GeO_2 taken, g.	0.1789	.2536	.1699	.1674	.1791	.1797	.2757
GeO_2 found, g.	0.1785	.2538	.1701	.1674	.1786	.1797	.2745
GeO_2 taken, g.	0.2495	.2654	.1050	.1093	.1508	.2016	.2972
GeO_2 found, g.	0.2489	.2640	.1044	.1092	.1509	.2013	.2972

The method was then used in the determination of germanium in two different samples of germanium-bearing zinc oxide. The method of Dennis and Papish[3] was followed to the point of precipitation of the germanium sulfide. From there on, the procedure here described was employed. Three analyses of each sample were made.

ZINC OXIDE NO. 1

Crude oxide G.	GeO_2 found G.	GeO_2 found %
100	0.1112	0.111
100	.1116	.112
105	.1159	.110
	ZINC OXIDE NO. 2	
50	.1054	.211
60	.1259	.210
102	.2150	.211

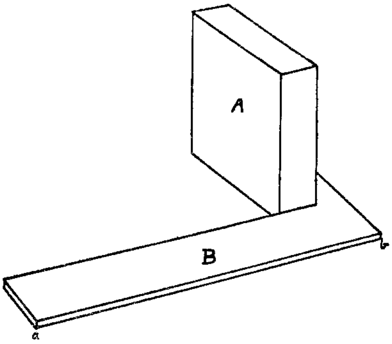
Summary

This article describes a method for the determination of germanium, in which the germanium is precipitated as the disulfide, the precipitate is oxidized with 3% hydrogen peroxide and the germanium is finally weighed as the dioxide.

ITHACA, NEW YORK

NOTES

A Simple Tangentimeter.—It is often of the utmost importance to the physical chemist to know the slope of a plotted curve at any point. It was to satisfy such a need that the instrument shown in the figure and described below was constructed and used, after a search for, and trial of the various methods given in the literature. The essential feature of the device is copied from a mechanical differentiator constructed and described by A. Elmendorf.[1] In the figure, A is a mirror (a plane polished block of speculum metal in this case) mounted on one leg of the steel square B, so that the mirror face extends to the plane of the bottom of the square and is normal to the edge ab.



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[1] Elmendorf, *Sci. Am. Suppl.*, Feb. 12, 1916.

When the mirror is standing across a given curve, and is normal to it, there will be no break between the curve and its image at the foot of the mirror; any deviation from the normal will cause a noticeable break. Obviously, then, the line ab will be parallel to the tangent at that point, and the numerical value of the tangent can be obtained from its intersection with the abscissas and ordinates of the paper on which the graph is plotted. This calculation is much simplified if ab is made of such length that ten or one hundred units can be used as one of the ordinates in calculating the tangent.

It is well to caution the novice that the curve must be drawn *very* smoothly or false tangents will result. With a little practise, considerable accuracy can be attained in the use of this instrument.

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RECEIVED MAY 24, 1924
PUBLISHED MARCH 5, 1925

The Influence of Intensive Drying on Inner Equilibria.—In relation to the publication of G. N. Lewis[1] concerning Baker's drying experiments, I will state here to prevent confusion that I had already discussed the problem in detail and published in the early part of 1922 an explanation corresponding exactly to that later published by Professor Lewis.

This explanation in its original form,[2] stated that by intensive drying the inner transformations in a unary phase are stopped and consequently the inner equilibrium is fixed and a mixture is obtained which, on distillation, generally gives a distillate with a lower boiling point and a residue with a higher boiling point than that of the original liquid. Further, it was concluded that the boiling points observed by Baker were abnormally high because the liquid mixture, before reaching the boiling point, had already partly evaporated.

After the publication of Baker's later investigations on the properties of extremely dry liquids[3] the author discussed these results in a chapter of his book "Theory of Allotropy" and considered, in view of these new experiments, whether the original explanation set forth above might be regarded as adequate, or should be supplemented by the assumption that the inner equilibrium is first displaced and then fixed. The conclusion arrived at was that for the purpose of providing a general explanation the original form should be supplemented by the assumption that, by the drying process, the inner equilibrium can be displaced—an assumption which is not in contradiction with thermodynamic considerations.

Moreover, the best way of answering the question as to what actually

[1] Lewis, THIS JOURNAL, **45**, 2836 (1923).

[2] *Z. physik. Chem.*, **100**, 477 (1922).

[3] Baker, *J. Chem. Soc.*, **121**, 568 (1922).

occurs during intensive drying was indicated, namely, by the determination of the vapor pressure, at the drying temperature, since a difference between the drying temperature and the temperature at which the vapor tension is measured, might have significance.

After this explanation of the behavior of an intensively dried liquid as a mixture had actually been verified,[4] Lewis' paper appeared, in which an explanation of Baker's observations is offered corresponding exactly with that which I had originally given. Lewis, however, makes no reference in his paper to my previously published explanation, either in the earlier or later form.

Although I have just published[5] a more detailed article on this point, it appears advisable to give here also a short statement of the results obtained. A year ago I and my assistants began experiments to determine whether the drying process is a fixation of the inner equilibrium or a displacement of the inner equilibrium, followed by a fixation, and probably these experiments will soon yield a solution to the problem. Furthermore, we have begun an extensive investigation of the influence of intensive drying on other properties of a large number of substances. Of these substances sulfur trioxide has already given most interesting results, behaving completely as a mixture, so that it has been possible to determine an important part of the pseudo-system.

Again, it had seemed to me that pure, freshly distilled phosphorus pentoxide, perhaps the dryest of all substances, would therefore be expected to be an extremely interesting material to study more closely. Accordingly, it was investigated, with the result that it confirmed completely my expectations of it, behaving very distinctly as a mixture over a wide range of temperature.

The first parts of the detailed reports of our work on these two substances, sulfur trioxide and phosphorus pentoxide, will appear shortly in the *Journal of the Chemical Society.*

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Moving Boundaries and the Phase Rule.—In a recent article[1] J. A. Beattie derived the phase rule as it applies to the equilibrium state of a system containing N components, P phases and S surfaces at which electric potentials exist. The equation is

$$F = N - P + S + 2 \qquad (1)$$

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[4] *Ann. Rep.*, **19**, 36 (1922).

[5] Smits, *J. Chem. Soc.*, **125**, 1068 (1924).

[1] Beattie, THIS JOURNAL, **46**, 2211 (1924).

in which F is the number of degrees of freedom. Beattie applied this equation, with success, to the equilibrium conditions of galvanic cells. It is of interest to note that the same equation applies as well to the equilibrium conditions obtained in the measurement of ionic mobilities by the moving-boundary method. As an illustration, consider the determination of the mobility of the potassium ion-constituent in potassium chloride, by means of a moving boundary between an indicator solution of lithium chloride and a solution of potassium chloride, represented by $LiCl \mid KCl$. The electrodes are considered to be so far removed from the boundary that the products of their reactions have no effect on its equilibrium conditions. In such a case, there are three components: water, lithium chloride and potassium chloride two phases and one surface of electric potential. Hence, $F = 3-2+1+2 = 4$. However, there is one restriction imposed on the equilibrium state of the system, namely, the velocity of the lithium ion-constituent must equal that of the potassium ion-constituent. It follows from this restriction that the relationship

$$C_{Li}/C_K = T_{Li}/T_K \qquad (2)$$

must be fulfilled,[2] in which C_{Li} and C_K represent the concentrations of lithium chloride and potassium chloride, respectively, and T_{Li} and T_K the corresponding transference numbers of the lithium and of the potassium ion-constituents. The number of degrees of freedom which can be applied to the variables is thus reduced to three. Now, there are four variables[3] to be controlled in this single boundary mobility determination, namely, temperature, pressure, concentration of potassium chloride, and concentration of lithium chloride, but only three of these are independent. It has been proved experimentally[4,5] that if the attempt is made arbitrarily to regulate all four of the variables, the measured mobility is not a constant, but varies with any arbitrary variation in the concentration of the indicator solution, or in the potential gradient. On the other hand, when Equation 2 is satisfied, and thus only three variables are taken arbitrarily, the mobility is a constant, as it should be, with respect to any variations in potential gradient (except, of course, when too large a current causes a heating effect greater than the thermostat can control). The phase rule, in the form derived by Beattie, considered in connection with the relation which must hold between the concentrations, indicates that erratic results might be expected unless Equation 2 is fulfilled, since otherwise the system is not in equlibrium. This does not mean that the phase rule predicts the Kohlrausch relationship, Equation 2, but it does indicate that there must be

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[2] Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

[3] Since mobility is defined as the velocity under unit potential gradient, neither the potential gradient nor the current can be counted as a variable.

[4] MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923).

[5] Smith and MacInnes, *ibid.*, **46**, 1398 (1924).

some relationship between two of the four apparent variables of the system, since only three of them can be independent.

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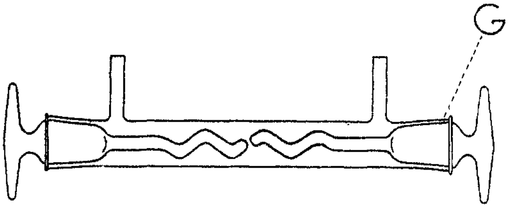
A Drying Tube for Phosphorus Pentoxide.—When phosphorus pentoxide is used for drying a gas, it is usually suspended on glass wool in an upright tube, or is spread over the lower half of a horizontal tube. In the first case phosphoric acid resulting from the union of pentoxide with moisture tends to clog the apparatus, and with a horizontal tube the surface of the phosphorus pentoxide soon becomes glazed and inactive.

If in this latter case the reagent could frequently be stirred or turned over, fresh oxide would be brought into contact with the gas, and the period of the efficiency of the drying agent would be greatly prolonged. To accomplish this, the tube shown in the figure was devised. It is used in the horizontal position, and is filled to about two-thirds its diameter with phosphorus pentoxide. The two hollow, glass stoppers in the end are very carefully ground and terminate in heavy glass rods which are bent as shown. The stoppers are lubricated with a rubber-vaseline-paraffin lubricant[1] at G to a distance of not over 5 mm. along the barrel of the stopper. The gas is passed in and out through the side arms. The phosphorus pentoxide in the tube can be stirred and fresh surface exposed simply by turning the two stoppers. The tubes that we have used have a length over all of 25 cm.



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Received November 12, 1924
Published March 5, 1925

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[1] Dennis, "Gas Analysis," The Macmillan Company, 1913, p. 115.