, 534 (1936).

Relativity Theory and the Universe

SINCE the relativity theory can be adequately interpreted in the space of Lobachevsky¹, may I be permitted to say a few words in connexion with a communication of Sir James Jeans².

In the finite space of positive curvature, the number of nebulae at great distances would increase less rapidly than x^3 . However, observations made at Mount Wilson "seem to indicate the exact reverse". This would speak in favour of the supposition that space is of infinite dimensions and of negative curvature. The area of the circle with radius x in Lobachevsky's plane is expressed by

$$A = \pi sh^2 x = \pi \left(x^2 + \frac{x^4}{3} + \dots \right);$$

that is, it is larger than the area of a circle of the same radius in the plane of Euclid. The volume of the sphere in Lobachevsky's space is given by

$$V = \pi (sh \ 2x - 2x) = \pi \left(\frac{4}{3}x^3 + \frac{4}{15}x^5 + \dots \right).$$

This volume increases more rapidly than the cube of the distance, so that if the nebulae are uniformly distributed in space, the number of nebulae would also increase more rapidly than x^3 ; and this would agree with the observations made at Mount Wilson.

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¹ NATURE, 114, 820 (1924).

² "The Size and Age of the Universe", NATURE, 137, 20 (Jan. 4, 1936).

Ebulliometric Determination of Small Amounts of Water*

THE sensitivity of the ebulliometric method of determining small amounts of water, which has been applied to measurements of the water content in standard samples of benzoic acid¹, to determinations of the degree of decomposition of organic substances on heating², and to measurements of adsorption of vapours on solid metallic surfaces³, may be considerably increased by the use of the azeotropic mixture *n*-propanol/toluene instead of ethanol/benzene used formerly.

The method¹ is based on the fact that the lowering of the condensation temperature of a binary

* Publication approved by the Director of the National Bureau of Standards of the U.S. Department of Commerce.

azeotropic mixture such as ethanol/benzene is proportional to the amount of water introduced into the apparatus. With the aid of the ebulliometer with several sections, it has been found possible to obtain a lowering of 0.033° C. per mgm. of water. This lowering depends on the dephlegmating power of the apparatus and on the nature of the ebulliometric liquid that is used.

Measurements of the lowering of condensation temperature caused by the addition of 1 mgm. of water to different azeotropic mixtures were carried out in the same apparatus. When the ebulliometer was filled with a constant-boiling mixture of ethanol and benzene, a lowering of 0.010° C. per mgm. of water was obtained, but when the azeotropic mixture *n*-propanol/toluene was used, there was obtained a lowering of 0.080° C. per mgm. of water.

The above data prove that the application of the azeotropic mixture *n*-propanol/toluene increases the sensitivity of the method about eight times in comparison with that obtained when the mixture ethanol/benzene is used.

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¹ W. Swietoslawski, M. Wojciechowski and S. Miernik, *Bull. intern. acad. Polonaise*, A, 59 (1935).

² W. Swietoslawski, NATURE, 135, 829 (1935).

³ M. Wojciechowski, NATURE, 135, 830 (1935).

Kinetics of a Bimolecular Association in Benzene Solution and in the Gaseous State

FOR the further development of the theory of reaction kinetics and polymerisation in the condensed state, it is important to compare the rate of an association reaction, of the type $a + b \rightarrow c$, in solution and in the gas phase. In this communication experiments are reported from which such a comparison is possible.

The example studied is the Diels-Alder reaction between acrolein (*a*) and cyclopentadiene (*b*) to give endomethylene-tetrahydrobenzaldehyde (*c*)¹. It was found that in benzene solution, as in the gaseous state², a homogeneous bimolecular association is involved. The results of the kinetic measurements are given in the accompanying table.

	Benzene solution	Gaseous state
Temp. range	5.7° - 76.5°	107.9° - 209.8°
<i>k</i> (l./gm.-mol.-sec.)	3.3×10^{-4} (<i>t</i> =40°)	3.3×10^{-4} (<i>t</i> =160°)
<i>E</i> (kgm.-cal.)	13.7 ± 0.5	15.2 ± 1
<i>Z</i> (l./gm.-mol.-sec.)	1.3×10^6	1.5×10^6
<i>Z</i> _{max.}	5×10^6	4×10^6
<i>Z</i> _{min.}	0.3×10^6	0.6×10^6
Measurements by:	Wassermann	Kistiakowsky and Lacher ²

In the first line of the table the temperature range over which the measurements were carried out is given. The rate constant *k* was calculated, taking into account all the experiments within this temperature range. *E* is the activation energy, and *Z* in the fourth line was calculated from *k* and *E* according to the Arrhenius equation $k = Ze^{-E/RT}$. The *Z* values of the last two lines have been calculated in order to demonstrate the influence of the experimental error: *Z*_{max.} corresponds to an activation energy 0.9 kgm.-cal. larger, and *Z*_{min.} to one 0.9 kgm.-cal. smaller than 13.7 kgm.-cal. or 15.2 kgm.-cal.