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 | 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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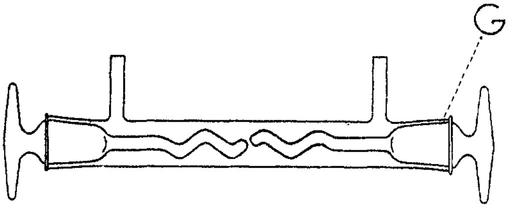
A Drying Tube for Phosphorus Pentoxide.—When phosphorus pentoxide is used for drying a gas, it is usually suspended on glass wool in an upright tube, or is spread over the lower half of a horizontal tube. In the first case phosphoric acid resulting from the union of pentoxide with moisture tends to clog 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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[1] Dennis, "Gas Analysis," The Macmillan Company, 1913, p. 115.