

In spodumene, $\text{LiAlSi}_2\text{O}_6$ and petalite, $\text{LiAlSi}_4\text{O}_{10}$, it is possible that oxygen ions (with $\Sigma s_i = 2$) are common to a silicon tetrahedron, an aluminum tetrahedron and a lithium tetrahedron (the radius ratio for lithium ion is 0.33).

No aluminum silicates of alkali metals are known in which the $\text{Al}^{+3}:\text{R}^{+1}$ ratio is less than 1:1.

Summary

A set of principles governing the structure of complex ionic crystals, based upon the assumption of a coordinated arrangement of anions about each cation at the corners of an approximately regular polyhedron, is formulated with the aid of considerations based upon the crystal energy. Included in the set is a new electrostatic principle which is of wide application and considerable power.

It is shown that the known structures of many complex crystals, in particular the complex silicates, satisfy the requirements of these principles.

As an illustration of the application of the principles in the prediction of structures with the coordination theory, some properties of the structures of the three forms of Al_2SiO_5 , cyanite, andalusite and sillimanite, are predicted.

It is further shown that the theory requires that no stable basic silicates of divalent metals exist, and that in aluminum silicates of alkali metals there should be at least one aluminum ion for every alkali ion.

The structures of aluminum silicates of divalent metals which are simplest from the coordination standpoint are shown to correspond to the formulas $\text{R}_3^{++}\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{R}_3^{++}\text{Al}_2\text{Si}_6\text{O}_{18}$, which include the most important minerals of this class, the garnets and beryl.

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SOLUBILITY IN THE GASEOUS PHASE, ESPECIALLY IN THE SYSTEM: $\text{NH}_3(\text{l})-\text{NH}_3(\text{g}), \text{H}_2(\text{g}), \text{N}_2(\text{g})$

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A number of investigators have found that a solubility effect may be shown within a gaseous phase, especially under circumstances in which the density of the gaseous phase is relatively high. Pollitzer and Strebel¹ were perhaps the first to mention this phenomenon.

The two-phase system $\text{NH}_3(\text{l})-\text{NH}_3(\text{g}), \text{H}_2(\text{g}), \text{N}_2(\text{g})$ in which the H_2 and N_2 were maintained at the constant mole ratio of $3\text{H}_2:\text{N}_2$ has been experimentally investigated by Larson and Black.² Concentrations

¹ Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 785 (1924).

² Larson and Black, *THIS JOURNAL*, **47**, 1015 (1925).

of ammonia in the gas phase were found to be as much as six times the concentrations calculated with the aid of the perfect gas laws, and an application of the Poynting equation³ for increase of vapor pressure with total pressure did not yield satisfactory results. These authors suggest that the observed concentrations are possibly due to a positive solubility effect of the gaseous phase for ammonia vapor.

Lurie and Gillespie⁴ have recently studied a similar system in which they measured the composition of mixtures of nitrogen and ammonia in equilibrium with a mixture of barium chloride and barium chloride octa-ammine, their experiments extending up to total pressures of approximately 60 atmospheres at 45°. At this temperature and within the pressure range studied it was found that the equilibrium concentrations of ammonia exhibited a considerable solubility effect when compared with values calculated with the assumption of Gibbs' rule of additive pressures. An application of the equation of state for mixtures of Keyes and Burks, however, yielded satisfactory agreement with the experimentally determined concentrations.

Considering the available data for a number of cases of gaseous solutions (including the $\text{NH}_3\text{-H}_2\text{-N}_2$ system), Randall and Sosnick⁵ have presented a series of curves of "activity coefficients" which enable rough quantitative predictions of values in other mixtures and at other temperatures.

A Concept of "Zero Solubility."—In order that we may further examine the nature of phenomena similar to those mentioned above, it will be necessary first to define what we mean by "solubility" in systems of this kind. For this purpose let us consider a closed system containing only a gaseous component, A. Let us next imagine this system to be partially filled with a non-volatile liquid component, B, allowing none of Component A to escape from the system. It is apparent that, when equilibrium is attained, Component A will be uniformly distributed throughout the liquid phase and uniformly distributed throughout the gaseous phase, but in general its distribution will not be uniform throughout the system as a whole. With a certain choice of components, Component A might be found to be almost entirely in the liquid phase, its density in the gaseous phase being much less than its original density before the introduction of the liquid phase. This might be expressed by stating that the gas is very soluble in the liquid. With another choice of components, Component A might remain largely in the gaseous phase, its density accordingly being greater than before the introduction of the liquid. In this case the gas might be said to be comparatively insoluble in the liquid.

³ Poynting, *Phil. Mag.*, [4] 12, 32 (1881).

⁴ Lurie and Gillespie, *THIS JOURNAL*, 49, 1146 (1927).

⁵ Randall and Sosnick, *ibid.*, 50, 967 (1928).

The unique case is that in which Component A remains uniformly distributed throughout the entire system, its density in each phase being identical with its original density before introduction of the liquid. As the spatial distribution of Component A is in this case entirely unaffected by the presence of Component B, it follows that the activity of Component A at each point throughout the system is dependent only on its volume concentration and temperature. It seems quite logical to consider this as a case of "zero solubility," and from this point of view we may define a "solubility effect" as being a change in the activity of one component which is due to the presence of other components.

Application to the System $\text{NH}_3(\text{l})\text{-NH}_3(\text{g}), \text{H}_2(\text{g}), \text{N}_2(\text{g})$.—Let us first consider a simple closed system containing liquid ammonia in equilibrium with ammonia gas at constant temperature. Under these conditions the pressure exerted by the ammonia vapor is the normal vapor pressure of ammonia at the temperature considered. Next let us imagine the liquid phase to be separated from the gaseous phase by a piston permeable to ammonia vapor but impermeable to ammonia liquid; by means of this piston let us exert a definite pressure upon the liquid phase, thus increasing the activity of ammonia in this phase. If equilibrium conditions are maintained, it is evident that the activity of ammonia in the gaseous phase will correspondingly increase; this increase in activity is developed by an increase in the density of ammonia in the gas phase. The net result is that increase of pressure on the liquid ammonia phase causes an increase in the density of ammonia in the gas phase; this phenomenon is often referred to as the Poynting effect. It is obvious that no solubility effects are involved in the Poynting effect, as the gas phase is assumed to contain no constituent other than ammonia.

We may, however, employ a different device for exerting pressure upon the liquid ammonia phase. In the absence of the semi-permeable membrane which has previously been assumed to exert this pressure, let us pump into the system an "inert" gas which is substantially insoluble in the liquid phase. By this means we may exert the same pressure on the liquid ammonia as was previously exerted through the assumed semi-permeable membrane. The significant difference between conditions in the two assumed cases is that in this second case the gas phase contains a high concentration of the "inert" gas. The question at once arises as to whether or not this "inert" gas has a solubility effect. It seems logical to consider that no solubility effect is exhibited if the volume concentration of ammonia in the gaseous phase is identical with what it would be were the same pressure applied to the liquid phase through the medium of a semi-permeable piston. This is in conformity with the definition of solubility effect which we have developed above, namely, that a solubility effect is a change in the activity of the solute due to the presence of the solvent; in this case the solvent is the "inert" gas by means of which we exert an increased pressure upon the liquid ammonia, while the solute is the ammonia in the gas phase.

We may now proceed to examine this system in greater detail, in accordance with our present conception of a solubility effect.

Activity of Ammonia in the Liquid Phase.—The activities of liquid ammonia at pressures greater than its normal vapor pressure, relative to its activity a' at the same temperature and under the pressure of its saturated vapor, have been calculated by applying the equation⁶

⁶ See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 225.

$$RT \ln a/a' = \int_{P'}^P V dP \quad (1)$$

This calculation has been made in a manner entirely similar to that used by Randall and Sosnick,⁵ except that approximate corrections have been made for the decrease in volume of the liquid ammonia at pressures greater than the vapor pressure, and for the solubility of the 3H₂:N₂ mixture in the liquid ammonia phase. For this purpose a rough value of 5×10^{-5} was used for the compressibility factor for liquid ammonia, and the solubilities of hydrogen and nitrogen in the liquid phase have been estimated by graphical interpolation and extrapolation of the data of Larson and Black,⁷ who worked in this instance at pressures up to 150 atmospheres. The activity values as given by Randall and Sosnick would probably have been used in these calculations had they been available at the time this material was in course of preparation.

Activity of Ammonia in the Gaseous Phase.—The calculation of the concentration of ammonia in the gas phase from its activity presents difficulty. In the absence of experimental information Lewis and Randall⁸ considered all gaseous solutions to be nearly perfect solutions, and assumed the fugacity of each constituent to be proportional to the mole fraction of that constituent, at every temperature and at every pressure. More recent experimental data have shown that gaseous mixtures at higher pressures may present the same kinds of deviations as liquid mixtures, although the deviations are not, in general, so large.^{5,9}

Keyes¹⁰ has employed his equation of state for similar calculations with gaseous mixtures, assuming a simple additive rule for combining the constants of the individual gases to obtain the constants for the mixture.

For our present purpose we shall make the very simple assumption that the activity of ammonia vapor is dependent only on its volume concentration and temperature, and is entirely independent of the other gases which may be present. This is equivalent, according to the definition which we have adopted above, to assuming that there is no solubility effect toward ammonia vapor in the gas phase, and agreement of calculated with observed results will be a strong indication of the relative unimportance of such an effect.

Because of its convenient form for the direct evaluation of certain desired integrals, the P - V - T relationships of ammonia vapor will be expressed by means of the Bureau of Standards equation.¹¹ While it is known that this equation well reproduces the experimental data, its

⁷ Larson and Black, *Ind. Eng. Chem.*, **17**, 715 (1925).

⁸ Ref. 6, p. 225.

⁹ Gibson and Sosnick, *THIS JOURNAL*, **49**, 2172-2179 (1927).

¹⁰ Keyes, *ibid.*, **49**, 1393 (1927).

¹¹ U. S. Bureau of Standards "Scientific Paper No. 501," 1925.

accuracy becomes increasingly uncertain as it is extrapolated to pressures which are increasingly greater than the normal vapor pressure of liquid ammonia at a particular temperature. Randall and Sosnick⁵ have clearly shown how certain equations of state may lead to erroneous values of fugacity when they are too far extrapolated. It is easy to show that similar limitations apply to the Bureau of Standards equation of state, and for this reason the present calculations have not been extended beyond total pressures of 600 atmospheres.

Method of Calculation

The activities of liquid ammonia in the presence of compressed $3\text{H}_2:\text{N}_2$ mixture at various pressures and temperatures, calculated as previously described, are shown in Table I, Col. 3. These activities are relative to the activity of $\text{NH}_3(\text{l})$ at the same temperature and under the saturation pressure of its own vapor. Under equilibrium conditions the activities in the liquid and gas phases are, of course, necessarily equal, when referred to the same standard state.

At a given temperature and total pressure it is next required to determine the pressure of ammonia vapor at which its activity will equal the activity of ammonia in the liquid phase. For this purpose Equation 1 has again been utilized, the integration being carried out by substituting for V its value in terms of P (at constant temperature), as given by the Bureau of Standards equation of state. At a given temperature this integral has been evaluated for a number of different values of P and a curve constructed in which a/a' has been plotted as ordinate against P as abscissa. From this plot it is then possible to read directly the value of P at which ammonia vapor has the same activity as its calculated value in the liquid phase. These values of P are given in Table I, Col. 4. Substitution of these values of P directly in the equation of state for ammonia vapor gives the corresponding values for the specific volumes of ammonia vapor. Multiplication by 17.03 gives the molal volumes as shown in Table I, Col. 5.

Let us now consider a volume of the compressed gaseous mixture in equilibrium with liquid ammonia, equal in cc. to RT , where RT is expressed in cc.-atm. At any given temperature and value of the molal volume of ammonia, $RT/\text{Molal Volume}$ will represent the number of moles of ammonia contained in this volume. These values are given in Table I, Col. 6.

The number of moles of the "inert" gas ($3\text{H}_2:\text{N}_2$) which are present in this same volume will be estimated by an application of the principle of additive pressures. Consider a volume of $3\text{H}_2:\text{N}_2$ mixture in equilibrium with the mixture containing ammonia, through a membrane permeable to hydrogen and to nitrogen but impermeable to ammonia. We

TABLE I
 OBSERVED AND CALCULATED DATA

| Total press., atmos. | Temp., °C. | Activ. of NH ₃ (l) | Press. of NH ₃ (g) | Molal vol. NH ₃ (g) | $\frac{RT}{\text{Molal vol.}}$ | Moles of 3H ₂ :N ₂ | Mole % of NH ₃ From data of Larson and Black | |
|----------------------------|---------------|----------------------------------|----------------------------------|--------------------------------------|--------------------------------|---|--|-------|
| | | | | | Molal vol. | | Calcd. | |
| 50 | -40 | 1.064 | 0.755 | 24762 | 0.772 | 48.0 | 1.59 | |
| | -20 | 1.062 | 1.991 | 9800 | 2.12 | 46.8 | 4.34 | 5.70 |
| | -10 | 1.060 | 3.05 | 6681 | 3.23 | 45.9 | 6.58 | 7.35 |
| | 0 | 1.057 | 4.50 | 4625 | 4.85 | 44.5 | 9.82 | 10.0 |
| | 10 | 1.057 | 6.46 | 3268 | 7.11 | 42.6 | 14.3 | 13.9 |
| | 20 | 1.056 | 9.00 | 2372 | 10.13 | 40.2 | 20.1 | 20.4 |
| 100 | -40 | 1.135 | 0.808 | 23096 | 0.828 | 93.8 | 0.88 | |
| | -20 | 1.126 | 2.122 | 9332 | 2.22 | 92.6 | 2.34 | 3.25 |
| | -10 | 1.123 | 3.23 | 6284 | 3.43 | 91.8 | 3.60 | 4.35 |
| | 0 | 1.120 | 4.82 | 4280 | 5.23 | 90.5 | 5.47 | 5.80 |
| | 10 | 1.116 | 6.85 | 3062 | 7.58 | 88.5 | 7.90 | 8.00 |
| | 20 | 1.112 | 9.45 | 2241 | 10.73 | 86.2 | 11.07 | 11.10 |
| 200 | -40 | 1.287 | 0.918 | 20254 | 0.944 | 176.0 | 0.53 | .. |
| | -20 | 1.264 | 2.42 | 8135 | 2.55 | 175.1 | 1.44 | .. |
| | -10 | 1.260 | 3.65 | 5509 | 3.91 | 174.7 | 2.20 | .. |
| | 0 | 1.250 | 5.40 | 3790 | 5.91 | 173.5 | 3.30 | .. |
| | 10 | 1.244 | 7.72 | 2670 | 8.70 | 172.1 | 4.82 | .. |
| | 20 | 1.240 | 10.70 | 1936 | 12.42 | 169.8 | 6.83 | .. |
| 300 | -40 | 1.458 | 1.040 | 17803 | 1.074 | 246.3 | 0.43 | |
| | -20 | 1.428 | 2.74 | 7120 | 2.92 | 246.4 | 1.17 | 1.50 |
| | -10 | 1.412 | 4.13 | 4814 | 4.48 | 246.0 | 1.79 | 2.20 |
| | 0 | 1.400 | 6.12 | 3280 | 6.83 | 245.0 | 2.71 | 3.25 |
| | 10 | 1.390 | 8.71 | 2321 | 10.00 | 244.3 | 3.93 | 4.60 |
| | 20 | 1.370 | 12.00 | 1685 | 14.27 | 242.7 | 5.56 | 6.45 |
| 400 | -40 | 1.649 | 1.180 | 15622 | 1.224 | 305.5 | 0.40 | .. |
| | -20 | 1.605 | 3.11 | 6210 | 3.34 | 307.0 | 1.08 | .. |
| | -10 | 1.583 | 4.68 | 4189 | 5.14 | 307.7 | 1.64 | .. |
| | 0 | 1.565 | 6.91 | 2855 | 7.85 | 307.7 | 2.49 | .. |
| | 10 | 1.549 | 9.87 | 1998 | 11.62 | 308.0 | 3.64 | .. |
| | 20 | 1.536 | 13.90 | 1398 | 17.20 | 307.0 | 5.31 | .. |
| 600 | -40 | 2.113 | 1.530 | 11924 | 1.603 | 399.0 | 0.40 | |
| | -20 | 2.023 | 3.95 | 4775 | 4.35 | 405.0 | 1.06 | 1.20 |
| | -10 | 1.983 | 6.06 | 3118 | 6.91 | 407.0 | 1.67 | 1.70 |
| | 0 | 1.950 | 8.96 | 2092 | 10.71 | 409.0 | 2.55 | 2.40 |
| | 10 | 1.925 | 12.80 | 1434 | 16.19 | 411.0 | 3.79 | 3.50 |
| | 20 | 1.900 | 18.65 | 910 | 26.41 | 411.0 | 6.04 | 5.05 |

shall assume the density of the 3H₂:N₂ mixture to be the same on both sides of the membrane, and the 3H₂:N₂ mixture in both cases to exert a pressure equal to $(P-p)$, where P is the total pressure exerted by the mixture containing ammonia vapor and p is the pressure exerted by the ammonia vapor itself, as given in Table I, Col. 4. The number of moles of 3H₂:N₂ mixture in the volume RT will accordingly equal the pressure $(P-p)$, in atmospheres, divided by a compressibility factor, F , where F is equal to the PV product for one mole of 3H₂:N₂ mixture, at the tem-

perature and pressure under consideration, divided by the value of RT at that temperature. Values for F have been estimated by graphical interpolation and extrapolation of the data of Bartlett, Cupples and Tremearne,¹² and the values thus calculated for the number of moles of $3\text{H}_2:\text{N}_2$ present in the volume RT are given in Table I, Col. 7.

The mole fractions of ammonia in the gaseous mixtures may be obtained by dividing the values given in Col. 6 for the number of moles of ammonia in the volume RT , by the sum of the values in Cols. 6 and 7. These values, in mole per cent., are shown in Col. 8. In Col. 9 are shown the corresponding values which have been graphically interpolated from the experimental data of Larson and Black.

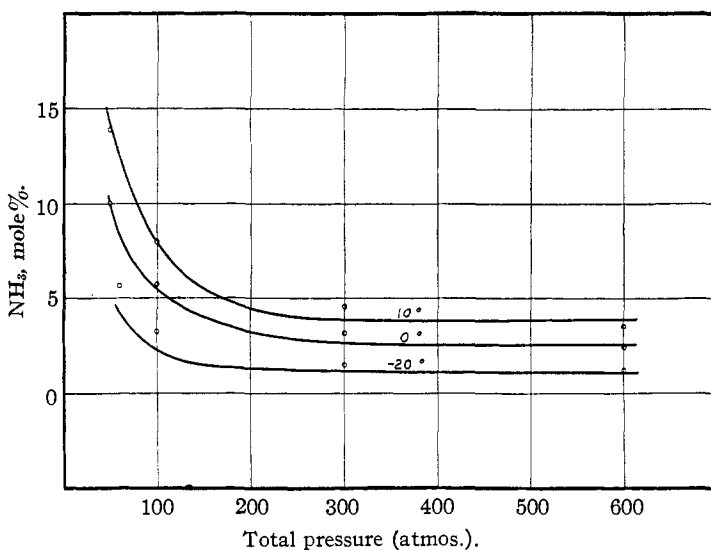


Fig. 1.—Mole percentage of ammonia in $3\text{H}_2:\text{N}_2$ mixture in equilibrium with liquid ammonia. Curves show calculated values; circles show experimental values.

Discussion

Considering the nature of the calculations and the assumptions which are necessarily involved, the calculated values may be said to be in good agreement with the experimental data. Within the pressure range covered by the calculations (600 atmospheres' total pressure), there seems to be no consistent deviation of substantial magnitude, such as would be shown if the gaseous phase had a significant solubility effect for ammonia vapor. Although there is a considerable deviation at the lower temperatures measured by Larson and Black, as illustrated in Fig. 1, it should be noted that this deviation *does not increase with increasing*

¹² Bartlett, Cupples and Tremearne, *THIS JOURNAL*, 50, 1275 (1928).

pressure, as would be expected if it were due to a solubility effect of the compressed gaseous mixture.

A point of interest which appears from these calculations is the fact that comparatively little reduction in the mole per cent. of ammonia in the gas mixture is to be expected on increasing the total pressure beyond 600 atmospheres. At 0° an increase of pressure from 600 to 1000 atmospheres will decrease the volume of the gas mixture to about 75% of its initial value, simultaneously increasing the activity of $\text{NH}_3(1)$ to 152% of its initial value. It is quite possible that at some pressure a minimum value is attained, beyond which the mole per cent. of ammonia in the gas phase increases with increasing pressure. A few of the calculated values do, in fact, indicate a somewhat higher molal concentration of ammonia at 600 atmospheres' total pressure than at 400 atmospheres' total pressure, but at these high pressures this may possibly be due, at least in part, to errors incident to the extrapolation of the equation of state for ammonia vapor.

Summary and Conclusions

A concept of solubility is presented which seems to be especially applicable to systems involving one or more gaseous components. According to this concept, a solubility effect is defined as being a change in the activity of one component which is due to the presence of other components.

A method is outlined by which the two-phase system $\text{NH}_3(1)\text{-NH}_3(\text{g})$, $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$ has been examined for the presence of such a solubility effect. It is concluded that, within the fairly large error of calculation, there is no indication of a solubility effect of the gas phase for ammonia vapor.

An analogous treatment can be applied to other similar systems for which the required data are available. It is to be expected that the conclusions which may be reached will vary in each individual case.

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