



POINT DEFECTS AND THEIR INTERACTION

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INTRODUCTION

An ideal crystal may be defined as a three-dimensional periodic array of atoms (or molecules). Real crystals, however, do not conform to this definition for various reasons. First, even at zero temperature, there are lattice vibrations. Second, in a metal, electrons are not located at well-defined sites but traverse the crystal more or less at random. Third, real crystals contain chemical impurities. Fourth, there are point defects, e.g. interstitial atoms, vacancies, atoms at wrong lattice sites. Fifth, most crystalline specimens involve one- and two-dimensional imperfections, in particular edge dislocations, screw dislocations, stacking faults, and small-angle grain boundaries. These imperfections are not only curiosities, but decisively determine technically important properties, e.g. mechanical strength, light absorption, electrical conductivity, and diffusivities.

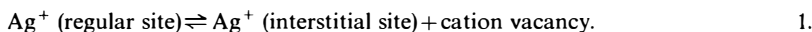
In this article, the history of point defects is briefly surveyed, analogies with imperfections in gases and liquid phases are delineated, and inherent limitations of the concept of point defects in crystals due to mutual interaction are discussed.

HISTORICAL

The concept of point defects evolved in many consecutive steps. In 1914 Tubandt & Lorenz (1) showed that upon passing current across solid AgCl, AgBr, or AgI between Ag electrodes, Faraday's law is obeyed, i.e. ions rather than electrons are the prevailing electrical carriers. Moreover, using the boundaries between pressed pellets as "markers," Tubandt (2) showed that in AgCl, AgBr, and AgI the current is carried virtually only by Ag^+ ions, whereas the anions are practically immobile. Subsequently, in 1926 Frenkel (3) published a most seminal theoretical paper. He suggested that in a state of thermodynamic equilibrium, some Ag^+ ions in face-centered cubic (fcc) AgCl and AgBr do not occupy regular lattice sites but instead occupy interstitial sites while an equal number of regular cation sites are vacant. Interstitial Ag^+ ions may jump from one interstitial site to a neighboring unoccupied interstitial site, or they may push an adjacent Ag^+ ion on a regular site

to a neighboring interstitial site (denoted as interstitialcy migration). Further, silver ions on regular lattice sites may move to adjacent cation vacancies.

The equation for the formation of interstitial Ag^+ ions and cation vacancies may be formulated as



Frenkel pointed out that this equation is analogous to equations for the dissociation of diatomic molecules in a gas. Accordingly, one may apply the law of mass action to this reaction. The equilibrium constant K_1 may be related to the standard Gibbs energy change ΔG_1° of reaction 1, which in turn is determined by the standard enthalpy change ΔH_1° and the standard entropy change ΔS_1° , such that

$$\ln K_1 = -(\Delta H_1^\circ - T\Delta S_1^\circ)/RT. \quad 2.$$

The fraction of interstitial cations or cation vacancies referred to the total number of cations is denoted as the degree of disorder α analogous to the degree of dissociation in gases and in liquid solutions. Hence

$$\alpha^2 = K_1, \quad \text{or} \quad \alpha = K_1^{1/2} \quad \text{if} \quad \alpha \ll 1. \quad 3.$$

The importance of Frenkel's paper cannot be overestimated. Up to 1926 other authors had advanced qualitative rather than quantitative ideas. Von Hevesy (4) used the term *Gitterauflockerung*, i.e. loosening of the crystal lattice. Smekal (5, 6) suggested that motion of ions occurs mostly in incidental pores or along internal surfaces, e.g. in cracks or grain boundaries. Motions of this kind may make a certain contribution to the conductivity but do not yield a conductivity as a well-defined physical property, i.e. a single-valued function of temperature and hydrostatic pressure as the decisive thermodynamic variables.

Between 200 and 400°C, the electrical conductivities of AgCl and AgBr range from 10^{-3} to $40 \Omega^{-1} \text{ m}^{-1}$, whereas the conductivities of molten AgCl and AgBr are about $300\text{--}400 \Omega^{-1} \text{ m}^{-1}$ (1). Assuming that the mobilities of lattice defects in the solid are of the same order as the mobilities of ions in the molten compounds, one arrives at the preliminary estimate that values of α must be at least 10^{-5} . Thus, according to equations 1 and 2, with $\Delta S_1^\circ \approx 0$, values of ΔH_1° cannot be higher than about 100 kJ.

Presuming a rigid lattice of hard-sphere ions as a model, one obtains a value of ΔH_1° which is of the order of the lattice energy = energy required for disintegration of 1 mole of the crystal into gaseous ions (≈ 800 kJ/mole). Actually, "polarization" around defects occurs. Using an admittedly crude model with the macroscopic dielectric constant as a measure of polarizability, Jost (7) has shown that the actual value of ΔH_1° is much less than the lattice energy. These calculations have subsequently been refined by other authors and numerical values have been compared with experimental data (8).

In 1935 Schottky (9) generalized Frenkel's treatment and analyzed theoretically thermodynamic equilibria in ionic crystals in which interstitial cations, cation vacancies, interstitial anions, and anion vacancies are present in finite concentrations. He showed that prevalence of some types of defects is determined by relatively low

enthalpy changes for their formation from the ideal lattice. In particular, he showed that in most alkali halides prevalence of cation vacancies and anion vacancies is to be expected in accord with experiments in which the partial conductivities of cations and anions are of the same order of magnitude.

As a counterpart to disorder in AgCl and AgBr Ure showed (10) that in CaF_2 , the prevailing defects are interstitial anions and anion vacancies in virtually equal concentrations.

An extreme situation occurs in α AgI (stable above 146°C). According to X-ray investigations (11), the anions constitute in essence a well-ordered body-centered cubic (bcc) sublattice with 2 I^- ions in the unit cell, whereas 2 cations are distributed essentially at random on $6+12+24$ sites of 3 different sublattices, i.e. most sites of these sublattices are vacant. Alternatively, according to the results of recent neutron diffraction investigations, it has been suggested that in essence 2 cations are distributed at random on 24 sublattice sites with considerable displacement of the neighboring anions (12).

The general idea of pronounced structural disorder in α AgI is in accord with the fact that the electrical conductivity due to motion of cations is very high ($\approx 250 \Omega^{-1} \text{ m}^{-1}$ at 500°C) and nearly independent of temperature. At the melting point (558°C), the conductivity of solid AgI is 12% higher than the conductivity of liquid AgI.

If the degree of disorder, α , in a crystal such as AgCl or AgBr is less than about 10^{-3} , the concept of interstitial Ag^+ ions or cation vacancies is unambiguous. In the case of α AgI, the situation is different. There are two possibilities: either, there are no "regular" cation sites and all Ag^+ ions occupy various types of interstitial sites; or alternatively, there are regular lattice sites (perhaps in different sublattices) and most of the sites are vacant. These two descriptions are equivalent and therefore not subject to serious controversy.

For the further development of structural models, comparative measurements of the electrical conductivity and the diffusivities in crystals involving small concentrations of foreign cations, e.g. Cu^+ in AgCl by Tubandt, Reinhold & Jost (13), have been important. In essence, it has been found that conductivity data and diffusivities are interrelated in accord with equations derived earlier by Nernst (14) and Einstein (15) for aqueous electrolytic solutions. Deviations from the classical Nernst-Einstein relation were found later. These deviations are formally described by introduction of correlation factors which in turn may be calculated theoretically for appropriate models (16).

In 1931 Wagner & Schottky (17) published a rather general statistical-mechanical treatment of defects in binary solid compounds of composition $A_m B_n$, especially intermetallics, e.g. Fe_4N or CuZn where atoms A and B are presumed to occupy sites of different sublattices in a state of ideal order. The following types of defects have been considered: atoms A and B on interstitial sites; vacancies in the sublattices of components A and B ; and finally atoms A on sites of the sublattice of component B and atoms B on sites of the sublattice of component A . The latter types of defects can practically be disregarded in ionic compounds where the constituent ions of the sublattices have electrical charges of opposite sign and the

enthalpy change for an interchange of the constituent ions between different sublattices is therefore exceedingly high. In intermetallics, however, the latter types of defects are important especially when atoms *A* and *B* have about equal size.

In the above description only first-order effects are considered. In addition, it must be recognized that around each defect, the neighboring atoms (or ions) are displaced to some extent from their regular lattice sites.

From general considerations and equations of statistical mechanics it follows that in a state of thermodynamic equilibrium at $T > 0$, the fractions of the aforementioned defects are greater than zero. Finite concentrations of the various defects are necessarily present in intermetallics involving deviations from the ideal stoichiometric composition. Thus lattice defects are decisive for the width of one-phase fields of intermetallics in a phase diagram T vs mole fraction of component *B*. Conversely, experimental data for the width of one-phase fields of intermetallics in combination with Gibbs energy data of the intermetallics may be used to estimate the concentration of lattice defects (17).

Other point defects of great significance are electrons and holes. Electrons as carriers of the electrical current in metals have been considered since about 1900. To interpret the positive Hall effect in some metals, the concept of holes was introduced by Peierls (18) in 1929 and Heisenberg (19) in 1931. At about the same time it was recognized that electronic conduction in oxides containing an excess of metal, e.g. ZnO, is due to excess electrons. In other oxides involving a deficit of metal, e.g. Cu₂O or NiO, electronic conduction is due to holes. In the language of a chemist, a hole in Cu₂O is represented by a Cu²⁺ ion which may exchange an electron with a Cu⁺ ion as the normal constituent of the cation sublattice in Cu₂O (20). Subsequently, electrons and holes were recognized as the predominant point defects in silicon and germanium, which are the most important elemental semiconductors.

The point defects listed above may form associates. In pure metals, e.g. Cu, self-diffusion at high temperatures is mostly due to monovacancies. In addition there is a small but discernable contribution from divacancies.

In ionic crystals and semiconductors, point defects involving excess electrical charges of opposite sign attract each other and may readily form electrically neutral associates.

Upon absorption of ultraviolet light by Ge or ZnO the primary product may be an excess electron next to an electron hole, denoted an exciton.

In alkali halides of ideal stoichiometric composition, associates of cation vacancies and anion vacancies occur which do not contribute to electrical conduction but do contribute to diffusion of isotopes.

In alkali halides with metal excess, at about 600°C there are only a few free electrons. Most electrons are associated with anion vacancies. Alternatively, one may say that electrons are substituted for anions. These associated defects are known as *F* centers. Their behavior has been investigated especially by Pohl and his associates since about 1925 (21). Since *F* centers are electrically neutral, they do not contribute to electronic conduction. Electronic conduction occurs only inasmuch as *F* centers dissociate into anion vacancies and excess electrons. In

addition, there are F' centers which may be described as two electrons at the site of an anion vacancy. Further associated defects have been found at and below room temperature. For example, there are associates of 2 or 3 F centers denoted as M and R centers, respectively. The properties of these defects have been studied very extensively by optical absorption measurements and in part by other methods, e.g. electron spin resonance (22).

Further, in AgCl doped with CdCl_2 , a cation vacancy and a Cd^{2+} ion substituted for a Ag^+ ion may form an electrically neutral associate, $\{\text{V}_{\text{Ag}}\text{Cd}_{\text{Ag}}\}^x$, in the Kröger-Vink notation (23).

The significance of equilibria between elementary defects and associates is discussed below in greater detail.

STRUCTURAL IMPERFECTIONS IN GASES AND LIQUIDS

Gases

A gas or a gas mixture is usually called "ideal" if at a given temperature the product of pressure P and volume V is constant. This definition of an ideal gas is supplemented by considerations from an atomic point of view. An assembly of atoms (or molecules) as given chemical entities represents an ideal gas if the constituent atoms (or molecules) are far enough apart from each other so that the volume of the atoms is much less than the total volume, and energetic interaction is negligible. Strictly speaking, the conditions for an ideal gas are satisfied only in the limiting case $V \rightarrow 0$. At a finite volume, deviations from the ideal gas law, $PV = \text{constant}$, occur. These deviations can be rationalized by the van der Waals equation as a first approximation.

Interaction between two atoms (or molecules) A and B may be accounted for by writing the energy excess ΔE at distance r_{AB} relative to the energy of A and B at infinite distance as the difference of two terms in accord with Lennard-Jones (24)

$$\Delta E = C_1/r_{AB}^m - C_2/r_{AB}^n, \quad 4.$$

where C_1 and C_2 are constants and the exponents of r_{AB} are set $m = 12$ and $n = 6$ by most authors. Equation 3 may be generalized for interaction among more than 2 atoms or molecules.

In addition, one may consider the occurrence of "anomalous" chemical species formed either by association, e.g.



or by dissociation, e.g.





Formation of associates is characterized by presence of pairs *AA*, *AB*, etc with a "lifetime" considerably longer than the time of a "collision." The formation of associates such as O_4 , $(\text{NO})_2$, or Na_2 has been ascertained especially by observation of characteristic absorption bands, in particular infrared absorption bands corresponding to intramolecular oscillations with frequencies of the order 10^{11} sec^{-1} .

Presence of dissociation products such as I atoms, CO, and Cl_2 may also be ascertained spectroscopically. Formation of ions and electrons may be established by measurements of the electrical conductivity of the gas.

Reactions 5, 6, 7, and 8 are typical examples of association if the species on the left-hand side prevail. Similarly, reactions 9, 10, 11, and 12 are typical examples of dissociation if the species on the left-hand side prevail. With increasing temperature (or decreasing total pressure), the degree of dissociation increases and finally the dissociation products may predominate. Thus use of the terms "association" or "dissociation" depends on temperature and pressure. Accordingly, different definitions of perfect states may be used.

Lewis & Randall (25) have stated expressly that an unambiguous definition of the degree of dissociation is required to devise appropriate experimental methods for its determination and to evaluate experimental data unambiguously. In many situations, e.g. in iodine gas, the resulting principal uncertainty is not serious since the errors of conventional measurements, e.g. determination of the *P-V*-relation, or optical absorption measurements are much greater. The principal uncertainty in the definition of the degree of dissociation, however, must be recalled especially in investigations on solutions of electrolytes, discussed below.

Liquids

The structure of a liquid may be described as a nearly close-packed assembly of atoms or molecules without long-range order. In one-component systems, a liquid may consist of virtually equal chemical species, e.g. argon atoms or benzene molecules. In some cases, however, dissociation and/or association occurs. Thus one has situations which are analogous to situations in gases delineated above.

The occurrence of electrolytic dissociation, i.e. the formation of positively and negatively charged dissociation products, is most conspicuous in conjunction with a well-defined electrical conductivity. A well-known example is the dissociation of water which may be described by the equation



as a first approximation. The affix (aq) indicates that hydronium ions H_3O^+ and hydroxyl ions OH^- do not occur as "free" ions in view of strong interaction with the surrounding water molecules (and their polymers) as electrical dipoles.

For many purposes, the simpler equation



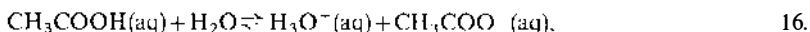
is used. Perhaps the equation



may be considered as a more appropriate approximation (26).

The conductivity of pure H_2O is rather low ($\approx 5 \cdot 10^{-6} \Omega^{-1} \text{m}^{-1}$ at 25°C). Much higher conductivities are observed in solutions involving "electrolytes" as solutes, e.g. HCl , KCl , CH_3COOH . For example, a 0.1 m KCl solution with a solute:solvent ratio of $2 \cdot 10^{-3}$ has a conductivity of $1.29 \Omega^{-1} \text{m}^{-1}$ at 25°C .

After van't Hoff and Arrhenius published their "revolutionary ideas" of electrolytic dissociation in 1887, the exploration of the structure of electrolytic solutions was the most important topic of physical chemistry for the next two decades. For this purpose, investigators used the results of conductivity measurements and further evaluated thermodynamic data derived from measurements of the depression of the freezing point, decrease of the vapor pressure of the solvent, emf measurements of galvanic cells, etc. In some solutions, electrolytic dissociation can be described adequately by a single reaction, e.g.



which obeys the ideal law of mass action (27).

In other solutions, the situation is more involved, inasmuch as more than 2 ionic species occur as dissociation products. For example, in a solution of HgCl_2 , the presence of HgCl^+ , HgCl_3^- , and HgCl_4^{2-} ions in addition to neutral HgCl_2 molecules as prevailing species has been ascertained.

After 1900, difficulties were encountered. First, calculations of the degree of dissociation of simple electrolytes such as HCl , KCl , or KOH yielded different values depending on whether conductivity measurements, emf measurements, or measurements of the depression of the freezing point of the solvent were evaluated. This was found for all electrolytes with apparent values of $\alpha \approx 1$ at concentrations of about 0.1 m. These electrolytes were classified as strong electrolytes. Second, systematic deviations from the ideal law of mass action for hypothetical equilibria such as $\text{HCl}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ were found. This awkward situation was denoted as the anomaly of strong electrolytes.

To represent experimental thermodynamic data regardless of atomic interpretation, Lewis (28) introduced the concept of activity. Subsequently, Noyes & Bray (29) introduced the activity coefficient. Similarly, experimental data have been reported in terms of osmotic coefficients and conductivity coefficients.

Finally, the anomaly of strong electrolytes was in essence resolved by Debye & Hückel (30), who took into account long-range electrostatic interaction among positively and negatively charged ions in accord with Coulomb's law and disregarded the presence of electrically neutral molecules as a limiting case. Similarly, the interpretation of conductivities and diffusivities has become possible (31–33).

Use of approximations in the treatment by Debye & Hückel without proper justification has been criticized. More elaborate calculations, however, have ascertained the validity of the limiting equations for sufficiently dilute solutions (34, 35).

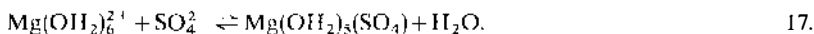
Theoretical equations for the limiting case of very dilute solutions do not involve adjustable parameters. For NaCl solutions, satisfactory agreement between calculated and experimental activity coefficients has been found up to about 0.001 m, corresponding to a molar solute:solvent ratio of about $2 \cdot 10^{-5}$ and an average activity coefficient $f_{\pm} = 0.965$. For NaCl solutions up to 0.1 m corresponding to a molar solute:solvent ratio of $\lesssim 2 \cdot 10^{-3}$, the agreement between calculated and experimental activity coefficients (≥ 0.78) is satisfactory if one introduces $4 \cdot 10^{-10}$ m as the distance of closest cation-anion approach as an adjustable parameter (36). For concentrations exceeding 0.1 m it is necessary to use higher-order approximations of the theory involving additional parameters.

The theory of concentrated solutions of electrolytes contains two principal difficulties. First, one has to know the energies of assemblies of ions for all possible configurations. Second, if one knows these energies, statistical-mechanical calculations of the Helmholtz or Gibbs energy are extremely involved (37).

For calculations of the energy, one has to recognize that at close distances ($\approx 10^{-9}$ m) the energy with respect to infinite distance is no longer determined exclusively by Coulomb's law. Use of the dielectric constant as a macroscopic quantity is not valid for distances comparable to the radii of the ions involved. Also, non-electrostatic interaction energies, e.g. polarization energies must be considered.

Further, one may consider presence of cation-anion pairs, i.e. electrically neutral molecules in accord with Bjerrum (38) and other authors. In this context it must be noted that there is a continuous transition between short-range interaction resulting in the formation of molecules and long-range interaction decisive for the limiting equations of Debye & Hückel. Bjerrum (38) suggested that the limiting value for short-range distance (\approx formation of molecules) is given by the distance at which the magnitude of the pair energy is equal to 2 kT. This definition, however, is arbitrary.

In the case of divalent and trivalent cations, approach of an anion results eventually in the formation of a well-defined inner-sphere complex whose formation may be described as replacement of a H_2O molecule by an anion as ligand. For example, in a solution of MgSO_4 , the reaction is



The rate constants of the consecutive steps of reaction 17 in both directions have been deduced from measurements of the absorption of acoustical waves (39–41), whereupon one may calculate the equilibrium constant of reaction 17. In this manner, the equilibrium constant of reaction 17 has been found to be $4.5 \cdot 10^{-3}$ mole/liter (41). Similarly, the formation of the complex $\text{Be}(\text{OH}_2)_3\text{SO}_4$ has been investigated (42, 43).

In these and other cases, it is expedient to describe the properties of a solution in terms of a superposition of the formation of ion pairs as well-defined associates

and long-range electrostatic interaction (44). In this context, one may introduce an adjustable equilibrium constant K of the reaction



This calculation, however, presupposes that cation-anion pairs, but no other associates such as CuCl_2^- in a solution of CuCl , are present in appreciable concentrations. Calculations of the concentrations of cation-anion pairs are therefore not unambiguous if only reaction 18 is taken in account.

Different kinds of associates occur especially in solutions involving divalent or trivalent cations with associates such as MgCl^+ and MgCl_2 in a solution of MgCl_2 , or CdCl^+ , CdCl_2 , CdCl_3^- , and CdCl_4^{2-} in a solution of CdCl_2 .

Therefore, one may ask whether a more direct experimental determination of the concentration of cation-anion pairs and other associates is possible. For this purpose, one may use optical absorption measurements in the visible region or in the ultra-violet. In this way it has been possible (45) to show the presence of PbCl^+ ions in an aqueous solution of PbCl_2 and to determine the equilibrium constant of the reaction



This brief outline of investigations on the constitution of electrolytic solutions illustrates the variety of questions to be answered. It is evident that real insight requires the use of different experimental methods. This is especially true for mixtures of electrolytes in which eventually many kinds of associates may have to be considered.

INTERACTION AMONG DEFECTS IN CRYSTALS

General Aspects

Interaction among point defects in crystals is in many respects similar to that in gases and liquids. It must be recalled, however, that many crystalline samples contain more impurities than gases or liquids and, therefore, experimental investigations yield reproducible results only if the concentration of defects is relatively high. For many purposes, a crystalline sample is denoted as pure if the content of foreign substances is less than 10^{-4} . Further purification, e.g. by zone melting, is possible but requires great effort (46). Zone melting is especially efficient for the purification of silicon and germanium. Zone melting has also made it possible to obtain KCl with an impurity content as low as 10^{-8} . For NaCl , however, a practical limit is reached at an impurity content of about 10^{-5} because of less favorable distribution coefficients of impurities between solid and liquid NaCl (47, 48).

It is now recognized that reproducible results can be expected only if single crystals with a small density of dislocations are investigated. It must be noted that small contents of additives may be anchored at dislocations and small-angle grain boundaries where they may be immobile. Alternatively, foreign atoms or ions may move along dislocations or small-angle grain boundaries at relatively high velocities; this effect is known as short-circuit diffusion.

In gases and liquids, equilibrium between rare molecular species and the bulk material is generally established within a millisecond or even shorter time intervals. In contrast, establishment of equilibrium in crystals at low temperatures may require much longer spans of time. Thus investigations with frozen-in defects are possible. Investigations on the gradual approach to equilibrium play an important part in solid state physics. In particular, the problem of radiation damage of structural materials and their recovery is mentioned in this context. There are apparently few analogous situations in gases or liquids, with the exception of the slow attainment of equilibrium among different molecular species in liquid sulfur (49).

Moreover, the preparation of crystalline specimens with well-defined compositions is more difficult than in the case of aqueous solutions. By and large, it is easy to prepare a 0.001 m solution involving a solute:solvent ratio of about $2 \cdot 10^{-5}$ with an accuracy of 1%. For crystalline specimens such an accuracy can rarely be attained.

Special difficulties are encountered in investigating the dependence of the properties of an oxide, sulfide, or halide on the excess or the deficit of metal with respect to the ideal stoichiometric composition. Classical chemical analysis does not permit a sufficiently precise determination of the metal:oxygen ratio in a metal oxide involving a small deviation from the ideal ratio. It is possible, however, to determine the amount of excess metal or the metal deficit with the help of other appropriate analytical methods. For example, the excess of metal in ZnO may be determined by dissolving the oxide sample in an aqueous HCl solution and measuring the amount of evolved hydrogen gas (50, 51). The deficit of metal in Cu₂O (equivalent to the concentration of Cu²⁺ ions) may be determined by dissolving Cu₂O in an aqueous solution and titrating the Cu²⁺ ions with a solution of CrSO₄ (52).

In other cases, e.g. Fe₄N, Ag₂S, Ag₂Se, Ag₂Te, CoO, NiO, CuI, one may evaluate the changes in the metal:nonmetal ratio as a function of the activity of metallic or nonmetallic component, which in turn may be determined by partial pressure measurements or by measurements of the emf of appropriate galvanic cells involving solid electrolytes (53).

In addition, one may evaluate physical measurements, e.g. measurements of optical absorption (54, 55), the magnetic susceptibility (56), paramagnetic electron spin resonance (57), or the Hall constant (58, 59). It must be recognized, however, that in some cases, the result depends on the model used for the evaluation of the experimental data.

Even under favourable conditions, the metal excess or the metal deficit has been determined only with an accuracy of about 10^{-4} referred to the ideal stoichiometric composition.

Pure Metals

In most pure metals, the prevailing point defects are vacancies, with a fraction of 10^{-3} or less near the melting point. Their concentration may be determined by combining data for the thermal expansion of the crystal by use of a dilatometer

with the increase of the lattice constant deduced from X-ray investigations (60). Thus the total fraction of vacant sites in Al at 650°C (i.e. 9°C below the melting point) is about $8 \cdot 10^{-4}$. In Ag at 950°C (i.e. 11°C below the melting point), the fraction of vacant sites is about $1.7 \cdot 10^{-4}$.

Vacancies are presumed to effect diffusion in metals and alloys. In a pure metal, self-diffusion may be investigated by use of radioactive tracers. Since the concentration of vacancies is small, one may assume that the temperature dependence of their concentration as well as the temperature dependence of the self-diffusion coefficient $D(T)$ can be represented by an Arrhenius equation

$$D(T) = D_0[\exp(-Q/kT)], \quad 20.$$

where Q is the overall activation energy. In view of equation 20, one may expect that a plot $\ln D(T)$ vs T^{-1} or $(kT)^{-1}$ yields a straight line. Actually, plots show often slight concave upward curvatures. This has been taken as an indication that diffusion is effected not only by monovacancies but in part also by divacancies (61).

Since in a state of thermodynamic equilibrium the concentration of monovacancies and divacancies is always small and since the attractive energy between vacancies due to stress release decreases rapidly with distance, there are few conceptual difficulties in the definition of these defects and their concentration. Further, it is safe to presume that the equilibrium of the reaction



obeys the ideal law of mass action.

It is difficult, however, to deduce the relative contributions of monovacancies and divacancies from a theoretical analysis of D as a function of T since measurements of D are experimentally possible only over limited temperature ranges, e.g. several hundred degrees, and the precision of the data is not extremely high.

Thus it is desirable to evaluate auxiliary data, e.g. measurements of the dependence of D on pressure (62), the isotopic effect (62), and especially the annihilation of positrons trapped at vacancies (62, 63).

Interstitial Alloys

In most metals, atoms of relatively small size, especially H, C, and N, are dissolved as interstitials. The hydrogen content is in essence proportional to the square root of the H_2 partial pressure in a coexisting gas phase in accord with the concept of H atoms rather than H_2 molecules in the metal. At higher hydrogen contents in the metal, however, deviations occur. In the α phase of the system Pd-H, experimental data may be represented by the semi-empirical formula (64, 65)

$$y = K_1 p_{H_2}^{1/2} + K_2 p_{H_2}, \quad 22.$$

where y is the H: Pd ratio in the alloy and K_1 and K_2 are constants. Equation 22 has been interpreted by the assumption that the alloy contains pairs of H atoms in equilibrium with unpaired H atoms,



The fraction of pairs of H atoms has been estimated by applying the ideal law of mass action to reaction 23. At 75°C and $y = 0.02$ about 20% of the hydrogen has been estimated to be present as the associate $\{H, H\}$.

Presence of pairs of H atoms may be assumed to be due to a lower strain energy for two neighboring H atoms in comparison to the total strain energy for H atoms far apart from each other (66).

Actually, the situation is more involved. First, the band structure of Pd is changed upon dissolution of H atoms as potential electron donors (65, 67). Second, the effect of lattice expansion with increasing hydrogen content must be taken into account. This is an indication that the size of an interstice in Pd is not sufficient to accommodate a hydrogen atom without displacement of the neighboring Pd atoms. It may be hypothesized that dissolution of hydrogen becomes easier when the lattice spacing becomes greater with increasing concentration of hydrogen. Evaluation of available data has shown that most of the deviation from the classical Sieverts formula $y = K_1 p_{H_2}^{1/2}$ for unpaired H atoms is due to the effect of the increase of lattice spacing (68). Thus previous investigators have considerably overestimated the concentration of pairs of H atoms. The situation in the systems V-H, Nb-H, and Ta-H is similar. This example shows the inherent difficulties encountered when one tries to deduce the concentration of associates of defects from one kind of experimental data alone. For full understanding, it is necessary to evaluate the results of other kinds of measurements.

Substitutional Alloys

In a substitutional solid alloy A - B with a small content of B , e.g. with a mole fraction $x_B < 0.001$, atoms of kind B may be denoted as defects in metal A as solvent. Conversely, if the mole fraction x_B is close to unity, e.g. $x_B > 0.999$ and $x_A < 0.001$, atoms of kind A may be denoted as defects in metal B as solvent. If the amounts of atoms A and B are of the same order of magnitude, however, the defect concept is not properly applicable. Accordingly, other concepts are used in order to characterize a substitutional alloy of intermediate composition.

In particular, one may consider the numbers of nearest (and next nearest) neighbors around a given atom. In what follows, the total number of nearest neighbors (=coordination number) is denoted by Z . For the limiting case of random distribution of atoms A and B in the lattice it follows from elementary equations of statistics that the mole fraction $x_{A(A_{Z-i}B_i)}$ of atoms A that have $(Z-i)$ atoms A and i atoms B as nearest neighbors is

$$x_{A(A_{Z-i}B_i)} = (1-x_B) \frac{Z!}{(Z-i)!i!} (1-x_B)^{Z-i} x_B^i. \quad 24.$$

For the same conditions, the mole fraction $x_{B(A_{Z-i}B_i)}$ of atoms B with $(Z-i)$ atoms A and i atoms B as nearest neighbors is

$$x_{B(A_{Z-i}B_i)} = x_B \frac{Z!}{(Z-i)!i!} (1-x_B)^{Z-i} x_B^i. \quad 25.$$

Random distribution of atoms A and B practically prevails if atoms A and B are isotopes. Then, in the terms of thermodynamics, one has an ideal solution with zero heat of mixing. Further, the partial pressures of A and B in a coexisting gas phase are proportional to mole fractions x_A and x_B , respectively.

In general, substitutional alloys A - B show deviations from ideality, i.e. the heat of mixing is not equal to zero and the partial pressures of A and B are not proportional to the respective mole fractions. This is an indication that deviations from random distribution of atoms A and B occur. In particular, a negative heat of mixing indicates that A atoms attract B atoms preferentially and vice versa, corresponding to preferential presence of B atoms around A atoms and preferential presence of A atoms around B atoms. Quantitative relations between structure and thermodynamic quantities such as heat of mixing and activities of A and B as functions of alloy composition are necessarily involved. Simple relations are obtained only upon introduction of special assumptions and approximations. Reference is made to the quasichemical theory of mixtures presented, e.g. in the monograph by Guggenheim (69). A basic assumption in the quasichemical theory is that the energy of the system can be written as the sum of the products of the number of "bonds," A - A ,

to be independent of the presence of other atoms in the surroundings. This assumption, however, is not realistic in view of cooperative effects in an alloy in accord with the band theory accounting for the contribution of electrons to binding among the cores of the atoms.

To overcome the limitations of the quasichemical theory due to nonrealistic approximations, Mathieu, Durand & Bonnier (70) and Lupis & Elliott (71) suggested the so-called central atom model. According to this theory, the bond energies between a central atom A or B and the surrounding atoms A and B as ligands are supposed to depend on the number of ligands ($Z-i$) and i of atoms A and B ,

coordination number Z equals 12. Thus one has $Z-1 = 11$ differences of bond energies as adjustable parameters whose numerical values must be deduced from available experimental thermodynamic data whose accuracy is limited. Thus a numerical evaluation of the parameters is practically possible only if one introduces simplifying assumptions, e.g. if one assumes a linear or a quadratic dependence on i .

In a fcc lattice with lattice constant a , the distance to the 12 nearest neighbors is $0.707a$. In addition, there are 6 next nearest neighbors at a distance $1.000a$. Since the distances of nearest and next nearest neighbors differ by only 29%, neglect of the interaction energy of a given atom with next nearest atoms seems controversial. If the next nearest neighbors are also taken in account, the number of unknown parameters is further increased. Then calculations become even less practicable.

In addition, one may evaluate the results of X-ray and neutron diffraction experiments. Even under favorable conditions, however, one obtains only average values for the number of atoms A and B surrounding a given atom A or B but one does not obtain the mole fractions $x_{A(A_{Z-i}B_i)}$ and $x_{B(A_{Z-i}B_i)}$ for $i = 0, 1, \dots, Z$.

Intermetallics

Next consider an intermetallic compound A_mB_n where atoms A and B occupy sites of different sublattices a and b in a state of ideal order. First suppose that an exchange of atoms between sublattices a and b at elevated temperatures occurs,



where the subscripts a and b indicate atoms on sites of the respective sublattices. If the numbers of atoms on wrong lattice sites, N_{A_b} and N_{B_a} are relatively small in comparison to the total number of atoms,

$$N_{A_b} \ll N_{A_a}; N_{B_a} \ll N_{B_b}, \quad 27.$$

one may use the ideal law of mass action as equilibrium condition for reaction 26. For further calculations it is convenient to introduce the mole fractions $x_{A_b} = N_{A_b}/N^I$, $x_{B_a} = N_{B_a}/N^I$, etc, where N^I denotes the total number of lattice sites. If equation 27 holds, the law of mass action may be written as

$$x_{A_b} \cdot x_{B_a} = K_{26}. \quad 28.$$

In an intermetallic compound of ideal composition, N_{A_b} necessarily equals N_{B_a} and, accordingly, $x_{A_b} = x_{B_a}$. The degree of disorder α may then be defined as

$$\alpha \equiv (x_{A_b} - x_{B_a})_{\text{ideal composition } A_mB_n}, \quad 29.$$

whereupon equation 28 may be written as

$$x_{A_b} x_{B_a} = \alpha^2. \quad 30.$$

Wagner & Schottky (17) used equation 30 for calculating x_{A_b} and x_{B_a} in samples involving a small excess of component A or B with respect to the ideal composition. Subsequently, the activities of A and B are obtained as functions of the deviation from the ideal composition. These equations, however, have not been applied to experimental data since these data refer to large defect concentrations x_{A_b} and x_{B_a} , beyond the validity of the ideal law of mass action.

If the number of atoms on wrong sites is relatively large, e.g. in AuCu, AuCu₃, or CuZn, it is expedient to introduce an alternative measure of order, following Bragg & Williams (72). In this case, no deviations from the ideal composition are considered; the degree of order s is defined by

$$s = (r_a - x_A)/(1 - x_A), \quad 31.$$

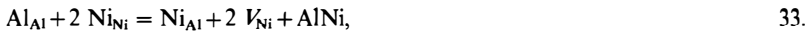
where x_A is the overall mole fraction of A and

$$r_A = N_{A_a}/(N_{A_a} + N_{B_a}) = x_{A_a}/(x_{A_a} + x_{B_a}) = x_{A_a}/x_A \quad 32.$$

is the fraction of sites in sublattice a which are correctly occupied by A atoms. For random distribution of atoms A and B (=complete disorder), one finds that $r_a = x_A$ and, accordingly, $s = 0$. For ideal order where all sites of sublattice a are occupied by A atoms, $r_a = 1$ and, accordingly, $s = 1$.

In this treatment, defects do not appear since only compositions of the sublattices averaged over large regions are considered. Use of the parameter s is expedient for the theoretical calculation of measurable quantities such as X-ray diffraction data or the enthalpy of the compound as functions of temperature T . For this purpose, explicit expressions for energetic interaction between atoms A and B must be introduced (73, 74). Thus, there are the same difficulties as in calculations for substitutional alloys.

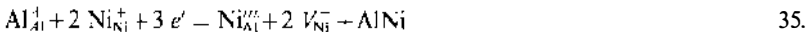
Another type of disorder occurs in AlNi and analogous intermetallic compounds, e.g. AlCo, GaNi, GaCo, InPd, with the bcc CsCl (=B2) structure at ideal stoichiometric composition. According to the results of pycnometric density measurements and X-ray investigations, AlNi with Ni excess contains two atoms per unit cell, corresponding to the presence of Ni atoms on sites of the Al sublattice. In AlNi with Ni deficit, however, the number of atoms per unit cell is less than 2, corresponding to vacant sites in the Ni sublattice (75). Instead of reaction 26 one has the reaction



where excess charges are not indicated. The equilibrium condition reads

$$x_{\text{Ni}_{\text{Al}}} x_{\text{V}_{\text{Ni}}}^2 \approx K_{33} \quad \text{if} \quad x_{\text{Ni}_{\text{Al}}} \ll 1, x_{\text{V}_{\text{Ni}}} \ll 1. \quad 34.$$

The validity of equation 34 is confined to very small deviations from the ideal composition because of pronounced changes of the band structure for the transition of AlNi with Ni deficit to AlNi with Ni excess in view of data for magnetic susceptibility (76), the Hall effect (77, 78), thermoelectric power (77), and optical properties (78–80). It has been suggested (81) that one may consider Al^{3+} ions, electrons, and electrically neutral nickel atoms as constituents of the ideal AlNi lattice. Accordingly, in terms of the Kröger-Vink notation (23), one may formulate the reaction



as an alternative to reaction 33. The pertinent equilibrium condition may be formulated in terms of activities of reactants and products. In view of the relatively large homogeneity range between the compositions $\text{Al}_{0.57}\text{Ni}_{0.43}$ and $\text{Al}_{0.63}\text{Ni}_{0.37}$ at 1000°C it is obvious that there must be pronounced energetic interaction among Al^{3+} ions on regular lattice sites, electrons, and nickel atoms substituted for Al^{3+} ions having a triple negative excess charge with respect to the ideal lattice, and vacancies in the Ni sublattice.

Under these conditions, the law of mass action applied either to reaction 33 or reaction 35 does not yield relations that permit an unambiguous representation of experimental data.

Another fairly simple case of disorder occurs in $\gamma' \text{FeNi}_{1+\delta}$ in which practically no defects in the Fe sublattice, but some interstitial N atoms and some vacancies in the nitrogen sublattice, are found. Theoretical calculations (17) yield a relation between nitrogen activity $a_{\text{N}} = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$ and the nitrogen excess δ with respect to

the ideal composition Fe_4N . Experimental data (82) agree with the theoretical relation

$$\delta = 6.4 \cdot 10^{-4} [(\alpha_N/2.1) - (2.1/\alpha_N)]$$

$$\text{at } 550^\circ\text{C for } -3.7 \cdot 10^{-3} < \delta < -0.4 \cdot 10^{-3}. \quad 36.$$

Ionic Compounds

GENERAL REMARKS In ionic compounds the most important defects are interstitial cations and anions, cation and anion vacancies, and excess electrons and holes, which have a positive or negative excess electrical charge. Thus one has long-range energetic interaction analogous to that in aqueous solutions of electrolytes. The following differences are noted.

1. Upon approach of cations and anions in aqueous solutions H_2O molecules, often firmly bound in the inner shell, must be replaced. Thus the formation of cation-anion pairs can sometimes be described as exchange of ligands as discussed above. In ionic compounds lacking the presence of a solvent no exchange of ligands occurs. Accordingly, the lifetime of cation-anion pairs and other associates is relatively short.

2. In aqueous solutions one measures the mean activity of an electrolyte and further the electrical conductivity of the solution as a function of concentration. In the case of ionic compounds, one may also measure the electrical conductivity as a function of composition, e.g. metal deficit in wüstite, $\text{Fe}_{1-\delta}\text{O}$. Further, conductivity is measured as a function of the concentration of additives (=dopes), e.g. AgCl (+ CdCl_2) or NaCl (+ CdCl_2). In the case of oxides and sulfides with small deviations from the ideal composition, however, conductivity is often measured as a function of the activity of the metallic or nonmetallic component, determined by the equilibrium with a coexisting gas phase with known oxygen or sulfur activity, or by use of a suitable galvanic cell upon which an appropriate voltage is imposed. In these measurements, the conductivity is determined by the composition of the compound but in some cases one does not measure the composition but establishes only the relation between conductivity and the activity of the metallic or nonmetallic component.

In addition, other measurements may be evaluated. For example, one may measure self-diffusion coefficients, the transference number of ions and electrons, the partial conductivity of ions for suppressed motion of electrons, the partial conductivity of electrons for suppressed motion of ions (83, 84), the interdiffusion coefficient \tilde{D} for transport in samples in an ionic compound with a given gradient of metal:nonmetal ratio, and the transport coefficient in samples with a given gradient of the activity of the metallic or nonmetallic component of an oxide. The results of these measurements are interrelated by the general equations of irreversible thermodynamics (85). In a binary compound without dopes there are three independent Onsager coefficients which may be determined experimentally. Ternary systems, e.g. a solid solution CoO-MgO or $\text{NiO-Cr}_2\text{O}_3$ or the spinel NiCr_2O_4 , have six independent coefficients. Their measurement is possible in principle but hardly practicable from the viewpoint of research economy.

In addition, one may evaluate the results of measurements of electron spin resonance, light absorption, dielectric loss, the absorption of acoustical waves, and specific heat measurements.

In what follows, some typical cases of interaction among elementary point defects in ionic compounds are discussed. First, metal deficient metal oxides with prevailing *p*-type electronic conduction and, second, metal halides with prevailing ionic conduction are considered.

Special reference is made to a previous review article on the thermodynamics of point defects and their associates by Schmalzried & Pelton (86).

METAL OXIDES Cation vacancies V_{Ni}'' and holes h^* have been suggested to be the prevailing defects in NiO at elevated temperatures (87). For the reaction



the ideal law of mass action reads

$$x_{V_{\text{Ni}}} x_{h^*}^2 / p_{\text{O}_2}^{1/2} = K_{37}. \quad 38.$$

Then, with $2x_{V_{\text{Ni}}} = x_{h^*}$ as the condition for electrical neutrality it follows that the hole concentration, and accordingly the electrical conductivity σ , is proportional to the sixth root of p_{O_2} if interaction among cation vacancies and holes is disregarded. Thus,

$$\partial \ln \sigma / \partial \ln p_{\text{O}_2} = \frac{1}{6}. \quad 39.$$

In accord with equation 39, a plot of $\ln \sigma$ vs $\ln p_{\text{O}_2}$ at 1000°C yields practically a straight line with the slope $\frac{1}{6}$ if the NiO sample is of high purity (88–90).

An auxiliary calculation shows that for NiO with a Ni deficit $|\delta| = 7 \cdot 10^{-5}$ at 1000°C and $p_{\text{O}_2} = 1$ atm, the Debye parameter κ is $\approx 5.6 \cdot 10^6 \text{ m}^{-1}$ corresponding to $\kappa a \approx 0.23$. In the pressure range $10^{-4} < p_{\text{O}_2} < 1$ atm, the mean activity coefficient f_{\pm} varies, therefore, only between 0.78 and 0.61. Thus, electrostatic interaction among defects in NiO is not significant.

The situation is different for metal deficient CoO. In the pressure range $10^{-4} < p_{\text{O}_2} < 1$ atm, several investigators (91–93) have found that at 1000°C

$$\partial \ln \sigma / \partial \ln p_{\text{O}_2} \approx \frac{1}{4}. \quad 40.$$

Under the same conditions virtually the same dependence of the cobalt deficit $|\delta|$ and the self-diffusion coefficient D_{Co}^* of Co has been found (93–98),

$$\partial \ln |\delta| / \partial \ln p_{\text{O}_2} \approx \partial \ln D_{\text{Co}}^* / \partial \ln p_{\text{O}_2} \approx \frac{1}{4}. \quad 41.$$

These results have been interpreted in terms of a model with nearly equal concentrations of singly ionized cation vacancies V_{Co}' and holes h^* as majority defects. For the reaction



the ideal law of mass action reads

$$x_{V_{\text{Co}}} x_{h^*} / p_{\text{O}_2}^{1/2} = K_{42}. \quad 43.$$

With $x_{V_{Co}} = x_h$, it follows from equation 43 that $x_{V_{Co}}$, x_h , σ , δ , and D_{Co}^* are proportional to $p_{O_2}^{1/4}$ in accord with experimental results according to equations 40 and 41.

For CoO with a metal deficit $|\delta| = 6.5 \cdot 10^{-3}$ at $p_{O_2} \approx 1$ atm and 1000°C and V_{Co}' and h^* as hypothetical defects in equal concentrations, the Debye parameter κ is $3.3 \cdot 10^5 \text{ m}^{-1}$ and $\kappa a = 1.39$. Under these conditions, one has to expect large electrostatic interaction among V_{Co}' and h^* defects. Use of the ideal law of mass action in equation 43 is not justified. The agreement between the experimental and the calculated dependence of σ , δ , and D_{Co}^* on p_{O_2} on the basis of the ideal law of mass action seems to be fortuitous. A model with equal concentrations of V_{Co}' and h^* in CoO at 1000°C is therefore not realistic. It seems possible that the majority effects in CoO at V_{Co}' and h^* , analogous to the defects in NiO, and that the relations in equations 40 and 41, in contrast to equation 39 for NiO, are in essence due to long-range electrostatic interaction among V_{Co}'' and h^* point defects and the presence of some V_{Co}' . For further clarification, additional experimental data, e.g. a determination of the partial ionic conductivity for suppressed transfer of electrons, may be helpful.

In wüstite, deviations from the ideal stoichiometric composition are very large. At 1000°C , the formula is $\text{Fe}_{0.95}\text{O}$ for equilibrium with $\gamma\text{-Fe}$, and $\text{Fe}_{0.87}\text{O}$ for equilibrium with Fe_3O_4 (99). In essence, one has a NaCl structure with virtually no defects in the fcc sublattice of the anions. In wüstite with the composition $\text{Fe}_{0.87}\text{O}$, one has 0.13 cation vacancies and 0.26 holes (chemically equivalent to 0.26 Fe^{3+} ions) per oxygen ion if other defects and associates are disregarded. In the ideal lattice, each cation has 12 other cations as nearest neighbors. Thus, for the hypothetical case of random distribution of the defects around a given cation vacancy with 12 neighboring cation sites, about 1.5 neighboring cation sites would be vacant and about 3 neighboring cation sites would be occupied by the trivalent cations Fe^{3+} . The elementary defects are in part in close vicinity and interaction must be quite significant. Under these conditions, the concept of a cation vacancy as a well-defined entity breaks down. Likewise, it is impossible to define unambiguously associates comprising a definite number of elementary defects. This situation should be treated as a cooperative phenomenon.

It is noteworthy that under these conditions, the dependence of the electrical conductivity on the oxygen equilibrium partial pressure does not differ very much from that for NiO. Experimentally, it has been found for wüstite that (100)

$$\partial \ln \sigma / \partial \ln p_{O_2} \approx \frac{1}{8}. \quad 44.$$

It is also remarkable that the mobility of iron ions in an electrical field is rather high. Upon comparing iron transport in the cell $\text{Fe} | \text{Fe}_{1-x}\text{O} | \text{Fe}$ with self-diffusion data, it has been found that, within the limits of error due to the uncertainty of the effective charge of the iron ions and the correlation coefficients, the Nernst-Einstein relation holds approximately (101).

At lower temperatures, more complex associates and clusters of defects, in part with iron ions on interstitial (=tetrahedral) sites, are present according to results of measurements of X-ray diffraction and neutron scattering (102–104).

The situation in other oxides has been surveyed by Libowitz (105). In addition,

investigations have been published on defects and their associates in ternary oxide systems. An unusual type of interaction has been found in solid solutions CoO-MgO and CoO-NiO (95, 106). At a given MgO:CoO ratio, the metal deficit at 1000°C and $1.3 \cdot 10^{-3} < p_{O_2} < 1$ atm depends on p_{O_2} in the same manner as in pure CoO. Upon addition of MgO, the metal deficit decreases sharply. At $x_{MgO} = 0.7$, the metal deficit is only about 1/50 of that in pure CoO. This sharp decrease cannot be explained by use of the law of mass action. Instead, the following explanation has been suggested. In pure CoO, a trivalent Co^{3+} may readily exchange an electron with 12 neighboring divalent Co^{2+} ions. This exchange lowers the energy of the system by virtue of quantum-mechanical resonance according to Pauling (107). Partial substitution of Co^{2+} by Mg^{2+} ions disturbs the quantum-mechanical resonance. Thus the energy of a Co^{3+} ion (equivalent to a hole) in CoO-MgO solid solutions is higher than in pure CoO.

For a quantitative treatment one may use the central atom model for substitutional alloys (70, 71). As an approximation one may tentatively assume that the energy required for removal of an electron from a Co^{2+} ion increases linearly with the number of neighboring Mg^{2+} ions. Then, using the mathematics for the theory of dissolution of oxygen in liquid binary alloys (108), one finds that the logarithm of the metal deficit in solid CoO-MgO solutions is expected to decrease about linearly with the MgO content x_{MgO} in accord with the experimental results. Analogous results have been obtained for the systems CoO-NiO (106) and Co_2SiO_4 - Mg_2SiO_4 (95, 109, 110).

Spinel has also been investigated. In general, deviations from the ideal stoichiometric composition are relatively large. Thus considerable interaction among elementary point defects must be anticipated. Nevertheless, it is possible to understand qualitatively important features in these systems upon applying the ideal law of mass action (111, 112), e.g. in the systems Co-Cr-O, Co-Al-O, Mg-Fe-O, Co-Fe-O, and Ni-Fe-O (113-115).

METAL HALIDES In AgCl and AgBr, the conductivity σ is given by the sum of the products of the concentrations of the defects Ag_i^+ and V'_{Ag} , their mobilities $u_{Ag_i^+}$ and $u_{V'_{Ag}}$, and the Faraday constant F ,

$$\sigma = (x_{Ag_i^+} u_{Ag_i^+} + x_{V'_{Ag}} u_{V'_{Ag}}) F / V_m, \quad 45.$$

where V_m is the molar volume and $x_{Ag_i^+} = x_{V'_{Ag}}$ in view of the condition of electrical neutrality. In order to determine the concentrations of the defects it is essential to know their mobilities. To determine $u_{V'_{Ag}}$ in AgCl one may dope AgCl with $CdCl_2$, whereupon one obtains a solid solution with Cd'_{Ag} and V'_{Ag} as prevailing defects if the concentration of $CdCl_2$ is large compared to the concentration of the defects in pure AgCl (116). The contribution of the defect Cd'_{Ag} to the conductivity can be disregarded. Thus, measuring the conductivity of AgCl- $CdCl_2$ solid solutions with known $CdCl_2$ contents, the mobility $u_{V'_{Ag}}$ is obtained if interaction between the defects Cd'_{Ag} and V'_{Ag} with opposite charges is negligible. Under these conditions, the conductivity is expected to increase linearly with the $CdCl_2$ content. Actually, deviations from linearity occur, indicating that interaction between Cd'_{Ag} and V'_{Ag} is not negligible. In view of long-range electrostatic interaction, the mobility of

V'_{Ag} is less than in an infinitely dilute solution. In addition, there may be associates $\{Cd_{Ag}V_{Ag}\}^x$ without excess charge that do not contribute to the conductivity. Essentially, the situation is the same as in aqueous solutions of strong electrolytes.

In a crystal $AgCl (+CdCl_2)$, the shortest distance between a cation vacancy and a cadmium ion Cd_{Ag}^* is essentially equal to $\frac{1}{2}\sqrt{3} = 0.87$ times the lattice constant of $AgCl$. In addition, there are associates at a distance equal to the lattice constant as a first approximation. The actual distances differ because of the distortion of the lattice around the dipole $V'_{Ag}Cd_{Ag}^*$. Thus the energy of the associates cannot be calculated definitively using Coulomb's law. In comparison, however, the associates $\{V'_{Ag}Cd_{Ag}^*\}$ have a more definite physical meaning than an ion pair in an aqueous solution of KCl .

The statistical mechanics and thermodynamics of solid solutions of type $AgCl (+CdCl_2)$ have recently been discussed by Allnatt (117).

At lower temperatures, associates have a sufficiently long lifetime that their physical properties may be investigated by use of appropriate methods which may also make possible a direct determination of their concentration. For example, associates $\{V_{Na}Mn_{Na}\}^+$ in $NaCl (+MnCl_2)$ solutions have been investigated using electron spin resonance between 25 and 450°C (118). In $NaCl$ with $x_{MnCl_2} \approx 10^{-3}$, the degree of association is about 2% at 600°C and 45% at 300°C. In addition, dielectric losses due to the reorientation of $V'_{Na}Mn_{Na}^*$ dipoles in an alternating electrical field have been evaluated.

These measurements provide clear-cut information for systems containing small amounts of a foreign halide. In systems containing large amounts of a foreign halide, e.g. in the solid solution $AgBr-CdBr_2$ with 20–35 mole % $CdBr_2$ at 300–400°C (119), point defects and associates as well-defined entities do not exist. Perhaps one may formulate equations for the mole fractions of Ag^+ ions, Cd^{2+} ions, and cation vacancies with specified numbers of these species as nearest neighbors analogous to equations for binary and ternary substitutional alloys in accord with the so-called central atom model (70, 71). Similarly, one may try to describe the state of ZrO_2-CaO , $ZrO_2-Y_2O_3$, and other solid solutions involving a large number of anion vacancies more or less associated with the cations of the solute oxides. These solid solutions with a high ionic conductivity at temperatures above 800°C are of special interest for emf measurements and fuel cells (86). The behavior of these solid solutions is somewhat complex inasmuch as the conductivity at a given temperature may vary with time. This indicates slow attainment of the equilibrium distribution of the elementary defects. Reference is made to a review article by Etsell & Flengas (120).

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