43. *The Vapour Pressure of Metallic Indium.*

By J. S. Anderson.

The vapour pressure of metallic indium has been determined by the effusion method between 800° and 1100°, corresponding to vapour pressures of 10^{-4} to 10^{-1} mm. The vapour pressure may be represented by $\log_{10}p = -12180/T + 8{\cdot}003$, whence the normal boiling point of the metal is calculated as approximately 2100°.

The measurements now reported were made, in the first place, in order to explain some observations as to the behaviour of traces of indium during the processes of large-scale, non-ferrous metallurgy. The behaviour of trace constituents of metal ores during the smelting of tin, lead, zinc, and copper is closely bound up with the problem of recovering indium and other rare elements on a technical scale from various smelter by-products. The vapour-pressure measurements serve also to fill a gap in the recorded physical properties of the elements of Group IIIB, since the vapour pressure of gallium has been measured by Harteck (*Z. physikal. Chem.*, 1928, **134**, 1), and that of thallium by Egerton and Coleman (*Phil. Trans.*, 1935, *A*, **234**, 177).

Experimental.

Material.—The indium was a sample extracted from Australian sources. Spectrographic analysis and comparison with samples obtained from Messrs. A. Hilger and from American technical sources indicated that the purity was probably not less than 99·9%. The principal impurities were traces of copper, nickel (which seems to be an invariable impurity in metallic indium), and tin, with small traces of cadmium and lead. Only the last two elements are more volatile than indium, and their amount would be insufficient to introduce any significant errors in the observed vapour pressures.

Measurements.—The vapour-pressure measurements were made by the Knudsen effusion method, whereby the mass of substance evaporating in time t through an aperture, from an enclosure in which there is equilibrium between vapour and condensed phase, into a high vacuum, is related to the vapour pressure by the equation

$$p = (GW/t)\sqrt{RT/M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where G is the weight evaporating, M is the molecular weight of the vapour, and W is the "resistance" of the aperture. For a hole, $W = \sqrt{2\pi/a}$ (where a is the area of the aperture); for a circular tube of length L and radius R, $W = \sqrt{2L/\pi R^3}$.

The general form of the apparatus followed the lines used by other workers (*e.g.*, Egerton and Coleman, *loc. cit.*). The indium was contained in a silica liner, within a small steel crucible, closed by a lid in which was the measured effusion aperture. The lid was ground away in the centre, so that the resistance of the aperture was practically that of a pure hole; a small correction could then be applied, if necessary, for the added resistance of the equivalent tube. Two different effusion apertures were used, with diameters of 1·975 mm. and 1·420 mm. These were measured under the microscope, and checked for circularity.

The silica apparatus was heated in an electric furnace. Temperatures were measured by a calibrated chromel–alumel thermo-junction, placed in direct contact with the steel crucible, and a potentiometer.

In effusion measurements, the procedures usually employed have been either (*a*) the vacuum-start method, in which the apparatus is first evacuated before being heated to the required temperature, or (*b*) the method in which an inert-gas atmosphere is pumped out only when the desired temperature has been attained. Either method is apt to introduce some uncertainty, *i.e.*, as to either the effective duration or the effective temperature of the experiment. Egerton and Coleman's method, whereby the effusion aperture is uncovered only after the steady state has been reached, furnished the most precise results. As, however, it was not possible to adopt this procedure, the following modification of the vacuum-start method was employed and gave very consistent results.

The furnace was brought up to the desired temperature, and the apparatus was evacuated to 10^{-4}—10^{-5} mm. pressure. The furnace was then raised about the silica tube containing the crucible, and the temperature of the crucible was measured at regular intervals (1 or 2 mins.) until, after 10—20 mins., the steady state was reached. Thereafter, temperature readings were made at intervals of 10—15 mins. to permit of furnace regulation, and to correct for temperature fluctuations in the final evaluation of the data. The usual duration of the experiments was 150—600 mins.

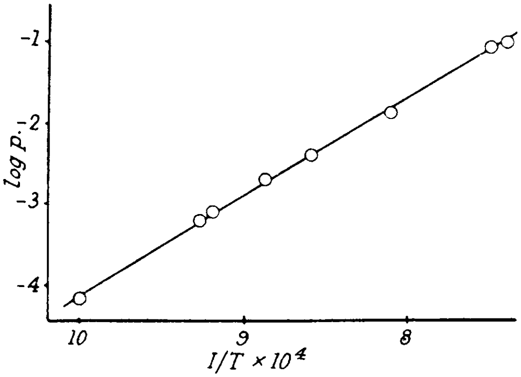
As a first approximation, the time for which the crucible was at the effective temperature of the experiment, $T_{\text{eff.}}$, was estimated directly from the observations; thence, an approximate vapour-pressure curve was constructed. Then, if $p_{\text{eff.}}$ be the vapour pressure at $T_{\text{eff.}}$, and p that at any other temperature T, we have that the total weight of material G effusing from the crucible in the time t is

$$G = Kp_{\text{eff.}}\, t_{\text{eff.}} = K\int_0^t p\,\mathrm{d}t$$

$$= Kp_{\text{eff.}}\int_0^t (p/p_{\text{eff.}})\mathrm{d}t$$

$$i.e.,\ t_{\text{eff.}} = \int_0^t (p/p_{\text{eff.}})\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$t_{\text{eff.}}$ being the effective time of the experiment. The value of $p/p_{\text{eff.}}$ at the moment of each temperature reading can be obtained with sufficient accuracy from the approximate vapour-pressure curve and the temperature record of each run. If the values of $p/p_{\text{eff.}}$ be then plotted against the time, the integral of equation (2) can be evaluated graphically, thereby determining $t_{\text{eff.}}$. This corrected time may then be used in equation (1) to recalculate the true vapour pressure at $T_{\text{eff.}}$.



The vapour pressure of metallic indium.

In calculating the vapour pressures from the effusion data, it was assumed that the vapour of indium is monatomic. This assumption, which might not be admissible in the case of gallium (cf. Harteck, *loc. cit.*), is here reasonable, since although indium does not crystallise in one of the close-packed metallic structures, there is no evidence of association in the solid.

A correction was applied to take account of the decrease in resistance of the effusion aperture consequent on the thermal expansion of the steel crucible. This effect is not quite negligible at the highest temperatures.

Results.—The experimental data are summarised in the following table. The observed vapour pressures, listed in col. 6, lie very well on the straight line

$$\log_{10} p = -12180/T + 8{\cdot}003 \quad . \quad . \quad . \quad . \quad (3)$$

as may be seen from the figure. From this expression are calculated the vapour pressures given in the last column. The average deviation of the results from the calculated values is not more than 8%, which, having regard to the rapid variation of vapour pressure with temperature, and the difficulty of avoiding temperature fluctuations at high temperatures, may be regarded as satisfactory.

Temp.	$T°$, K.	Diam. of aperture, mm.	$t_{\text{eff.}}$, mins.	G, mg.	$p_{\text{obs.}}$, mm.	$p_{\text{calc.}}$, mm.
727°	1000°	1·420	294·0	0·35	$6{\cdot}26 \times 10^{-5}$	$6{\cdot}65 \times 10^{-5}$
807	1080	1·975	546·8	11·2	$5{\cdot}78 \times 10^{-4}$	$5{\cdot}35 \times 10^{-4}$
815	1088	1·975	245·3	6·7	$7{\cdot}72 \times 10^{-4}$	$6{\cdot}50 \times 10^{-4}$
855	1128	1·420	128·4	3·57	$1{\cdot}55 \times 10^{-3}$	$1{\cdot}60 \times 10^{-3}$
890	1163	1·975	207·0	26·5	$3{\cdot}74 \times 10^{-3}$	$3{\cdot}58 \times 10^{-3}$
960	1233	1·420	213·7	44·8	$1{\cdot}22 \times 10^{-2}$	$1{\cdot}35 \times 10^{-2}$
1060	1333	1·975	86·3	231·4	$8{\cdot}36 \times 10^{-2}$	$7{\cdot}50 \times 10^{-2}$
1075	1348	1·420	147·8	228·8	$9{\cdot}38 \times 10^{-2}$	$9{\cdot}40 \times 10^{-2}$

From the vapour-pressure equation (3), the b. p. of indium is calculated to be 2382° K./760 mm. This, however, depends upon a very long extrapolation from the observed data, and it is probably more reliable to make a comparison with the data recorded for thallium, using Egerton and Coleman's vapour-pressure curve (*loc. cit.*) and the normal b. p. of thallium, *viz.*, 1730° K. (Leitgebel, *Z. anorg. Chem.*, 1931, **202**, 305). This gives for indium $T_{760} = 2360°$ K., which is probably close to the true value. With reference to the original topic of investigation, it is apparent that indium is more volatile than is tin, and is thus somewhat enriched in tin smelter flue dusts, as compared with the bulk of the furnace charge. Indium is, however, very much less volatile than lead or the metals of the zinc–cadmium group, and any indium present remains in the retort residues when those metals are refined by distillation.

Below, we collect the available data for the metals of Group IIIB. There is a steady trend apparent in the " liquid ratio," $(T_{760}-T_m)/T_{760}$ (Hume-Rothery, *J. Physical Chem.*, 1940, **44**, 808), from gallium to thallium, but the b. p. of gallium appears to be lower than would be expected.

Element.	T_m, °K.	T_{760}, °K.	Liquid ratio.	Latent heat of evaporation, cals.
Ga	302·8	2300	0·868	—
In	429·4	2370	0·819	55,400
Tl	430	1730	0·751	39,700

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