

from liquid helium II, or an analogous substance, if such exists; since a temperature difference across a semi-permeable membrane separating two masses of such a mixture would normally lead to a flow of heat, by means of the permeable component, which would ultimately result in the disappearance of this difference. In the case of liquid helium II, however, where the semi-permeable membrane is replaced by a fine capillary through which only the superfluid component may pass, a continuing temperature difference is possible because the superfluid, having zero entropy, is entirely incapable of transporting any heat from one container to another. If this analysis is correct, the supposed zero entropy of the superfluid component has a practical rather than a theoretical importance for the thermo-mechanical effect in liquid helium II.

*Note added in proof.* The more general relationship  $(\partial p/\partial T)_B = \rho s$  may be derived immediately from equation (8) by varying conditions in  $A$  while keeping those in  $B$  constant.

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<sup>1</sup> London, F., *Nature*, **141**, 643 (1938).

<sup>2</sup> Gorter, C. J., *Physica*, **15**, 523 (1949).

<sup>3</sup> Smits, A., "Die Theorie der Allotropie" (Barth, 1921).

<sup>4</sup> London, H., *Proc. Roy. Soc., A*, **171**, 484 (1939).

### Molecular Weight and Volatility

I WISH to direct attention to the fundamental effect of molecular mass on volatility, since it does not support the widely accepted view that volatility decreases with increase in molecular weight. The latter view relies on the various *empirical* relationships between molecular weight and boiling point, but it has no theoretical basis. Indeed, detailed arguments will be presented elsewhere suggesting that these empirical relationships are fortuitous and that the apparent increase in boiling point with molecular weight is due to other causes. By contrast, the *fundamental* effect of mass on volatility has a theoretical background and affords a rational explanation of certain boiling-point 'anomalies'.

The fundamental effect is clearly revealed by the comparison of vapour pressures of compounds differing only in isotopic composition ('isotopic molecules'). These comparisons are least complicated by differences in intermolecular forces, and it can be assumed that differences in vapour pressures are due to the effects of mass alone. The relative vapour pressures of 'isotopic molecules' vary in a complex manner, and it is intriguing to find that the lighter species is not always the more volatile. In fact, the review by Clusius<sup>1</sup> of hydrogen and deuterium compounds shows that the relative vapour pressures vary with temperature in the sense that higher temperatures favour the volatility of the heavier species. Similar behaviour by other 'isotopic molecules' was reported by Urey<sup>2</sup> and Stokland<sup>3</sup>. However, this peculiar behaviour is explicable in terms of statistical thermodynamics<sup>1,2,4</sup> although a rigorous treatment seems to be confined to simple cases such as that given by Ubbelohde<sup>5</sup>.

If this mass-effect is fundamental, then it should be a general phenomenon recognizable whenever

vapour pressures of two compounds are compared. However, it is a second-order effect usually obscured by the greater effect caused by differences in intermolecular forces, and is only disclosed in favourable circumstances, for example, isotopic molecules. Nevertheless, a novel example of this phenomenon was recently reported by Bradley, Mehrotra and Wardlaw<sup>6</sup>. They found that some tetra-alkoxides of hafnium,  $\text{Hf}(\text{OR})_4$ , were more volatile than the corresponding alkoxides of the lighter element zirconium, and preliminary vapour-pressure measurements showed the molar heats of vaporization of the tertiary amyloxides  $M(\text{OCMe}_2\text{Et})_4$  ( $M = \text{Zr}$  or  $\text{Hf}$ ) to be practically equal. Clearly, because of the equalization of intermolecular attraction, due to shielding of the central atom, the fundamental effect of mass on volatility is being asserted in a 'super-isotope effect'. Moreover, this theory predicts a super-isotope effect as a general phenomenon occurring in centro-symmetric systems such as  $M^{\text{I}}X_n$  and  $M^{\text{II}}X_n$ , where  $M^{\text{I}}$  and  $M^{\text{II}}$  are  $n$ -valent elements with nearly identical atomic radii and  $X$  is a univalent shielding group. Besides zirconium and hafnium, it seemed likely that compounds of niobium and tantalum and also molybdenum and tungsten might fulfil these conditions. A survey of the literature revealed that this is indeed the case, as is shown in Table 1, which gives data for pairs of compounds in which the heavier species is the more volatile.

Table 1

	NbF <sub>5</sub> : TaF <sub>5</sub> (ref. 7)		NbCl <sub>5</sub> : TaCl <sub>5</sub> (ref. 8)		MoF <sub>6</sub> : WF <sub>6</sub> (ref. 9)	
Formula weight	187.9	275.9	270.2	358.2	210.0	297.9
Boiling point, °C.	234.9	229.2	254.0	239.3	35.0	17.5
Radius of central atom (A.) (ref. 10)	1.34	1.34	1.34	1.34	1.36	1.37
Molar heat of vaporization (k.cal./mole)	12.9	13.0	13.2	13.6	8.34	8.69

The relative boiling points of these 'anomalous' pairs are quite inexplicable in terms of the conventional empirical rule connecting volatility and molecular weight, yet this behaviour is expected on the basis of what is here proposed as the fundamental effect of molecular weight on volatility. This theory will be presented in full elsewhere; meanwhile, experimental work is proceeding to test further these ideas.

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<sup>1</sup> Clusius, K., *Z. Elektrochem.*, **44**, 21 (1938).

<sup>2</sup> Urey, H. C., *J. Chem. Soc.*, 576 (1947).

<sup>3</sup> Stokland, K., *Kgl. Norske Videnskab. Selskabs Forh.*, **12**, 122 and 126 (1939).

<sup>4</sup> Bradley, D. C., *Nature*, **173**, 260 (1954).

<sup>5</sup> Ubbelohde, A. R., "Modern Thermodynamics", 169 (Oxford, 1952).

<sup>6</sup> Bradley, D. C., Mehrotra, R. C., and Wardlaw, W., *J. Chem. Soc.*, 1634 (1953).

<sup>7</sup> Frith, W. C., and Fairbrother, F., *J. Chem. Soc.*, 3051 (1951).

<sup>8</sup> Alexander, K. M., and Fairbrother, F., *J. Chem. Soc.*, S 223 (1949).

<sup>9</sup> Burg, A. B., "Fluorine Chemistry", **1**, 113 (Academic Press Inc., 1950).

<sup>10</sup> Sidgwick, N. V., "The Chemical Elements", **1**, xxix (Oxford, 1950).