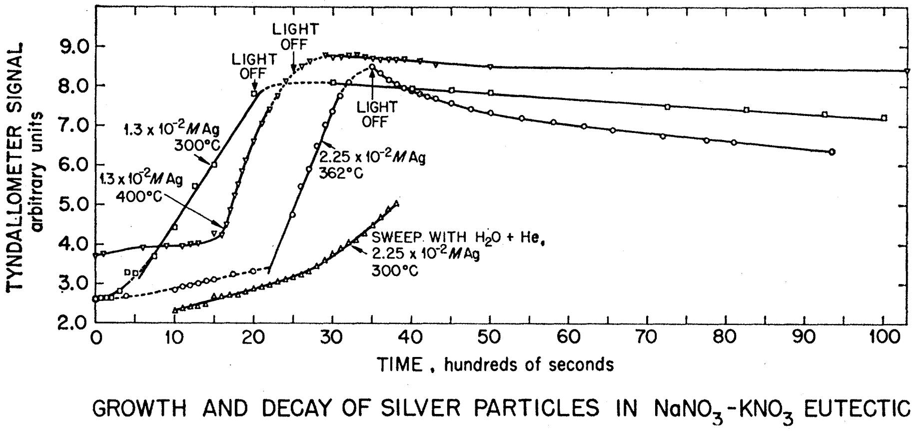

Fig. 2. Rate of formation of colloidal silver from photolysis of $NaNO_3$-KNO_3 eutectic that also contains $AgNO_3$.

Tyndallometer decreased to half its initial value on standing overnight. When the colloid was heated to 400°C, it dissolved and did not re-form on cooling.

Experiments to determine how these colloids are stabilized have been inconclusive. Electrophoretic plating of the gold sol gave negative results. None of the sols absorbed fluorescein dye (the staying power and ionization of this material in molten nitrates is also open to question). Mixing aged silver iodide sol, containing excess Ag^+ or excess I^-, with gold sols did not give mutual flocculation (*9*), as one would expect for these sols in a water system. However, addition of gold chloride to the silver iodide sol did reduce the amount of silver iodide scattering; thus there must be some interaction of the freshly formed gold sol with the silver iodide. However, since gold sol and silver iodide sol can coexist in the same solution, their interaction is not complete as it is in water solution.

The apparent stability of these colloids is not well understood. Both Voet (*3*) and Burkard (*5*) invoke a tightly bound layer of solvent molecules as a stabilizing influence on their sols. Indeed, Burkard (*5*) found that removing all solvents (for example, CS_2 from As, CS_2 from Se, C_6H_6 from P) from the glacial acetic acid sols caused them to precipitate rapidly. Such a picture could also be applied to these molten salt colloids; it is preferred to the alternative, proposed by Ostwald and Wannow (*4*), which calls for low conductivity in concentrated solutions and is thus clearly inapplicable here. Kreyger, Kirslis, and Blankenship (*10*) observed a change in the contact angle between molten salts and metal or graphite, depending on whether the salts contained water. This indicates a change in the affinity of salt for the metal interface induced by the presence of water, because of the adsorption and reaction of water itself. That the water in association with the solvent salt molecules then assumes an image charge due to the contact potential of the metal, or assumes a charge due to preferential cation hydration, then seems reasonable. The observation of ion-exchange phenomena in molten salt solutions also indicates that some sort of charge layer can occur in molten salts; but again, water or some form of bound water is a prerequisite for this ion exchange (*11*). A serious drawback to the model is that in view of the high conductivity of the molten salt solution, the repulsion from such a charge layer could operate only through a small distance (one or two atomic layers) unless further ordering of quasi-lattice structures by these surface charges is possible in the molten salt.

A group of Italian investigators (*12*) has prepared metallic dispersions of colloidal dimensions in fused sodium chloride. Copper, silver, and nickel were vaporized in the melt by the Bredig arc method (*13*). However, the many differences in their systems and ours, namely the difference in electrophoretic behavior, particle size distribution, temperature, and melt composition lead us to believe that these two groups of colloids have very little in common.

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Oxytocin: Crystal Data of a Seleno Analog

Abstract. *The sulfur atom in position 6 of deamino-oxytocin (1-β-mercaptopropionic acid–oxytocin) was replaced by selenium. The crystals of the resulting deamino-6-seleno-oxytocin are similar to those of the "wet" form of deamino-oxytocin, but they are stable upon prolonged exposure to air.*

The major obstacle to x-ray crystallographic analysis of neurohypophyseal principles (*1*) has been the small size of the crystals available.

The replacement of a sulfur atom in the disulfide bridge of deamino-oxytocin by selenium may overcome this difficulty (*2, 3*). Selenium, with its higher electron density, could serve as a heavy-atom marker, thus permitting the analysis of structure from smaller crystals. Biological and conformational studies in soluiton (*3, 4*) indicate that the selenium replacement introduces differences in the parent molecule; but this replacement does not affect the overall molecular conformation.

Crystals of deamino-6-seleno-oxytocin

Table 1. Crystal data of deamino-6-seleno-oxytocin with deamino-oxytocin.

Form	Unit cell dimensions					Space group	Measured density (D_m) (g/cm^3)
	a (Å)	*b* (Å)	*c* (Å)	β (deg)	*V* (10^3 Å^3)		
			Deamino-6-seleno-oxytocin				
Wet	27.1	9.1	23.0	102.2	5.54	*C*2	1.36
			*Deamino-oxytocin**				
Wet	27.3	9.07	23.1	102.4	5.60	$P2_1$	1.305
Dry	28.1	9.43	24.5	124.0	5.38	*C*2	1.328

*Data from (*1*).

of a more substantial size (0.5 by 0.08 by 0.03 mm) have been secured from an ethanol-water mixture. These crystals are monoclinic laths, elongated along the *b*-axis, lying on (001). Preliminary x-ray photographic studies with CuKα radiation showed that the unit cell dimensions (Table 1) of these crystals are comparable to those of the "wet" form of deamino-oxytocin (*1*). In addition, the density of these crystals, determined by flotation, is compatible with that of the "wet" form of deamino-oxytocin. Nevertheless, the analogs crystallize in different space groups: deamino-6-seleno-oxytocin in *C*2 and deamino-oxytocin in $P2_1$. However (*1*) the diffraction pattern of "wet" deamino-oxytocin showed marked pseudo face-centering related to the space group *C*2. In fact, a comparison of the diffraction patterns of all three principal planes and two general planes of the crystals of these analogs showed such similarity that we believe that the overall conformations of both peptide molecules are alike.

In contrast to the "wet" crystals of deamino-oxytocin, those of the selenium analog do not lose crystal water upon prolonged exposure to air or upon soaking in xylene, as manifested by the constancy of the unit cell dimensions and of the diffraction pattern. Therefore the collection of intensity data is facilitated.

Avian vasodepressor assays (*5*) reveal that the biological activities remained unchanged during x-irradiation, indicating that deamino-6-seleno-oxytocin is essentially stable to x-rays.

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Estimating Proportions in Petrographic Mixing Equations by Least-Squares Approximation

Abstract. *Petrogenetic hypotheses involving fractional crystallization, assimilation, or mixing of magmas may be expressed and tested as problems in least-squares approximation. The calculation uses all of the data and yields a unique solution for each model, thus avoiding the ambiguity inherent in graphical or trial-and-error procedures. The compositional change in the 1960 lavas of Kilauea Volcano, Hawaii, is used to illustrate the method of calculation.*

Fractional crystallization, assimilation, and mixing of magmas are often cited in petrographic literature as important mechanisms by which compositional variation in igneous rock series is produced. Graphical constructions or trial-and-error calculations (*1, 2*) have sometimes been used to test the ability of the proposed mechanism to produce the observed compositional changes. Consistent symbolic formulation of the problem shows at once that it fits readily into the framework of least-squares approximation. As in the graphical and trial-and-error methods, the objective of the least-squares analysis is to determine whether an assumed residual liquid might be derived from an assumed parent magma by removal or addition of components which have the compositions of mineral phases or contaminants such as wall rock or xenolith material. Although graphical or trial-and-error solutions are restricted to problems having only three or four components, this very serious limitation does not apply to the least-squares solution.

In this discussion x_{ij} is the observed amount of the *i*th oxide in the *j*th component, where $i = 1,n$, and $j = 1,k$; y_i is the observed amount of oxide *i* in the composition to be approximated; $\hat{b}_j$ is the estimated amount of component *j* required; and $\hat{y}_i$ is the estimated amount of oxide *i*.

For each of the *n* oxides we may thus write a linear equation containing one term in y_i and *k* terms in $b_j x_{ij}$, or, in matrix notation

$$\mathbf{XB} = \mathbf{Y} \tag{1}$$

where

$$\mathbf{X} = \begin{bmatrix} x_{11} & x_{12} & x_{13} \cdots & x_{1k} \\ x_{21} & x_{22} & x_{23} \cdots & x_{2k} \\ x_{31} & x_{32} & x_{33} \cdots & x_{3k} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ x_{n1} & x_{n2} & x_{n3} \cdots & x_{nk} \end{bmatrix} \tag{2a}$$

$$\mathbf{B}' = [b_1, b_2, b_3 \cdots b_k] \tag{2b}$$

and

$$\mathbf{Y}' = [y_1, y_2, y_3 \cdots y_n] \tag{2c}$$

where **B′** and **Y′** are, respectively, the transposes of the column vectors **B** and **Y**.

Interpretations of the results of conventional subtraction diagrams or their numerical analogues (*3*) are rarely free of ambiguity. Usually the number of oxides (*n*) is considerably greater than the number of components (*k*), but graphical and numerical procedures proposed thus far require that the number of oxides used in any solution be equal to or less than *k*.

Using any of these methods, the petrologist must work with no more than *k* of the *n* rows of Eq. 1 in any particular solution; each solution thus ignores at least $(1 - k/n)$ of the available information. Any of the unused rows of Eq. 1 which are linear combinations of those used in a solution are