85 % Sn or 16 % Sb and 84 % Sn by whirling at a constant temperature of 270° (the commencing solidifying points of the alloys are 284° and 290°) are partly found loose (fig. 2); near the narrowing of the tube they are partly united to a loose cake by the adhering motherliquor.

By mixing with 1 % of Ag it could be ascertained how much motherliquor had been retained by the crystals (VAN BYLERT, l. c.).

The amount of Ag in the loose crystals was so small that it could not be estimated. In the loose crystalline cake 8 % of motherliquor, was found.

The crystals contain 32.5 % of Sb, Sb Sn$_2$ contains 33,6 % of Sb. In the case of Sn Cu crystals (fig. 3) which were obtained by whirling at 300° an alloy containing 4.5 % of Cu, the amount of loose crystals is much smaller and insufficient for analysis.

Several alloys containing 4.5 % of Cu were therefore whirled and the loose crystals (fig. 3) collected as far as possible and analysed. Found 67,9 % of Sn, calculated 65 % of Sn.

The crystals cannot therefore be completely freed from motherliquor by whirling, but by operating in this manner it will be as a rule easy to ascertain whether pure metals, compounds or mixed crystals are deposited from the alloy.

If a change takes place in the composition of the alloy, the separated crystals in the first two cases will remain of constant composition within a few per cent, while in the case of mixed crystals a gradual change will be observed.

Physics. — Communication n⁰ 78ª from the Physical Laboratory at Leiden: "*Isotherms of diatomic gases and their binary mixtures. II. The determination of density with the piezometer of variable volume for low temperatures*". (By Prof. H. KAMER-LINGH ONNES and H. H. FRANCIS HYNDMAN).

§ 7. *The measurements.*

These are of two kinds. 1st. The density being given in terms of the normal density d_N (at 0.0° C. and 1 At.) the quantity of gas contained in the piezometer tube is determined by measurements of the normal volume V_N. 2nd. The volume of the compressed gas is measured under known conditions of pressure and temperature. The measurements of V_N are made both before and after the measurements at higher pressure. In general this is very desirable and

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to make it possible the closure of the piezometer tube by a U-tube with mercury was devised (see Comm. n⁰ 50). In our case however it is absolutely necessary because the screw joints g_2, g_3 (Comm. n⁰ 69) can develope a leak.

1. The normal volume is in principle determined in the manner employed by SCHALKWIJK Comm. n⁰ 70 V.

The bath used by him was not large enough to enclose the whole piezometer, but only the whole of the large volume. The graduated stem b_4 and the piezometer bulb were thus outside the bath and the constancy of the temperature of these parts had to be otherwise provided for. Had we sought the same accuracy as required by SCHALKWIJK, a new waterbath of the total length of the piezometer would have been required.

However as we could not from the other measurements expect such a high accuracy, we were satisfied here also with a somewhat less degree and found that the temperatures of the divided stem b_4 and of the piezometer bulb f_1 could be sufficiently determined by the use of simple water baths. Owing to the great length of the large reservoir and to its near equality with that of the bath for constant temperature, it was particularly necessary to avoid real differences in temperature between the bottom and top of the bath. To attain this it was necessary to arrange that the temperature of the room should not differ more than a few degrees from that of the bath. The latter was thus set at a temperature that could be reasonably attained in the room, and the room kept as near as possible to this temperature.

A small change was also made in the xylene regulator. The tube t (see Plates, Comm. n⁰. 70, III) which was formerly of glass was now brass above and steel where it entered the mercury, the requisite form could thus be given to the end and narrower tubes employed. In this way a greater sensitiveness was attained combined with an adjustability of some five degrees by merely moving the upper brass tube up or down in its brass support, without the troublesome removal or addition of mercury which was necessary before and which would also be required for greater changes.

The thermostat was also raised some 1.5 M. to obtain a quicker flow, which was shown to be desirable before (Comm. n⁰. 70, V).

In the earlier measurements the pressure was read by a controlled aneroïd at intervals. When however the barometric height is changing rapidly a larger error may arise from this than is allowable. In the later measurements the arrangement of Comm. n⁰. 60 was employed, the joint b (Plate II, Comm. n⁰. 69) being connected by

glass tubes to an air reservoir at 0.0° C. and a barometer, the whole forming a perfectly closed system at constant pressure. The barometer was placed on a screw stand of the type of Comm. n⁰. 60 and was read by the cathetometer used to read the mercury menisci in the U-tube of the piezometer.

The normal volume was ordinarily determined at least twice both before and after the measurements of compressed volume.

2. When the normal volume has been determined the piezometer tube is removed to the pressure cylinder A (Plate I, Comm. n⁰. 69) previously filled with mercury, it is then carefully warmed so that the air shall be completely expelled from the outer leg of the U-tube. When this operation is finished the small piezometer reservoir is brought into the bath necessary for the particular constant temperature required for the isotherm ; the construction of this bath and the constancy of the temperature will be considered with the various isotherms.

The graduated tube b_4 is kept at a constant temperature by a stream of water through the water bath b_8 from a similar thermostat to the one above mentioned. Although this must be at a distance of 10 M. the connecting tube is so well wrapped with wool that the temperature at b_4 is constant to 0.02 deg C. It was set at either 15.6° C. or 20.0° C. and determined to the above accuracy.

Finally we must consider the temperature of the steel capillary which sometimes is 130 cm. long and owing to its exposed position usually shows considerable differences of temperature although it was carefully wrapped in wool and enclosed in paper. In many cases the difference at different parts reaches 1 deg. C. As however the influence of this uncertainty depends upon the relative volumes of the capillary and the piezometer, this question will be further considered with the measurements.

§ 8. *The calculation of the measurements.* 1. *The normal volume.*

For this calculation we divide the volume of gas in the piezometer tube into 4 parts (Comm. N⁰. 69) at the four temperatures t'_1, t'_3, t'_4, t'_5. The constants are as follows:

V'_1 the volume of the small piezometer reservoir f_1 with the glass capillary f_2

V'_3 of the steel capillary from f_2 to a mark on the top of the glass tube b_5

V'_4 from this mark to the zero point of b_4

V'_5 from this zero point to the zero point of the U-tube b_2

v' from the zero point to the surface of the meniscus in the graduated leg of the U-tube [1])

B the pressure on the outer meniscus of U-tube

H the height of the top of the meniscus in the outer above the top of that in the graduated limb
expressed in cms of mercury at 0.0° C. at Leiden.

h, h' the capillary depressions of the menisci in the graduated and outer limbs of the U-tube

A the pressure of 1 atmosphere.

Then neglecting the differences in PV_A due to the difference between the pressure at the mercury meniscus in the graduated limb of the U-tube and A, and also the difference between this pressure and the mean pressure of the gas together with the change in the mean expansion coefficient α_N from 0.0° C to the various temperatures we have

$$V_N = \frac{B + H - h + h'}{A}\left\{\frac{V'_1}{1 + \alpha_N t'_1} + \frac{V'_3}{1 + \alpha_N t'_3} + \right.$$
$$\left. + \frac{V'_4}{1 + \alpha_N t'_4} + \frac{V'_5 + v'}{1 + \alpha_N t_5}\right\}$$

which is more convenient for calculation when written

$$V_N = \frac{B + H - h + h'}{A}\left\{ V_1 + V_3 + V_4 - v_1 - r_3 - v_4 + \frac{V_5 + v' + v''}{1 + \alpha_N t_5}\right\}.(1)$$

where V_1, V_3, V_4, V_5 are the volumes of the various parts at 17° C. found by calibration and

$$v_1 = V_1 \alpha_N t'_1, \quad v_3 = 17\, V_3\, \alpha_N, \quad v_4 = V_4\, \alpha_N t'_4, \quad v'' = V_5\, k\, (t_5 - 17).(2)$$

where k is the expansion coefficient of the glass and

$$\alpha_N = \frac{1}{v_0}\left[\left(\frac{\overline{dv}}{dt}\right)_p\right]_0^{17} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The last corrections can be conveniently tabulated.

2. *The measurements at higher pressure.* In this calculation we may neglect the corrections for the capillary depression in the graduated tube b_4 (the inner diameter is about 0.6 c.m.), and for the pressure of the gas due to its own weight, which corrections can easily be applied to the result if necessary.

The volume of gas under the pressure p at the surface of the meniscus in b_4 is divided into four parts each at its own temperature

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[1]) The volume of the supplements of the menisci used are all determined after Comm. N° 67, I.

t_1, t_2, t_3, t_4, which parts do not correspond exactly with those of the former calculation. Let (cf. Plate II, Conn. N⁰. 69) U_1 be the volume of the small piezometer reservoir with x cm. of glass capillary, U_2 that of the remaining glass capillary, $U_3 = V_3$ again that of the steel capillary with the joints g_2 and g_3 to a mark on b_5, U_4 the remaining volume from this to the mean mercury meniscus.

The volumes are all calculated to 17° C. and so with sufficient accuracy we may put the volumes U_1', U_2', U_3', U_4', of these parts at the temperatures t_1, t_2, t_3, t_4 under the pressure p as

$$U_1' = U_1 + w_1 + w_1', \ U_2' = U_2, \ U_3' = U_3, \ U_4' = U_4 + w_4 + w_4' \Big\}$$
$$w_1 = k (t_1 - 17) U_1, w_4 = k (t_4 - 17) U_4, w'_1 = \beta_1 p \ U_1, w_4' = \beta_4 p U_4 \Big\} \quad . \ (4)$$

where β_1 and β_4 are the coefficients for the elastic deformation of the glass walls calculated after the formulae of CLEBSCH and LAMÉ which agreed satisfactorily with some direct determinations.

If we call V_{N1} the normal volume of the gas in the piezometer volume U_1' and V_{N2} that of the gas in U_2, U_3, U_4 together then is

$$V_{N1} = V_N - V_{N2} = V_N - (U_2 \ d_{Apt2} + U_3 \ d_{Apt3} + U_4 \ d_{Apt4}) \ . \ . \ (5)$$

where d_{Apt2} etc. are the densities at p and t_2 etc. in terms of the normal density.

If further we call τ_2 etc. the difference $t_x - t_2$ of the temperatures t_2 etc. from a given temperature t_x not far removed from them at which the values of d_{Apt} are known.

Let U_2'', U_3'', U_4'' be such quantities that $U_2'' d_{Aptx} = U_2' d_{Apt3}$, etc. and put

$$U_2'' = U_2' + u_2 \text{ etc.,} \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (6)$$

If then we replace d_{Apt} by (pv_A), where the volume v_A of the gas is expressed in terms of the normal volume, we have with (5)

$$(pv_A)_{t1} = \frac{p}{d_{Apt1}} = \frac{pU_1'}{V_N - \dfrac{p}{(pv_A)_{tx}} \Big\{ U_2'' + U_3'' + U_4'' \Big\}} \ . \ . \ . \ (7)$$

The quantities u_2 etc. in (6) are calculated by

$$u_2 = \alpha_{p2} \ U_2 \ \tau_2, \quad u_3 = \alpha_{p3} \ U_3 \ \tau_3, \quad u_4 = \alpha_{p4} \ U_4 \ \tau_4 \ . \ . \ (8)$$

where owing to the small difference of t_4 from t_x, either at 15.°6 C. or 20.°0 C.

$$\alpha_{p4} = \left[\frac{1}{v_A} \left(\frac{dv_A}{dt} \right)_p \right]_{t_x} \ . \ . \ . \ . \ . \ . \ (9)$$

as t_3 lies between 15.°6 and 20° C. we put

$$\alpha_{p3} = \left[\overline{\frac{1}{v_A} \left(\frac{dv_A}{dt} \right)_p} \right]_{15.6}^{20} \ . \ . \ . \ . \ . \ (10)$$

assuming the same mean expansion coefficient for all cases, but

$$\alpha_{p2} = \frac{1}{-v_{t_2}} \left[\left(\overline{\frac{dv_A}{dt}} \right)_p \right]_{t_2}^{t_\alpha} \quad \cdots \cdots \quad (11)$$

must be determined for each value of t_2.

After determining $(pv_A)_{t_1}$ it is necessary to reduce it from its value at t_1 to that of the required isotherm t_s not much removed from it, this reduction is only possible when approximate values of the change in $(pv_A)_{t_1}$ due to temperature are known.

If we put $\tau_1 = t_s - t_1$ we have

$$(pv_A)_{t_s} = (pv_A)_{t_1} (1 + u_1) \quad \cdots \cdots \quad (12)$$

$$\text{where } u_1 = \alpha_{p1} \tau_1 = \left[\frac{1}{V_A} \left(\frac{dv_A}{dt} \right) \right]_{t_1 p} \tau_1, \quad \cdots \cdots \quad (13)$$

for the reduction at constant pressure, and correspondingly

$$(pv_A)_{t_s} = (pv_A)_{t_1} (1 + u'_1) \quad \cdots \cdots \quad (14)$$

$$\text{where } u'_1 = \alpha_{v_1} \tau_1 = \left[\frac{1}{p} \left(\frac{dp}{dt} \right) \right]_{t_1 V_A} \tau_1 \quad \cdots \cdots \quad (15)$$

for the reduction at constant volume, and thus to another pressure.

§ 9. *The constants necessary for the calculations.*

$A = 75,9467$ cm. after Comm. no. 60.

k was assumed at the ordinary temperature to be equal to $0,000024$ as for the kind of glass used it cannot differ much from that of Jena glass.

The values of α_v and α_p are calculated for each gas from the series of Comm N⁰. 70 when no better data are at hand.

In the calibrations of graduated tubes and determinations of the volumes V and U no very special precautions where taken beyond those oidinarily employed in accurate calibration. U_1 was determined by treating the piezometer as a barometer, pumping free of gas and filling in vacuum, it was then placed in ice. U_2 was calibrated by a mercury thread. U_3 can be directly determined by screwing the end g_1 of the steel capillary onto the end of b_5 and providing the other end of the capillary with a steel connecting tube carrying a glass cock. By connecting b_2 to the air pump the whole can be then well evacuated and the mercury slowly admitted through the above mentioned cock, until it reaches above the top divisions of the tube b_4. When dry air has been admitted the tube is placed vertically and the steel connecting tube carefully removed. By adjustment the mercury is brought just to the end of the capillary and its position in the tube b_4 read by a cathetometer, the temperature being also observed. To check these determinations the volume is calibrated in parts, the steel capillary after the method of Comm. N⁰. 60 and the glass either by a mercury thread or by screwing

a nut carrying a glass cock unto b_5, evacuating and reading as before
In the same way the area of the graduated tube b_4 was determined
but with more precautions as to constancy of temperature, and of
the large volume V_5 with the area of b_2. The precautions as to
constancy of temperature and accuracy of reading and weighing were
always referred to a higher accuracy than the one actually sought.

Physics. — Communication n⁰. 78ᵇ from the Physical Laboratory
at Leiden: "*Isotherms of diatomic gases and their binary
mixtures. III. The isotherms of Oxygen at* 20.°0 *C.* 15.°6 *C.*
0°.0 *C."* (By Prof. H. KAMERLINGH ONNES and H. H.
FRANCIS HYNDMAN).

(Communicated to the meeting of March 29, 1902).

§ 10. *The purpose of the research at ordinary temperatures.*
Measurements were made in this region for two purposes.

1⁰. In order to calculate our observation at low temperatures by
equation (7) it is necessary to know the values of pv_A at the given
pressures to at least the same accuracy as that sought for in the
measurements at low temperatures. In Comm. n⁰. 69, § 6 we have

given $\dfrac{1}{1000}$ as the accuracy aimed at and to this accuracy there

are no data at present available. The most trustworthy measurements
of AMAGAT [1]) commence at 100 At. and even should they have no
constant error they do not admit of interpolation for the values of
pv_A to this accuracy.

2⁰. We wished to so test our apparatus at ordinary temperatures
in a region where the results could be compared with and linked
into the above mentioned measurements of AMAGAT, that we could
satisfy ourselves of the accuracy of the method at low temperatures.

Measurements were made at 15°.6 C. to compare directly with
AMAGAT, but the majority at 20° C. because it is a more generally
useful temperature and can always be obtained. At the same time
as the measurements at ordinary temperature we give a series at
0.0 C. as this can also be directly compared with AMAGAT.

With the help of these measurements we can improve the coeffi-
cients in the series for pv_A given in Comm. n⁰. 71 and can also
obtain the expansion coefficients required for the small temperature
differences τ_3 and τ_4, more accurately than heretofore.

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[1]) Ann. de Chim. et de Phys. 1893,