von etwa 600 Å bis 1100 Å reicht. Als Anregungsmechanismus kommt wahrscheinlich ein Dreierstoß zwischen einem angeregten und zwei normalen Atomen in Frage. Ein ähnlicher Prozeß führt nämlich zur Bildung von Edelgas-Molekelionen in einer Entladung[3].

Fig. 3 zeigt das sichtbare Spektrum einer derartigen Corona-Entladung in He von 500 bzw. 0,1 Torr. Bei hohen Drucken erscheint außer dem He-Atomspektrum nur eine Bandenserie bei 4640 Å, die mit abnehmendem Druck allmählich schwächer wird. Falls sie mit der in diesem Spektralbereich liegenden He₂-Bande identisch sein sollte, wäre dies eine Stütze für die oben geäußerte Vermutung über den Ursprung der bei höheren Drucken gefundenen UV-Strahlung, da das erwähnte Kontinuum meist zusammen mit dem He₂⁻ Bandenspektrum beobachtet wird[1],[2].

Bei Drucken unter 1 Torr tritt in He, Ne und Ar eine gasionisierende Strahlung auf. Die Photoionisations-Wirkungsquerschnitte der Edelgase gegenüber ihrer eigenen Strahlung betragen $1,5 \cdot 10^{-17}$, $5 \cdot 10^{-17}$ bzw. $10 \cdot 10^{-17}$ cm². Es handelt sich hier mit größter Wahrscheinlichkeit um Funkenlinien der Edelgase. Wie aus Fig. 3b zu ersehen ist, wird nämlich bei diesen Drucken das Spektrum des He-Ions angeregt.

Physikalisches Institut der Universität, Würzburg

WOLFRIED BEMERL und HANS FETZ

Eingegangen am 25. April 1956

*) Das von der Firma Linde bezogene Reinsthelium wurde noch einer speziellen Nachreinigung unterzogen.
[1] FINKELNBURG, W.: Kontinuierliche Spektren. 1938.
[2] HOPFIELD, J.: Physic. Rev. 35, 1133 (1930); 36, 784 (1930).
[3] HORNBECK, J.: Physic. Rev. 84, 615 (1951). — HORNBECK, J., u. J. MOLNAR: Physic. Rev. 84, 621 (1951).
[4] BEMERL, W., u. H. FETZ: Z. angew. Phys. 8 (1956).

Temperature Variation of Surface Tension as a Free Volume Problem

Recently in a number of communications[1] the authors have tried to establish a general parallelism among the phenomena of viscosity (η), vapour pressure (p), and surface tension (S) of liquids, specially as regards their temperature variation. It was known for a long time that fluidity (reciprocal of viscosity) and free volume are connected by some simple relation[2]. BATSCHINSKI'S[3] empirical relation between viscosity and specific volume may be considered as one of the first attempts in this direction. Very recently MUKHERJEE[4] has correlated ultrasonic velocity in liquids with their free volume from the free volume theory of EYRING and coworkers. An experimental test of this relation has revealed that for most of the unassociated simple liquids fluidity is proportional to free volume. This piece of information was of great importance in deducing a relation between η and T, as was done by one of us[5a]. As it is suspected that there is a close resemblence between the phenomena of viscosity and surface tension, an attempt was made also to establish a functional relation between free volume (V_f) and S and, further a relation between S and T. From a very simplified structure of liquid one of the authors[5b] has shown that S and V_f are related as

$$S = C/V_f^{n/3}, \qquad (1)$$

where C and n are constants and, S and T are related as

$$\log S = a + b/T - c \log T. \qquad (2)$$

In the present communication it is intended to establish a simple relation between S and T starting from equation (1). From the consideration of partition function in a liquid it was shown by EYRING et al[6] that the free volume of a liquid is related to its molar volume by the expression

$$V_f = \left(\frac{c\,R\,T}{\Delta E_{\text{vap.}}}\right)^3 V, \qquad (3)$$

where V represents the molar volume, $\Delta E_{\text{vap.}}$ is the energy of vaporisation, and as a first approximation the packing factor c may be considered constant. Since $\Delta E_{\text{vap.}} = L - R\,T$ one gets from equations (1) and (3)

$$S = (C'/V^{n/3}) \cdot (L/T - R)^n,$$

where L is the normal latent heat of vaporisation and C' is a constant. But for many substances the variation of L with T may be represented[7] by $L = L_0 - a\,T$, hence

$$S = (C'/V^{n/3})(A/T - B)^n. \qquad (4)$$

Now, since the variation of S with T is much more faster than that of V with T in liquids, we shall assume that it remains constant over a reasonable range of temperature. So equation (4) becomes

$$S = (\alpha/T - \beta)^n. \qquad (5)$$

It is a well known fact that the surface tension tends to vanish near the critical region because the interface between liquid and vapour phases disappears here. Applying this condition, equation (5) is further simplified to

$$S = C \cdot [(T_c - T)/T]^n, \qquad (6)$$

where C and n are constants and T_c is the critical temperature. Fig. 1 gives a plot of $\log S$ versus $\log [(T_c - T)/T]$ for a number of liquids over a reasonable range of temperature remembering our assumption, namely, that of considering V to be constant. It is gratifying to note that even in the case of the highly associated liquid like water, where the assumption of constancy of packing factor also fails, we get nearly a straight line plot in the range from melting to the boiling point of the liquid. Table 1 records the values of S calculated from the relation (6) along with its observed values (c.g.s. units) in the case of benzene, which are in very good agreement.
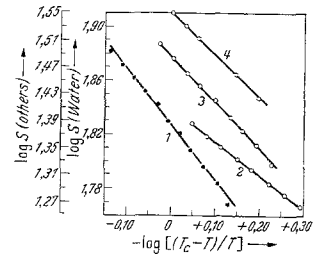
Fig. 1. Log S versus log $[(T_c - T)/T]$. 1 water; 2 ethyl-alcohol; 3 benzene; 4 carbon disulphide

Table 1. *Benzene, $T_c = 561,5\,°K$, $n = 0,6813$ and $C = 30,61$*

$T°$ K	273	283	293	303	313	323	333	343	353
S(obs.)	31·58	30·22	28·88	27·56	26·26	24·98	23·72	22·48	21·26
S(calc.)	31·78	30·27	28·84	27·50	26·16	24·90	23·68	22·51	21·38

The authors' grateful thanks are due to Prof. S. GHOSH, Dr. K. MAJUMDAR and Dr. Y.P. VARSHNI for their interest in the investigation.

Departments of Physics and Chemistry, Allahabad University, Allahabad, India

SHASHANKA SHEKHAR MITRA*) and
DHIRENDRA NATH CHAKRAVARTY

Eingegangen am 15. Mai 1956

*) Present address: H.M. Randall Laboratory of Physics, University of Michigan, Ann Arbor (Mich.), U.S.A.
[1] MITRA, S.S.: J. Chem. Physics 22, 349 (1954). — ERRATUM: J. Chem. Physics 22, 1471 (1954). — J. Indian Chem. Soc. 31, 444 (1954). — Sci. and Cult. 1956. — MITRA, S.S., and S.N. SRIVASTAVA: J. Chem. Physics 22, 1134 (1954). — J. Indian Chem. Soc. 31, 813 (1954). — MITRA, S.S., and D.N. CHAKRAVARTY: J. Chem. Physics 22, 1775 (1954). — Z. physik. Chem. 205, 1 (1955).
[2] HATSCHEK: The Viscosity of Liquids, p. 70. London: G. Bell 1928.
[3] BATSCHINSKI: Z. physik. Chem. 84, 643 (1913).
[4] MUKHERJEE, A.K.: J. Indian Chem. Soc. 28, 363 (1951).
[5] MITRA, S.S.: a) Current Sci. 24, 44 (1955). — J. Indian Chem. Soc. 32, 297 (1955). — b) Unpublished.
[6] EYRING and HIRSCHFELDER: J. Physic. Chem. 41, 249 (1937). — GLASSTONE, LAIDLER and EYRING: The Theory of Rate Processes, p. 479. New York: Mc Graw-Hill 1941.
[7] SAHA, M.N., and B.N. SRIVASTAVA: A Treatise on Heat, p. 472. Allahabad: Indian Press 1950.

Das Intensitätsverhältnis $K_{\bar{\alpha}} : K_\beta$
als Hinweis auf selektive Veränderungen an Legierungsanteilen

Das Intensitätsverhältnis $K_{\bar{\alpha}} : K_\beta$ ist etwa 4:1, wenn man an einer Netzebene eines Stoffes reflektiert, dessen chemische Bestandteile hinsichtlich ihrer K- oder L-Absorptionskanten-Wellenlängen hinreichend große Wellenlängenunterschiede gegen die eingestrahlte K-Strahlung besitzen. Anders werden die Verhältnisse, wenn man z.B. Eisen mit Kobalt-K-Strahlung bestrahlt. Die Wellenlänge der K-Absorptionskante von Fe liegt mit 1,740 kX zwischen den Werten für Co-$K_{\bar{\alpha}}$ mit 1,787 kX und Co-K_β mit 1,617 kX. Dadurch erfolgt eine Absorption der Co-K_β-Komponente im Eisen, so daß das Intensitätsverhältnis Co-$K_{\bar{\alpha}}$:Co-K_β nunmehr etwa 35:1 wird.