

The Critical Points of Ternary Systems with a Polymer Component

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Citation: *The Journal of Chemical Physics* **17**, 1006 (1949); doi: 10.1063/1.1747073

View online: <http://dx.doi.org/10.1063/1.1747073>

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Carrier-Free Radioisotopes from Cyclotron Targets. II. Preparation and Isolation of Cd^{109} from Silver*

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August 29, 1949

THE radionuclide, Cd^{109} , produced by the nuclear reaction $\text{Ag}^{109}(d, 2n)^1$ has been isolated without added isotopic carrier by a solvent-extraction procedure based on the selective solubility of cadmium pyridine thiocyanate in chloroform. Radioactive palladium, 13-hr. Pd^{109} , produced by the reaction $\text{Ag}^{109}(n, p)$, was allowed to decay out prior to the separation of 185-day Cd^{109} . This activity, however, is not extracted with cadmium and the method may be used in isolating 6.7-hr. Cd^{107} from an un-aged target.

The target was a block of spectrographically pure silver² ($\frac{1}{4}$ in. thick), soldered to a water-cooled copper plate. It was bombarded with 19-Mev deuterons for a total of 100 $\mu\text{a-hr.}$ in the 60-in. cyclotron at Crocker Laboratory. The bombarded surface of the silver was removed from the target by milling off to a depth of $\frac{1}{4}$ in.

The silver turnings were dissolved in a minimum volume of 16N HNO_3 and the solution was evaporated to dryness on a steam bath. The AgNO_3 plus activity was dissolved in 25 ml of H_2O and the silver was complexed with excess NH_4CNS . The solution was adjusted to pH 5 with sodium acetate and the Cd^{109} was extracted with chloroform containing 5 percent pyridine. This procedure, originally developed³ for the separation of micro amounts of cadmium, quantitatively extracted Cd^{109} from solutions containing presumably less than 10^{-8} g of stable cadmium.

To remove traces of silver, the chloroform phase was evaporated to dryness on a steam bath, redissolved in 2 to 3 ml of 1 percent H_2SO_4 , and extracted with 0.005 percent dithizone in chloroform.⁴ The final solution of Cd^{109} contained less than one microgram of silver.

A small portion of the activity was added to a solution containing silver and cadmium in carrier amounts, and the silver was precipitated as AgCl . Ninety-nine percent of the activity remained in the supernatant.

Absorption measurements in aluminum showed conversion electrons of approximately 0.1 Mev and the 22-keV x-ray of the Ag^{109} daughter. These data agree with the previously reported values.¹

The authors wish to express their appreciation to the crew of the 60-in. cyclotron for the bombardments, and to Mrs. Alberta Mozley and Mrs. Helen Haydon for technical assistance in counting.

* This document is based on work performed under Contract No. W-7405-eng-48-A for the AEC.

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¹ A. C. Helmholtz, Phys. Rev. **70**, 982 (1946).

² The silver was obtained from Johnson Matthey and Company. Cadmium was not detected by spectrographic analysis.

³ H. Fischer and G. Leopoldi, Mikrochim. Acta **1**, 30 (1937).

⁴ E. B. Sandell, *Colorimetric Determination of Traces of Metals* (Interscience Publishers, Inc., New York, 1944).

The Critical Points of Ternary Systems with a Polymer Component

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August 31, 1949

IN a recent paper R. L. Scott¹ has derived two equations giving the critical or plait points of ternary systems containing one-polymer component. As these equations are of the third and fourth order, respectively, they have twelve solutions, of which Scott has shown two to be spurious; he has shown how to calculate the remaining ten roots for polymers of infinite chain-length, and has indicated how to obtain the roots for large polymers as expansions by the reciprocal chain-length.

It is the purpose of this note to show that one more of the solutions is spurious and to indicate a numerical method for calculating the nine plait points for any value of the chain-length, should this be required.

Introducing constants $\mu_1 = \mu_{12} + \mu_{13} - \mu_{23}$ and similarly, μ_2 and μ_3 , Scott's Eqs. (26) and (27)² can be written, in his notation:

$$\varphi_1(1 - \mu_2\varphi_2)(1 - m\mu_3\varphi_3) + \varphi_2(1 - \mu_1\varphi_1)(1 - m\mu_3\varphi_3) + m\varphi_3(1 - \mu_1\varphi_1)(1 - \mu_2\varphi_2) = 0, \quad (1)$$

$$\begin{aligned} &\varphi_3(1 - \mu_1\varphi_1)[\varphi_1(1 - m\mu_3\varphi_3) + m\varphi_2(1 - \mu_1\varphi_1)] + \varphi_3(1 - \mu_2\varphi_2) \\ &[\varphi_2(1 - m\mu_3\varphi_3) + m\varphi_3(1 - \mu_2\varphi_2)] \\ &\quad - [\varphi_1(1 - \mu_2\varphi_2) + \varphi_2(1 - \mu_1\varphi_1)]^2 = 0. \quad (2) \end{aligned}$$

Equation (1) is symmetrical with respect to the volume fractions φ , except for the intrusion of m_1 , while Eq. (2) is not; it can, however, be made symmetrical most easily by introducing new variables U , V , and W , defined by

$$U = \varphi_1/(1 - \mu_1\varphi_1), \quad V = \varphi_2/(1 - \mu_2\varphi_2), \quad W = m\varphi_3/(1 - m\mu_3\varphi_3). \quad (3)$$

Equations (1) and (2) then become

$$U + V + W = 0 \quad (4)$$

$$U(1 + \mu_1 U)^2 + V(1 + \mu_2 V)^2 + mW(1 + \mu_3 W)^2 = 0, \quad (5)$$

where Eq. (4) has been used to simplify Eq. (5). These equations together with Eq. (6)

$$U/(1 + \mu_1 U) + V/(1 + \mu_2 V) + W/m(1 + \mu_3 W) = 1 \quad (6)$$

which results from $\varphi_1 + \varphi_2 + \varphi_3 = 1$, have nine roots and determine the nine critical points. It is easily confirmed that for infinite chain-length ($m = \infty$), nine of the ten points given by Scott satisfy these equations, while the point given by his Eq. (47) does not and is spurious. Incidentally, this solution satisfies his Eqs. (26) and (27) for all values of m . This solution, and the other two spurious ones quoted by Scott, are introduced during the algebraic manipulation of the equations by the necessity of multiplying with factors of the form $1 - \mu_i\varphi_i$; had n_1 and n_3 , or n_2 and n_3 , been used in the fundamental equations of the plait points (Scott's Eqs. (20) and (21)), instead of n_1 and n_2 , then three other spurious solutions would have been introduced. None of these spurious roots appear if the plait points are calculated from the expression for the free energy of mixing for "one mole of sites," $n_1 + n_2 + mn_3 = 1$, using two of the φ as independent variables, in extension of the treatment of Van der Waals and Kohnstamm³ for divariant binary systems to divariant ternary systems.

Solutions for any value of m can be obtained by assuming a trial value of U and calculating V and W from Eqs. (4) and (6); Eq. (6) reduces to a quadratic for given U , Eq. (5) is then used to ascertain whether the chosen value of U is correct; if it is not, the value of the l.h.s. of Eq. (5) can be used as a guide for the choice of a better U ; the process may be repeated until Eq. (5) is satisfied to any desired degree of accuracy.

Equations (4), (5), and (6) can be written in terms of the φ 's in the following symmetrical forms:

$$\varphi_1/(1 - \mu_1\varphi_1) + \varphi_2/(1 - \mu_2\varphi_2) + m\varphi_3/(1 - m\mu_3\varphi_3) = 0 \quad (7)$$

$$\varphi_1/(1 - \mu_1\varphi_1)^2 + \varphi_2/(1 - \mu_2\varphi_2)^2 + m^2\varphi_3/(1 - m\mu_3\varphi_3)^2 = 0 \quad (8)$$

$$\varphi_1 + \varphi_2 + \varphi_3 = 1. \quad (9)$$

After multiplication these equations are of the third, seventh, and first order, respectively; they have therefore twenty-one solutions, of which the following are spurious: $\varphi_1 = 1/\mu_1$, $\varphi_2 = 1/\mu_2$, $\varphi_3 = 1 - 1/\mu_1 - 1/\mu_2$, and two analogous ones, three times each, and three solutions at infinity, obtained by making the equations homogeneous by means of a fourth variable z in the form $(1, -1, 0, 0)$, $(-1, 0, 1, 0)$, and $(0, 1, -1, 0)$. We are thus left with nine genuine critical points.

The author is grateful to Mr. J. Crank and Dr. J. G. Oldroyd for helpful discussion of some of the points arising in this note.

¹ R. L. Scott, J. Chem. Phys. **17**, 268 (1949).

² The + sign in front of φ_3 in the third line of Eq. (27) should be replaced by a - sign.

³ Van der Waals and Kohnstamm, *Lehrbuch der Thermodynamik* (Leipzig, 1927).