

Measurements of the Height of a Large Drop of Mercury.

IN determining the surface tension of mercury and other liquid metals, many workers have used the method of measuring the height from the maximum section to the summit of a large drop. Most agree as to the method of setting on the maximum section, but a variety of ways are used to define the top of the drop. Two recent papers¹ describing measurements made after using every care to obtain pure mercury and high vacuum, and with no essential difference in technique except in the method of defining the summit of the drop, give respectively 515 ± 6.8 dynes and 432.2 ± 0.3 dynes for the maximum surface tension of mercury at 31° C. In view of this discrepancy and the fact that it corresponds to a difference of only about 0.2 mm. in height of the drop, the following notes on methods tried out in this laboratory may be pertinent.

(1) A collimated beam of light from a small distant source set carefully at the height of the drop shines over the summit, and the top of the drop is seen in the horizontal microscope, accompanied by diffraction lines. The definition is good, and the very small correction for diffraction can be determined by setting on to a similarly disposed mercury drop in the open laboratory, when the exact surface may be located by bringing a spherometer point almost into the surface and taking readings on both point and reflection.

(2) A card ruled with slanting lines is placed behind the drop and the setting is made on the intersection of the lines and their reflection.² The definition is sharp, but, of course, the telescope must be focused on the card and not on the drop, and there is thus a considerable horizontal distance between the points, the vertical separation of which must be measured. This increases any error due to inaccurate levelling, and, if the aperture is small, it is not easy to see reflections from a horizontal surface using a truly horizontal telescope.

(3) If the drop is enclosed in a box and light admitted through a ground-glass window on one side while observing through a window on the opposite side of the box, the drop appears as a sharply defined black body. What appears to be the upper surface of the drop, however, is really the lowest curve on the drop which will reflect rays coming from the top of the ground-glass window so that they pass into the telescope. The position of this curve depends on the size of the drop and its position relative to the top of the window. Using a window 4 cm. from the centre of a drop 6 cm. in diameter, the following readings were taken as the window was blackened out strip by strip from the top downward:

Height from top of drop to top of window.	Reading of microscope set on apparent top of drop.
1.0 mm.	3.343 mm.
2.2 "	3.328 "
5.1 "	3.274 "
8.3 "	3.222 "

The setting on the top of the drop, using method (1), was 3.367 mm., and the correction for diffraction about +0.01 mm. M. Kernaghan uses an enclosed drop and a ground-glass window, but the method of defining the summit is not very clearly stated. It is remarkable that the difference of 83 dynes quoted above is in the direction to be expected if the workers had used methods (2) and (3) respectively without completely eliminating the sources of error mentioned.

In spite of individual workers obtaining consistent values, the question of the value of the surface tension of mercury in vacuum remains unsettled, and it is obviously desirable that workers should check their

readings for the top of the drop by using two distinctly different methods of illumination and finding if the setting is unaltered. It may be said that measurements made here, both with glass and using an apparatus entirely of fused silica made by the Thermal Syndicate, indicate a greater height for the drop than those recorded by M. Kernaghan.

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July 10.

¹ Cook, *Phys. Rev.*, August 1929, and Kernaghan, *Phys. Rev.*, April 1931.

² Cook, *l.c.*

Polarity and Vapour Pressure.

IN considering the effect of polarity on the vapour pressure and association of a liquid, a simple case is its influence on the partial vapour pressures of a polar liquid in its binary mixtures with a non-polar liquid, which, except for lack of polarity, should preferably be closely related in chemical structure to the polar liquid.

It is convenient to consider as 'perfect' a solution in which the restraining force on a polar molecule about to be vaporised is the same as in an infinitely dilute solution of the polar in the non-polar liquid. Perfect solutions are then represented by the tangent to the partial vapour pressure curve of the polar liquid at the limit of zero concentration. It is proposed to consider the effect of polarity in producing deviations from this tangent. To take deviations from Raoult's law as measures of imperfection is unsatisfactory, since to do so implies that all pure liquids are perfect, whilst admitting that mixtures of liquids may be imperfect.

Let the activity of the polar liquid be equal to b times its vapour pressure. Then in a perfect solution the free energy (F_i) of the polar liquid per molecule is $kT \log_e bp_i$, where p_i is the partial vapour pressure of the polar liquid, and k is Boltzmann's constant. Let the partial vapour pressure of the polar liquid in a solution of the same concentration in reality be p : the corresponding free energy (F) being $kT \log_e bp$. The free energy of transference of a molecule from a perfect to a real solution of the same concentration is $F - F_i = kT (\log_e bp - \log_e bp_i)$, that is

$$\frac{p}{p_i} = e^{(F - F_i)/kT}.$$

For such a dipolar molecule as is under consideration, F may be identified with the energy due to the field of the dipole in a medium of dielectric constant equal to that of the real solution of the concentration involved. Similarly F_i is the energy in a medium of dielectric constant equal to that of the pure non-polar liquid (since under perfect conditions the environment of a polar molecule remains the same as in an infinitely dilute solution in the non-polar liquid). If the polar molecule be treated as two charged spheres in contact with each other, for simplicity assuming that each sphere is completely immersed in the dielectric and integrating up to a sphere, the radius of which may be called the molecular radius, it has been shown¹ that this energy is given by $\mu^2/3a^3D$, where μ is the dipole moment, D is the dielectric constant, a is the molecular radius. Therefore

$$\frac{p}{p_i} = e^{-\frac{\mu^2}{3a^3kT} \left(\frac{1}{D_i} - \frac{1}{D} \right)}$$

Unfortunately the data required to test this relation are very scanty. The values of a necessary to