

III. "On the Variation of Surface Energy with Temperature."

By WILLIAM RAMSAY, Ph.D., F.R.S., and JOHN SHIELDS, B.Sc., Ph.D. Received March 14, 1893.

(Abstract.)

It is shown that a close analogy exists between the equation for gases,

$$pv = RT,$$

and an equation expressing the relation of surface energy to temperature,

$$\gamma s = \kappa \tau,$$

where γ is surface tension; s , surface; κ , a constant; and τ , temperature measured downwards from a point about 6° below the critical point of the fluid. As the origin of T in the gaseous equation is where $p = 0$, so the origin of τ should be where $\gamma = 0$. Correcting the above equation so that τ shall represent the number of degrees measured downwards from the critical point, the equation becomes

$$\gamma s = \kappa (\tau - d).$$

But even this equation does not express the whole truth. For at temperatures less than 30° below the critical temperature, the relation between surface energy and temperature is not a rectilinear one; a correction is therefore introduced in the form of a second term, which becomes insignificant at temperatures more than 25° or $30^\circ \tau$; it is

$$\gamma s = \kappa \tau - \kappa d (1 - 10^{-\lambda \tau}).$$

The liquids examined were: ether, methyl formate, ethyl acetate, carbon tetrachloride, benzene, chlorobenzene, acetic acid, and methyl and ethyl alcohols; in fact, the only ones for which data are available. For, in order to calculate γ from the rise in a capillary tube, it is necessary to know the density of the orthobaric liquid and gas; and reliable data exist only for these liquids, and for a few others which resemble them closely, *e.g.*, fluorobenzene, bromobenzene, &c. Also to calculate s , *i.e.*, molecular surface, it is necessary to know the molecular volume of the liquid, and to raise it to the power $\frac{2}{3}$ rds. Hence $v^{\frac{2}{3}} = s$, or molecular surface; *i.e.*, it is possible to compare different liquids on the surfaces of which equal numbers of molecules lie.

Measurements were made at -89.8° , the boiling point of nitrous oxide under atmospheric pressure, with ether, methyl formate, ethyl acetate, and the two alcohols; the other substances are solid at that low

temperature. These observations confirmed the rectilinear relation with the first three; but in the case of the two alcohols, evidence was obtained of molecular association, as also with acetic acid. It is possible to calculate the amount of association at any temperature in such cases. For, assuming the constancy of κ for the molecular surface of the "normal" liquids, the equation

$$\kappa/d = x^3,$$

where d is the differential coefficient of an associating liquid, and x is the molecular aggregation, gives the number of simple molecules which have united to form a compound at the temperature chosen. For the alcohols at -90° , and for acetic acid at 20° , the association of molecules approximates to $(C_2H_4O_2)_4$, $(CH_4O)_4$, and $(C_2H_6O)_4$.

We have thus a method by which it is possible to ascertain the molecular complexity of undiluted liquids. The results with the alcohols are shown to agree within reasonable limits with those obtained from strong solutions by Raoult's method.

It is incidentally shown in the course of the paper that there is no angle of contact between liquid and glass, when the liquid surface is in contact only with its own vapour. Ordinary measurements of capillarity give inconstant, and probably inaccurate, results, for it is not the surface tension of the liquid which is measured, but that of a solution of air in the surface film of the liquid.

The paper contains tables and curves exemplifying and illustrating the statements given.

IV. "The Absolute Thermal Conductivities of Copper and Iron." By R. WALLACE STEWART, B.Sc. (Lond.), Assistant Lecturer and Demonstrator in Physics, University College, Bangor. Communicated by LORD KELVIN, P.R.S. Received March 2, 1893.

(Abstract.)

The experiments described in the paper were undertaken with the object of determining the theoretical conductivity at different temperatures of iron, and, in particular, of pure electrolytically deposited copper.

The method adopted was that due to Forbes, with two modifications.

(a.) The thermo-electric method of determining temperature was employed. The thermo-electric couple used was one of German silver and iron, giving, between 0° C. and 200° C., a uniform deflection on the galvanometer scale of about four divisions for a difference of one degree centigrade between the temperatures of its junctions.