THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 24 MAY, 1939 No. 5

THE MECHANISM OF THE GENESIS OF POLYMORPHOUS FORMS

MORTIMER C. BLOOM, *Mineralogical Laboratory, Massachusetts Institute of Technology.*

INTRODUCTION

Despite the steady growth of our knowledge of polymorphic phenomena,[1] we have at present almost no knowledge of the factors which determine what particular crystalline form will be generated when a solid is deposited from a vapor, from a melt, or from a solution. We have learned that only one modification of a given chemical species can be thermodynamically stable over certain ranges of temperature and pressure, and that within this region all other modifications tend to transform to this modification. We find in nature, however, many polymorphous forms far from their regions of thermodynamic stability. If this were due to the fact that high temperature forms, generated at temperatures within their region of stability have subsequently cooled without transformation, the presence of such high temperature forms would be an excellent basis for geological thermometry. Unfortunately, the hypothesis that high temperature forms, generated at temperatures within their thermodynamic stability region, have subsequently cooled without transformation, is not adequate to explain the known phenomena. To mention a few examples, cristobalite, with a stability range above 1470°C., has been formed by heating silica gel[2] with a melt of $NaPO_3$ at temperatures under 750°C. Wurtzite, with a stability range above 1020°C., has been obtained at 250° from an acid solution.[3,4] Metacinnabarite and marcasite, for which no stability regions have yet been

---

[1] BUERGER, M. J. and BLOOM, M. C., Crystal polymorphism: *Zeits. Krist.* (A) **96**, 182–200 (1937).

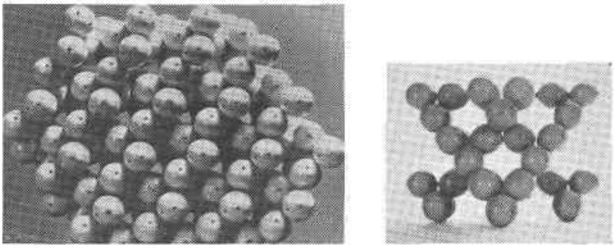
[2] PEYRONEL, GIORGIO, Cristallizzazione della Silice in $NaPO_3$: *Zeits. Krist.*, **95**, 274 (1936).

[3] ALLEN, E. T., CRENSHAW, J. L. and MERWIN, H. E., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions: *Am. Jour. Sci.*, Series 4, **34**, 341 (1912).

[4] ALLEN, E. T., CRENSHAW, J. L. and MERWIN, H. E., Effect of temperature and acidity in the formation of marcasite (FeS_2) and wurtzite (ZnS): *Am. Jour. Sci.*, Series 4, **38**, 393–431 (1914).

found, have similarly been generated from acid solutions at moderate temperatures[3,4] and aragonite, whose stability region is below 0°C. at atmospheric pressure[5] is readily generated under normal pressure conditions at room temperature by the addition of small quantities of extraneous material, such as strontium or lead salts to solutions which in their absence precipitate the stable calcite.[6]

A few workers have suggested possible causes for this anomalous behavior. Johnston, Merwin, and Williamson,[7] in 1916, offered the hypothesis with regard to aragonite, that since its solubility is close to that of calcite, a small amount of solid solution in the aragonite structure might make it less soluble than calcite in contact with certain solutions, and thus make it a truly stable phase as precipitated from such solution. They made no attempt, however, to give reasons why such solid solution should take place in the aragonite structure in preference to the calcite structure.



Low
Quartz

High
Cristobalite

FIG. 1

More recently, Buerger,[8] on the basis of crystal structure evidence, has offered an explanation of why the high temperature forms of certain minerals should have a preferential capacity for forming solid solutions with extraneous materials. He pointed out that of the three major stable crystalline forms of silica, quartz is a relatively closely packed structure, while the stable high temperature forms, tridymite and cristobalite, are very open ones (Fig. 1). Hence the high temperature forms might be expected to show a marked preferential tendency for interstitial solid solution. He reasoned that the high cristobalite solid solutions produced in this manner would have stability ranges different from those of the

---

[5] BACKSTROM, H. L. J., Über die Affinität der Aragonit-Calcit Umwandlung: *Zeits. phys Chem.*, **97**, 179 (1921).

[6] CREDNER, H., *J. prakt. Chem.*, **2**, 292 (1870).

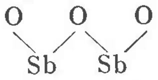
[7] JOHNSTON, J., MERWIN, H. E., and WILLIAMSON, E. D., The several forms of calcium carbonate: *Am. Jour. Sci.*, Series 4, **41**, 473–512 (1916).

[8] BUERGER, M. J., The silica framework crystals and their stability fields: *Zeits. Krist.*, **90**, 186–192 (1935).

pure substance, and that high cristobalite found at room temperature in opals and elsewhere may be, or may have been, such a stable solid solution.

One other hypothesis, which has been made in this connection, is that of Cohen and Moesveld.[9] These authors postulated that when the solution of a substance reaches the saturation point, adsorption of impurities on the nuclei of the stable form may inhibit the precipitation of this form and induce supersaturation. If the supersaturation concentration of an unstable form is thus exceeded, the unstable form may appear. If the unstable form has much less adsorptive tendency for the impurities than the stable form, the unstable form may appear exclusively; or a mixture of the two forms may be obtained. An apparently identical mechanism was subsequently postulated by C. H. Saylor[10] as a result of additional studies of the calcite-aragonite relation. This picture of the mechanism of the genesis of unstable forms requires a knowledge of adsorption phenomena on nuclei for its verification. Such knowledge is not available.

THE Sb_2O_3 SYSTEM

In order to test the hypothesis of solid solution in open structures as a cause of the genesis of unstable forms, a study of the Sb_2O_3 system was undertaken. This system has properties which make it particularly suitable and convenient for this purpose. The low temperature form senarmontite, stable up to 570°C.,[11] is an isometric arrangement of discrete Sb_4O_6 molecular clusters[12] (Fig. 2). Such clusters are apparently very stable units, for gas density measurements indicate their presence even in the vapor phase. The high temperature form, valentinite, stable between this temperature and the melting point,[11] is an orthorhombic structure[13] (Fig. 3) made up of chains of 

linkages which fit into each other (as shown on the *bc* projection) to form nearly planar rectangular sheets one linkage wide. Each sheet extends indefinitely in the *c* axis direction and is connected through O—O contacts to a neighboring sheet, leaving an interstitial hole parallel to the *c*

---

[9] COHEN, ERNST and MOESVELD, A. L. TH., Die Metastabilität der Elemente und Verbindungen als Folge von Enantiotropie oder Monotropie, I: *Zeits. phys. Chem.*, **94**, 450–481 (1920).

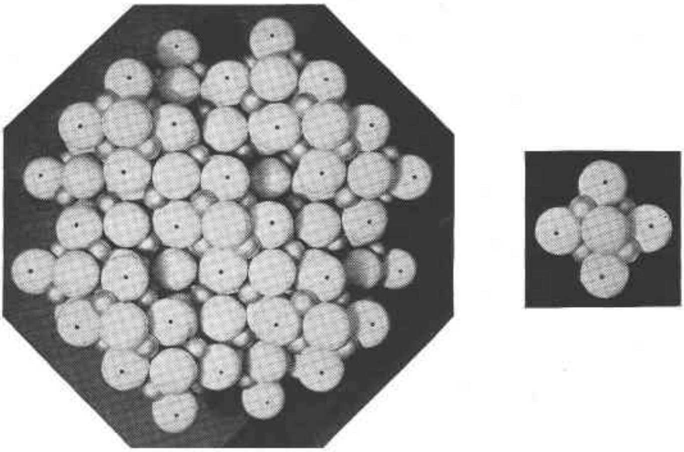
[10] SAYLOR, C. H., Calcite and aragonite: *Jour. phys. Chem.*, **32**, 1460 (1928).

[11] ROBERTS, E. J. and FENWICK, F., The antimony electrode: *Jour. Am. Chem. Soc.*, **50**, 2134 (1928).

[12] BOZORTH, R. M., The crystal structures of the cubic forms of arsenious and antimonous oxides: *Jour. Am. Chem. Soc.*, **45**, 1621 (1923).

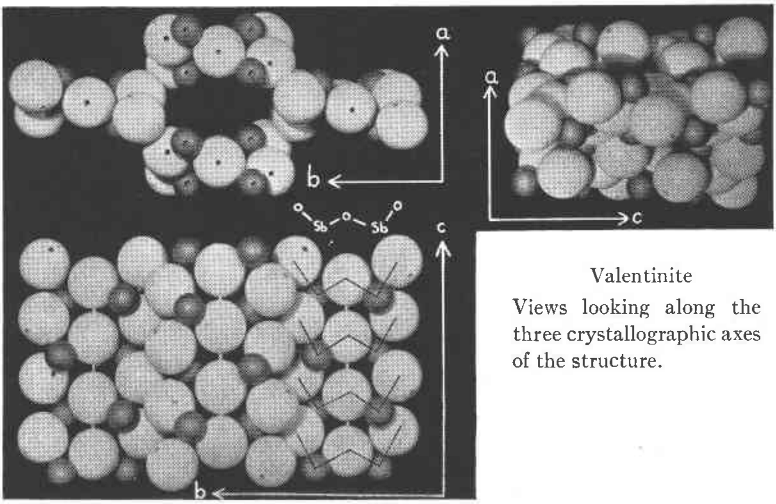
[13] BUERGER, M. J. and HENDRICKS, S. B., The crystal structure of valentinite (Orthorhombic Sb_2O_3): *Zeits. Krist.* (A), **98**, 1–30 (1937).

axis between each four sheets (as shown in the *ab* projection). The difference in crystal systems makes microscopic identification a comparatively simple matter of looking for birefringence, and the very very marked difference in structure simplifies the structural reasoning.



Senarmontite Sb_4O_6 Molecule

FIG. 2



Valentinite
Views looking along the three crystallographic axes of the structure.

FIG. 3

Moreover, the anomalous genesis of a high temperature form is shown to a marked degree by this system in nature; and the anomaly is readily reproduced in the laboratory. Thus the high temperature form (valentinite) is found widely distributed in nature as a surface alteration product of stibnite, despite the fact that its normal stability range is in excess of 570°C.

In the laboratory, valentinite is readily obtained by hydrolysis of antimony chloride with distilled water at room temperature.[14] During the course of this hydrolysis, HCl is generated by the reaction:

$$2\ SbCl_3 + 3\ H_2O \rightarrow Sb_2O_3 + 6\ HCl$$

and the products retain HCl so firmly at room temperature that three months' washing with distilled water under constant agitation does not suffice to remove this HCl completely. It may be removed by treatment with alkali, but in this case, the removal is accompanied by transformation to the stable senarmontite. These facts are all in accord with the hypothesis of solid solution in the high temperature form as the cause of the genesis of this form.

THERMODYNAMIC STABILITY CONSIDERATIONS

It now becomes of interest to ask whether these HCl-bearing solid solutions in the valentinite structure are truly stable phases in contact with the solutions from which they were generated. To make a rigorous test of the thermodynamic stability of this HCl-bearing valentinite, solubility measurements were made as follows:

Antimony trichloride, prepared as previously described,[14] was melted and poured in varying quantities into bottles each of which contained five liters of water (distilled from alkaline permanganate). The flocculent precipitates initially obtained were allowed to equilibrate in contact with their respective solutions for six months at laboratory temperatures. At the end of this period, one liter of supernatant liquor was removed from each sample and to it was added finely powdered pure senarmontite. This senarmontite had been prepared by triple sublimation, at 500°C. in vacuo, of an antimony chloride hydrolysis product which had been washed with distilled water under constant agitation for three months and which contained, prior to the sublimation, less than 0.05% chloride as an impurity. The solutions were allowed to remain side by side in contact with their respective solid phases for two more months at laboratory temperatures. At the end of this period, analysis yielded the following results:

Run No. 1	*Chloride* in Solution*	*Antimony** in Solution*
Valentinite	.0083 normal	.000093 normal
Senarmontite	——	.000039
Run No. 2		
Valentinite	.0055 normal	.000090 normal
Senarmontite	——	.000036

---

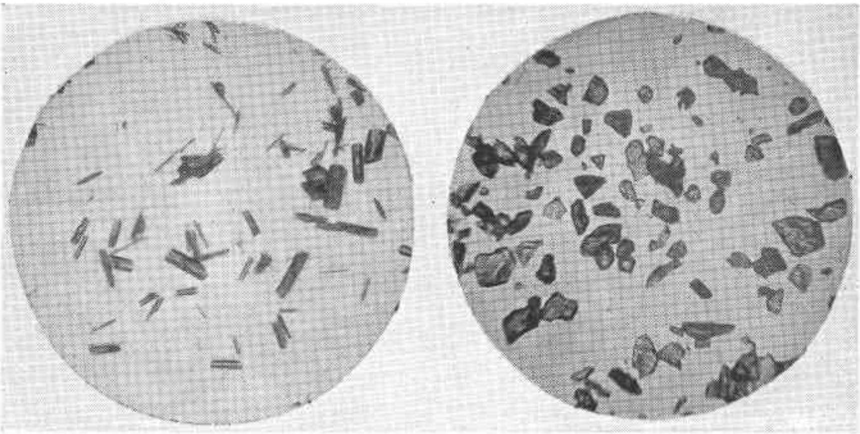
[14] BLOOM, M. C. and BUERGER, M. J., On the genesis of polymorphous forms—Sb_2O_3: *Zeits. Krist.* (A), **96**, 365–375 (1937).

Re-analysis, after standing an additional twelve months in contact with the respective solid phases as before, yielded:

Run No. 1	*Chloride in Solution*	*Antimony in Solution*
Valentinite	.0084 normal	
Senarmontite	.0084	
Run No. 2		
Valentinite	.0056	.000092 normal
Senarmontite	.0056	.000040

* Accuracy ± .0002
** Accuracy ± .000003

The conclusion seems unavoidable that the valentinite is the more soluble and hence the unstable phase unless it is showing excess solubility due to small crystal size. To test this possibility, microscopic examination was made and it was found that the valentinite crystals were of the same order of magnitude as the senarmontite crystals (Fig. 4).



Valentinite ×65 Senarmontite ×65

FIG. 4

The evidence seems conclusive that the valentinite is not a thermodynamically stable phase, except in the sense that it is apparently in equilibrium with the solution from which it was grown. Evidently the passive resistance to reorganization of the structure allows equilibrium to exist at a higher free energy than the minimum for the system.

THE MECHANISM OF PRECIPITATION

Since true thermodynamic stabilization by solid solution in the high temperature structure does not account for the observed phenomenon, we must look to extra-thermodynamic causes for the explanation of this anomalous genesis of the high temperature form. The fact that we must look to extra-thermodynamic causes for the explanation of crystallization phenomena has been demonstrated by a series of researches by DeCoppet,[15] Tammann[16] and Othmer[17] which, apparently, have not received the attention which they deserve in this connection. The idea of metastable and labile regions, and the so-called "Law of Stages" which have long been associated with the name of Wilhelm Ostwald, and which are still used in the explanation of the genesis of crystal forms, have been shown by the above mentioned researches to be not very useful, and, in some cases, hardly tenable concepts. These investigators present evidence that the region of metastability, postulated by Ostwald, is a function of the time one is willing to wait for the observance of the formation of crystals, as well as of the size of the sample used. They show that the use of very long times and very large samples enables spontaneous crystallization to be observed at temperatures close to the melting point. They have demonstrated that there is no general rule governing what particular form will appear when solid phases are generated; that in some cases only the unstable form is obtained, in other cases only the stable form is obtained, but that in many cases both forms appear simultaneously. They have shown further, that the presence of small quantities of impurities often have a marked effect upon the number and the nature of the nuclei formed; some impurities favor the formation of the stable form, and others favor the formation of unstable forms. The data of these investigations leave little room for doubt that the development of crystalline nuclei from vapor, from melt, or from solution is a chance phenomenon.

If the development of crystal nuclei is a chance phenomenon, it follows that the type of structure generated from solution should depend, first, upon the nature of the groups present in the solution prior to the deposition of the solid phase and, second, upon the nature of the available crystal structures into which these groups may aggregate. The presence of dissolved impurities may affect the probability of precipitation in a given structure in a number of ways. Several ways in which they may be thus effective are:

(1) They may induce changes in the numerical relationships between

---

[15] DeCoppet, L. G., Recherches sur la surfusion et la sursaturation: *Ann. chim. phys.*, (8) **10,** 457–527 (1907).

[16] Tammann, G., The transition of an unstable into a stable stage of aggregation: Chapter IX of "States of Aggregation," translated by R. F. Mehl, D. Van Nostrand, *New York* **(1925).**

[17] Othmer, P., Studien über das spontane Kristallisations-vermögen: *Zeits. anorg. Chem.*, **91,** 209–247 (1915).

groups already present in the solution (change of *pH*, of ionization, etc.).

(2) They may cause the formation of new groups (complex ion formation, etc.).

(3) They may act as local disturbances causing local changes of orientation and energy distribution.

(4) They may act as inert obstructions reducing the number of collisions of molecules of the precipitating substance. In any of these cases, the probability of crystallization would in general be diminished and the probability of supersaturation correspondingly enhanced. This is in accord with the known effect of solute impurities on supersaturation.[15,18] If, however, there is a solid structure which can readily house the given impurity in solid solution, the effect of this impurity in inhibiting aggregation into such a structure should be small. Consequently, it is to be expected that the probability of precipitation of a structure of this type will be greater, in the presence of the impurity, than that of structures which cannot readily accommodate the foreign material. The precipitated solid may be thermodynamically stable or unstable with respect to forms of the ideally pure compound, since the postulated factors affecting the probability of precipitation have no necessary relation to thermodynamic stability. However, solid solution in a structure as here postulated will decrease the solubility of the structure and, if a sufficient amount of the impurity can be accommodated in the solid solution, it may effect true thermodynamic stabilization of a structure which in the absence of such solid solution is not the stable one.

We shall now apply these considerations to the precipitation of Sb_2O_3. It has previously been mentioned that Sb_4O_6 clusters are evidently very stable units. It is these that are found as the molecular unit in the gas phase and it is these that we would expect to find as the un-ionized aggregates in solution. In the case under consideration, the hydrolysis of $SbCl_3$, HCl is generated giving as impurities in the solution hydrogen ion (H^+) and chloride ion (Cl^-). The effect of H^+ upon aqueous antimonous solutions is revealed by the data of Schuhmann.[19] The effect is the production of SbO^+ according to the equation:

$$Sb_4O_6 + 4\ H^+ = 4\ SbO^+ + 2\ H_2O.$$

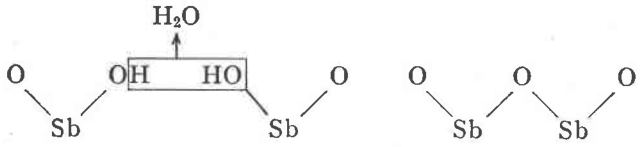
The effect of Cl^- is presumably that of cases (3) or (4) above. Let us ask, therefore, "what is the relationship between the presence of SbO^+ and Cl^-, and the development of the high temperature structure?"

---

[18] COHEN, ERNST and MOESVELD, A. L. TH., Kristallisations-vermögerung in übersättigen Losungen: *Zeits. phys. chem.*, **94**, 482-504 (1920).

[19] SCHUHMANN, REINHARDT, The free energy of antimony trioxide and the reduction potential of antimony: *Jour. Am. Chem. Soc.*, **46**, 57 (1924).

The mechanism of formation of oxides from aqueous solution is, in general, the initial formation of groups containing hydroxyl ion (OH^-) and subsequent dehydration. This must be the case unless we assume an appreciable concentration of oxide ion (O^{--}). In the cases of iron, aluminum and manganese, the intermediate hydroxyl-bearing products are known in the solid state and recent crystal structure evidence has shown that they are respectively FeOOH,[20] AlOOH[21] and MnOOH[22] linkages. If we postulate the formation of such a linkage in the case of antimony, we should obtain SbOOH which, by elimination of H_2O between two such groups, would give rise to a chain of the following character:



It has previously been pointed out that such a chain is the fundamental unit of the valentinite structure. It has also been pointed out that the low temperature senarmontite structure is composed of discrete Sb_4O_6 molecules and it might be expected, therefore, that acid solutions which break up these molecules into SbO^+ would tend to produce the high temperature structure. Turning now to the effect of Cl^-, detailed examination of the valentinite structure reveals that the "holes" in the structure are capable of housing a spherical atom of approximately 1.6 Å in radius. This is apparently adequate for the housing of HCl, which in the gas phase has an equilibrium distance of 1.272 Å between atomic centers.[23] Looked at from another point of view, the chloride ion radius[24] is 1.81 Å in six co-ordinated ionic crystals, and contraction due to decrease of co-ordination might well allow interstitial accommodation in the above structure. We should not expect the presence of Cl^-, therefore, to inhibit the development of the valentinite structure.

Additional experimental results are summarized in the following table:

---

[20] Goldsztaub, S., Structure de la goethite: *Bull. Soc. Franc. Min.*, **58**, 25–43 (1935).

[21] Takané, K., Crystal structure of diaspore: *Proc. Imp. Acad. Japan*, **9**, 113–116 (1933).

[22] Buerger, M. J., The symmetry and crystal structure of manganite, Mn(OH)O: *Zeits. Krist.* (A), **95**, 163–174 (1936).

[23] Jevons, W., Report on band spectra of diatomic molecules: *Physical Society, London*, page 276 (1932).

[24] Stillwell, C. W., Crystal Chemistry, Chapter II. The Sizes of Atoms and Ions. McGraw-Hill Book Company, **1938**.

THE INFLUENCE OF SOLUTION COMPOSITION UPON THE STRUCTURE OF THE PRECIPITATED PHASES OF Sb_2O_3

Method	*Temperature*	*Precipitated Phase*
Air oxidation of antimony under distilled water	25°	Senarmontite
Precipitation from .01 *N* HCl	25°–100°	Valentinite
Precipitation from .01 *N* H_2SO_4	25°–100°	Valentinite
Precipitation from .01 *N* $HClO_4$	25°–100°	Mixture mostly senarmontite
Precipitation from .06 *N* $HClO_4$	25°–100°	Valentinite

It will be observed that when Sb_2O_3 is generated by air oxidation of antimony under distilled water, that is, in the absence of dissolved impurities, that the stable senarmontite structure is obtained. H_2SO_4 acts just as HCl does, and we see here the mechanism of the genesis of valentinite by weathering of stibnite. The oxidation of the sulphide produces sulphate, which with water produces H_2SO_4 and thus causes the generation of valentinite. It will be noted, however, that in the case of $HClO_4$ it is necessary to raise the acid concentration to much higher values than in the case of HCl or H_2SO_4 in order to obtain the exclusive generation of the valentinite structure. For an explanation of this, we must look to the difference in the influence of the Cl^-, SO_4^{--}, and ClO_4^-. The sulphate radical is known from crystal structure evidence to consist of a tetrahedral arrangement of oxygens about the sulphur, the O—O distance along the tetrahedral edge being 2.44 Å.[25] The direct interstitial accommodation of such a tetrahedron would not be possible without some distortion of the structure, but if one of the oxygens of the SO_4^{--} radical replaces the normal oxygen of the valentinite structure, the tetrahedron could easily be accommodated within the available space without any distortion, and the requirements of valence and electrical neutrality would be satisfied. Since such a replacement would alter neither the Sb—O relations of the valentinite structure nor the type of Sb—SO_4^{--} bonds which may be presumed to exist in $Sb_2(SO_4)_3$, this mechanism of solid solution appears quite probable.

The perchlorate radical is known from crystal structure evidence to consist of an entirely analogous tetrahedral arrangement of oxygens

---

[25] *Zeits. Krist.*, *Strukturbericht*, Bd. II, page 84 (1937).

about the chlorine, the O—O distance (along the tetrahedral edge) in this case being 2.65 Å.[26] The distortion of the structure necessary to accommodate such an ion by direct interstitial solid solution is of course still greater and no analogous substitution mechanism satisfying valence and neutrality requirements is available. The presence of ClO_4^- would therefore be expected to hinder development of the valentinite structure. This is the probable explanation of the fact that higher hydrogen ion concentrations are required for the exclusive generation of the valentinite structure in the presence of $HClO_4$ than in the presence of HCl or H_2SO_4.

Discussion and Conclusions

In the precipitation of antimony trioxide from aqueous solutions, the presence of acid impurities introduces two effects. The H^+ causes a marked change in the number and nature of the groups present, and the anion of the acid acts as an obstruction to the aggregation of the groups into a solid structure. A study of the crystal structures of the two forms in relation to the nature of the groups in solution prior to precipitation gives a picture of the probable mechanism of the genesis of the polymorphous forms of this substance. The profound effect of hydrogen ion concentration as well as the subsidiary effect of the anion upon the genesis is satisfactorily accounted for by this mechanism. The reason that the high temperature form (valentinite) is found widely distributed in nature as a surface alteration product of stibnite is indicated.

We may expect to find analogous mechanisms in operation with other oxides, with sulphides, and with carbonates, for in all these cases, H^+ will have a marked effect upon the number and nature of the groups present in solution. In the case of sulphides, the instability of sulphide ion (S^{--}) makes X—(SH^-)* bonding and subsequent elimination of H_2S an almost inevitable mechanism of sulphide formation from acid solutions. For example, the complete precipitation of Hg, Cd, Cu, Bi, As, Sb, Sn as sulphides is commonly effected in analytical chemistry from solutions approximately 0.3 normal in acid. Using the solubility and equilibrium constant data of the International Critical Tables, one may calculate that such a solution contains not more than one sulphide ion (S^{--}) in 100 cc. of solution. There are approximately 2×10^{15} hydrosulphide ions (SH^-) in the same volume.

It would appear that the anomalies connected with the genesis of unstable polymorphous forms are due to the fact that the development of crystal nuclei is a chance phenomenon and depends, therefore, upon

---

[26] *Zeits. Krist.*, *Strukturbericht*, Bd. **II**, page 88 (1937).

* X = any positive ion, (SH^-) = hydrosulphide ion.

two major factors: (1) the groups present in the vapor, melt, or solution prior to the development of the solid phase, (2) the possible crystal structures into which these groups may aggregate. As a result, the solid phase which precipitates may be thermodynamically stable or unstable since the factors, above outlined, which determine the structure of the precipitated phase have no necessary relation to thermodynamic stability. In the case of precipitation from solution, the presence of dissolved impurities may change the nature of the structure which is precipitated due to two major effects: (1) They may change the number or the nature of groups present, (2) they may act as obstructions to the aggregation of the groups into a solid structure. The second of these effects might be expected to favor the precipitation of open structures capable of housing the dissolved impurities in solid solution. Such solid solution in a structure will reduce the solubility and may thus, if a sufficient amount of the impurity can be accommodated, effect true thermodynamic stabilization of an otherwise unstable structure. This is not, however, a necessary condition for its appearance.