NASA TR R-112

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNICAL REPORT
R-112

A METHOD FOR THE CALCULATION OF LATTICE ENERGIES OF COMPLEX CRYSTALS WITH APPLICATION TO THE OXIDES OF MOLYBDENUM

By WILLIAM S. CHANEY

1961

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. Yearly subscription, $15; foreign, $19; single copy price varies according to size --------- Price 50 cents

TECHNICAL REPORT R-112

A METHOD FOR THE CALCULATION OF LATTICE ENERGIES OF COMPLEX CRYSTALS WITH APPLICATION TO THE OXIDES OF MOLYBDENUM

By WILLIAM S. CHANEY

Langley Research Center
Langley Air Force Base, Va.

CONTENTS

	Page
SUMMARY	1
INTRODUCTION	1
SYMBOLS	2
THE OXIDATION PROBLEM	2
INTRODUCTORY DISCUSSION OF THEORETICAL CONCEPTS	3
Coulombic Energy	4
Vector System of Expressing Crystal Structure	4
Polarization Energy	5
Van der Waals Energy	5
Repulsion Energy	5
Born-Haber Cycle	5
Unique Layer Structure of Molybdenum Trioxide	6
Covalent Energy	6
CRYSTAL STRUCTURE	7
LATTICE ENERGY	12
Coulombic Energy	13
Polarization Energy	15
Van der Waals Energy	17
Repulsion Energy	18
Summary of Energies	21
INTERLAYER ENERGY	21
COVALENT EFFECTS	24
DISCUSSION	25
Model	25
Experimental Work	27
Temperature	27
CONCLUDING REMARKS	27
APPENDIX A—CRYSTAL-STRUCTURE CALCULATIONS	29
Crystal-Structure Data	29
Atom Positions and Bonds	30
APPENDIX B—METHODS OF ENERGY CALCULATIONS	34
Calculation of Coulombic Energy	34
Calculation of Polarization Energy	36
Calculation of Van der Waals Energy	38
Calculation of Repulsion Energy	39
APPENDIX C—METHOD OF OBTAINING POLARIZABILITIES OF IONS	40
APPENDIX D—THERMOCHEMICAL DATA AND THE BORN-HABER CYCLE	43
Thermochemical Data	43
Lattice-Energy Calculations by Born-Haber Cycle	43
REFERENCES	44

TECHNICAL REPORT R–112

A METHOD FOR THE CALCULATION OF LATTICE ENERGIES OF COMPLEX CRYSTALS WITH APPLICATION TO THE OXIDES OF MOLYBDENUM

By William S. Chaney

SUMMARY

A theoretical study has been made of molybdenum dioxide and molybdenum trioxide in order to extend the knowledge of conditions and factors involved in the oxidation of molybdenum. The lattice energies have been calculated by using an improved and more generalized method which is based on the electrostatic model. The crystal structure has been examined and the details of the structure have been correlated with the valence mechanisms contributing to the lattice energy.

There are several energy-producing valence mechanisms which contribute to the lattice energy. Those studied herein are coulombic energy, polarization energy, Van der Waals energy, and repulsion energy. The methods used to compute these energies have been modified and improved making them applicable to many types of crystals which could not be readily studied with the old methods. In particular, the new method permits the calculation of lattice energies of distorted crystal structures such as those found in the oxides of molybdenum.

The data reported by X-ray crystallographers have been transformed into a vector system. This system is easier to apply in the energy calculations and easier to use in sketching the crystal structure.

Covalent effects have been examined in the molybdenum oxide crystals but a quantitative calculation of covalent energy was not attempted. A postulated covalently induced electrostatic energy was briefly investigated and appears to be feasible.

It is felt that the overall study has provided much insight as to the nature of the bonding mechanisms responsible for the stability of these oxides. In particular, the layer structure and weak interlayer bond found in molybdenum trioxide are believed to be responsible for the high vapor pressure of this oxide.

Perhaps of more general significance, the methods developed in this research should be useful in extending the knowledge of complex crystals which have not been subject to this type of study before.

INTRODUCTION

The electrostatic theories of valence have been used for many years to compute lattice energies and to study the relationships among crystal structure, lattice energies, and physical properties of crystals. The established methods are limited, however, to relatively simple crystal structures possessing great symmetry. The mathematical methods that are employed take advantage of the crystal symmetry to express the energy relationships in terms of mathematical series which may be resolved by established techniques. Although the complexity of the established methods limits their application to relatively simple symmetrical crystal structures, many real crystals are amenable to these methods.

In this investigation, the electrostatic theories of valence were applied to the dioxide and trioxide of molybdenum. Because of the unusual and distorted crystal structure of these oxides, the usual method of computing the components of lattice energy could not be applied. A new method has been developed which is more general in its scope. This method is discussed in great detail and it is applied to these two oxides of molybdenum. Because of the more general character of this method, it should be possible to apply the electrostatic theories of valence to the many complex crystals which have not been

investigated by this means before.

Molybdenum is a metal which has attracted interest. It possesses properties which make it a potentially useful structural material in high-temperature environments. However, in an environment with very high temperatures and an oxygen containing atmosphere, such as the environment for very high-speed terrestrial flight, molybdenum combines with oxygen catastrophically.

The oxidation of molybdenum has been studied by many investigators using empirical and experimental methods. Apparently no theoretical study has been made of this problem. A theoretical study was undertaken here to extend the knowledge of the conditions and factors involved in the oxidation of molybdenum.

The author wishes to express his appreciation to Dr. O. K. Rice, Professor of Chemistry, University of North Carolina, for constructive criticism and helpful advice.

SYMBOLS

A_M	Madelung constant
a_o	Bohr radius
a,b,c	crystal cell dimensions
B	repulsion constant
c	conversion factor, kcal/erg
$\vec{D}$	vector between two ions
d	distance between ions
E_I	ionization potential
e	electronic charge
$\vec{F}$	electric field vector
$\vec{G}$	position vector of a polarizable ion
g	repulsion exponential law parameter
$\vec{I}$	general position vector of an ion
$\hat{i},\hat{j},\hat{k}$	unit vectors in an orthogonal system
J	Van der Waals dipole-dipole coefficient
L	Van der Waals dipole-quadrupole coefficient
M_{ij}	number of bonds between ions i and j
$\vec{Mo}^l$	molybdenum ion position vector
N	number of polarizable electrons
N_{Av}	Avogadro's number or number of polarizable ions
n	repulsion power law parameter
$\vec{O}_l^l$	oxygen ion position vector
P	number of outer shell electrons in an ion
p_r	repulsion coefficient defined by equation (74)
q	electric charge
R	interionic distance at equilibrium
$\vec{R}$	vector from the origin of one cell to the origin of another cell
R_j	ionic refraction of the jth ion
r	ionic radius
U	energy
U_c	coulombic energy
U_{dd}	Van der Waals dipole-dipole energy
U_{dq}	Van der Waals dipole-quadrupole energy
U_p	polarization energy
U_r	repulsion energy
U_s	stabilization energy
U_t	total lattice energy
x,y,z	Cartesian coordinate system axes
Z	valence
α	polarizability
α,β,γ	interaxial angles of the crystal cell
$\hat{\alpha},\hat{\beta},\hat{\gamma}$	unit vectors in the directions of the crystal-cell axes
η	parameter, layer number
ρ	scaling parameter
τ	number of ions per unit cell
$\vec{\mu}$	electric dipole moment
ξ	number of moles or stoichiometric units per unit cell

THE OXIDATION PROBLEM

In general, all metals except certain noble metals have a natural tendency to react with oxygen gas and form an oxide. The usefulness of a metal as a structural material is greatly dependent on the rate at which this oxidation process proceeds. The basic method of controlling the oxidation process is to interpose a barrier between the metal surface and the atmosphere. This barrier may be an artificial device, such as a coat of paint; however, for metals known to be inherently oxidation resistant, the barrier is usually a tough tightly adherent oxide film.

The oxide of a metal is a very important factor in the oxidation characteristics of the metal. The oxide film may be loose, porous, or flaky and provide little protection to the underlying metal. A protective oxide will form a tough and tightly adherent film. If a break in this film should occur then subsequent oxidation will repair the defect. This is said to be a self-regenerative film.

The oxidation process that occurs in the presence of a self-regenerative protective oxide film is controlled by the rates of diffusion of either the oxygen atoms or the metal atoms or both. The force that drives the diffusion of atoms through the film is related to the gradient of the chemical potential of these atoms across the film. As the film becomes thick and the gradient of the chemical potential small, the oxidation process may reach a virtual standstill. Nonprotective oxides may occur where the oxide is in the gas state rather than the solid state. Molybdenum trioxide exists as a solid at lower temperatures but readily vaporizes at higher temperatures affording practically no protection for the metal. At high temperatures, molybdenum oxidizes very rapidly and this imposes a serious limit on the usefulness of the metal as a structural material.

There are several oxides of molybdenum known to form under various conditions with compositions ranging from a metallic oxide Mo_3O to the trioxide MoO_3. The formation of oxides on the metal surface is probably a complex transition through several of the possible compositions. At high temperatures the dioxide changes to the trioxide. The trioxide is unstable in the sense that it does not remain solid and certainly does not form a protective coating. The trioxide melts at a temperature of 1,068° K under pressures as low as 10 mm Hg. At a temperature of 1,428° K and a pressure of 1 atmosphere, the molten molybdenum trioxide vaporizes. Direct sublimation occurs at 0.3 mm Hg and 973° K.

There are two general areas of importance in research on oxides as they are related to the oxidation of metals. The first pertains to the physical nature of the oxide itself and to the underlying reasons for the failure of the oxide to form a protective film. The second pertains to modifications of the oxide to make it more stable and to reduce the diffusion controlled oxidation rate. The feasibility of research in this second area has been demonstrated by Wagner in his theory of oxidation (discussed in ref. 1) where it is shown that small additions to the base metal can modify a diffusion controlled oxidation rate. Also, some double oxides are more stable than the single oxides forming them. These two areas of research are related in that the first provides a foundation of knowledge on which the second may be based.

The present research is devoted to an exploration of the kinds of forces holding the oxides of molybdenum together, of the relative magnitudes of the energies involved, and of the relationship of these features to the crystal structure.

INTRODUCTORY DISCUSSION OF THEORETICAL CONCEPTS

An introductory discussion of the underlying concepts which form the basis for the theoretical developments in this investigation is given here. Readers who are familiar with this field of work may desire to omit reading this section.

The electrostatic theory of valence is a very old theory and contains contributions from many early workers. The method of computing the bonding energy of molecules and the lattice energy of crystals has long been established for certain compounds. This method is capable of yielding accurate quantitative results in many cases, especially for crystals that are essentially ionic in the nature of their bonds. It is possible to account for the structural configuration of many presumably covalent compounds on the basis of the electrostatic theory.

The model used in the electrostatic theory is based on the assumption that ions are formed by the transfer of electrons from the more electropositive element to the more electronegative element, thus forming cations and anions, respectively. The ions are assumed to exist in the crystal as quasi-spheres with a moderate amount of hardness and with a variation in size over a small range. Except when the ions are polarized, the electric charge is assumed to be concentrated at the center of the sphere. In the presence of an electric field, the ions may be polarized by acquiring an induced separation of the centers of positive and negative charge. The ions contain "orbiting" electrons which, on a short-time basis, act with the nucleus to produce a revolving electric dipole and in two adjacent ions the revolution of these dipoles may become synchronized to produce an attractive force between the ions. When forced together the ions repel one another by repulsion forces (other than coulomb forces) which presumably act in compliance with the Pauli exclusion principle. In most computations the temperature is presumed to be 0° K. The ions in crystals vibrate about their mean positions with zero-point vibrational energy. In cases

where the cation has partially filled d-orbitals, crystal field effects may be present. The crystal field effects are not present in the trioxide of molybdenum and are assumed to be ineffective in the case of the dioxide.

In lattice energy calculations based on the electrostatic theory, there are several energy contributions which are computed individually. These include coulombic energy, polarization energy, Van der Waals energy, and repulsion energy. Zero-point vibrational energy and crystal field effects are not included in this work. The theoretical concepts are developed in the text and the application of these concepts is carried out in appendixes A to D.

COULOMBIC ENERGY

The coulombic energy is the electrostatic potential energy of a molecule or stoichiometric unit located in an infinitely large crystal. Since the charge of each ion is assumed to be concentrated at the center point of that ion and potential energy contributions of neighbors are additive, the computation of coulombic energy amounts to a summation of potential energy contributions from an infinite array of point charges. The electrostatic potential energy of one ion due to another is proportional to the reciprocal of the distance between them and decreases in magnitude as the distance increases. However, for one reference ion in an infinite crystal, the number of neighbors increases rapidly with the distance away from that ion. The overall crystal is electrically neutral and there are positive and negative energy contributions resulting from the different pairings of positive and negative ions. The net effect is that for a reference ion the electrostatic potential energy increases in magnitude as neighbors are added in an array about it and rapidly levels off to a fixed value. In simple crystals, the potential energy contributions may be arranged in the form of a mathematical infinite series and the limiting value of the sum determined by analytical techniques. This method has been used, in several variations, to effect such a summation for most common types of simple crystals.

Where a crystal is found to be distorted with very little periodicity of the ion spacing within a single cell, the labor involved in the method just described would be very great and the results would be applicable to only one anomalous crystal. In this research a method of effecting the summation is developed that requires no symmetry at all within a crystal cell. This method takes advantage of the periodic arrangement of the cells themselves and the electrostatic potential energy of a cell of ions in an infinite crystal of cells is determined. The summation of potential energy contributions for a single reference cell as neighboring cells are added in layers around it is expressed in terms of a distance parameter η. The calculation is made on an automatic computer with the lattice expanding until covergence is established. The final contribution of long-distance neighbors is determined by extrapolating to the limit of the potential energy as η approaches infinity. This method is applicable to any crystal and is limited only by the computational speed of the computer.

VECTOR SYSTEM OF EXPRESSING CRYSTAL STRUCTURE

Consideration of the problem of computing the coulombic energy of a crystal should make it apparent that a system is needed to express the position of each ion within a unit cell and to express the position of any cell with respect to a selected reference cell. A vector system has been selected because of the convenience of the vector notation and established vector methods of computation. The system adopted is actually a compound system consisting of reference systems located at each point in a larger reference system. Each cell in the crystal constitutes a reference system with the cell edges parallel to the cell reference system axes. The origin of the cell is the origin of the cell reference system. The position of each ion in the cell is specified by a position vector in the cell reference system. In the larger reference system, a single cell is selected as a reference cell and the origin of the cell is the origin of the system. The axes are again parallel to the cell axes but distances along each axis are measured in units of cell dimensions. In this system, a vector specifies the position of the origin of a cell with respect to the origin of the reference cell.

The advantage in using this compound system is that the relative position of any one ion with respect to any other ion may be simply expressed as an algebraic sum of vectors. The notation is particularly convenient for the methods of computation developed in this research.

The position of each ion or atom in the cell of a crystal has been determined, for many substances, by experimental measurements using X-ray diffraction techniques. The experimental data which are used in this work are given in appendix A.

POLARIZATION ENERGY

Polarization energy exists for an ion in a crystal when there is an electric field present at the position of the ion. The electric field acts to cause a separation of the centers of positive and negative charge in the crystal producing an electric dipole. This electric dipole then acquires an electrostatic potential energy in the electric field. The net energy effect is called the polarization energy. Most simple symmetrical crystals have a symmetric distribution of positive and negative charges for which the associated electric fields cancel at the position of each ion and polarization energy does not exist. The requirement of symmetry that made possible the calculation of coulombic energy with mathematical series effectively eliminated crystals in which polarization energy would be expected. Polarization energy is to be expected in many distorted crystals and isolated molecules.

The computation of the electric field at some selected point in an array of point charges requires a vector summation of the electric fields associated with each charge since the electric field is a vector quantity. This summation is somewhat analogous to the coulombic energy problem except that convergence is much more rapid.

VAN DER WAALS ENERGY

Van der Waals energy, a kind of potential energy, is associated with Van der Waals forces, a term applied to general forces of attraction and repulsion of uncharged molecules. This term includes the interaction of molecules which possess permanent electric dipole moments. The interaction of molecules, atoms, and ions not possessing permanent dipole moments is the kind of Van der Waals energy being considered in this research. The associated forces are also called London forces. The presence of a charge on an ion does not prohibit the existence of Van der Waals forces; rather, these forces are superimposed on the coulombic forces which are attributable to the charges.

A mechanical model frequently used to explain the Van der Waals forces between atoms is described by the synchronized revolving dipoles mentioned previously. The theory of Van der Waals energy is discussed in almost every textbook on quantum chemistry and will not be repeated in detail in this paper.

Van der Waals energy is a relatively small contribution to the total lattice energy of an ionic crystal. It can be an important factor in some crystals in determining which of two possible similar structures is most stable.

REPULSION ENERGY

Whenever two atoms or ions are forced together they tend to resist this force; that is, they tend to occupy a certain volume in space and resist any action which would reduce this volume. This behavior presumably is attributable to the Pauli exclusion principle. The methods of computing the energy associated with this repulsion force are empirical. There are two methods in general use known as the "inverse power law" and the "exponential law." Each method employs an expression with two unknown parameters. One parameter is eliminated by setting the derivative of lattice energy with respect to the interionic distance equal to zero at the experimentally determined distance. It is presumed that at the experimentally determined distance, the potential energy forces are all in equilibrium. The second unknown parameter may be determined by using experimentally determined compressibilities or by using empirical constants. The inverse power law was used in this research because it was mathematically simpler. Both laws are valid for ions the potential energy forces of which are in equilibrium. The exponential law is considered by many investigators to be better where the forces are not in equilibrium.

BORN-HABER CYCLE

The validity of the model used in these calculations of energy may be tested by comparing the theoretically determined lattice energy with the experimentally determined lattice energy. The Born-Haber cycle is used to determine the experimental lattice energy from thermochemical measurements of the heats of formation. The heat of formation of a crystal is the energy

released when the crystal is formed from the elements in their natural state at standard conditions. The lattice energy is energy released when the crystal is formed from the elements in the state of gaseous ions. The Born-Haber cycle allows for such factors as heats of vaporization and dissociation and also for ionization potentials and electron affinities in computation of empirical lattice energy.

UNIQUE LAYER STRUCTURE OF MOLYBDENUM TRIOXIDE

Upon examination of the crystal structure of molybdenum trioxide, it becomes apparent that this crystal is made up of layers. In nonlayer crystals, the metal and nonmetal atoms are in alternate positions so that like atoms are not adjacent to one another. Layer crystals, in this sense, are typified by structural layers the boundaries of which are defined by like atoms in the surface of one layer being adjacent to like atoms in the surface of the neighboring layer. Layer structures are believed to result from directed covalent bonds or large polarization of the anions. This same structural concept can be carried further to include crystals made up of chains or crystals of small individual molecular configurations wherein the boundaries are still defined by like adjacent atoms.

The importance of layer structures in consideration of their stability characteristics lies in the kind of bonding between the layers. It is not necessary that a crystal have every bond in it broken in order that it lose its solid state. In the sense of becoming nonsolid, the crystal may fail by separating into small structural units. Only a small part of all the bonds in a crystal may break and, in view of this, it is worthwhile to examine the different kinds of bonds in a crystal to see which might be the weakest.

It is generally believed that the interlayer bonding in ionic crystals is predominantly Van der Waals bonding. This conclusion is reached by elimination of the other types of bonds. The most influential type of bond that might be present in an ionic crystal is the coulombic bond. The section entitled "Interlayer Energy" is devoted to an effort to make a quantitative estimate of how much coulombic contribution there is in the interlayer bond. It is shown there that Van der Waals bonding is not predominant.

COVALENT ENERGY

Covalent energy is sometimes discussed in connection with ionic crystals as a sort of residual energy that represents the difference in measured lattice energy and lattice energy computed on the basis of the electrostatic model. This is not a good explanation of the lack of agreement in energy calculations although where the difference in energy is small the error in concept is probably not so objectionable as when this difference is large. Generally, the concept of the covalent bond implies a utilization of the valence electrons that would make the assumptions in the electrostatic theory invalid. However, in the case of molybdenum dioxide, there are two d-electrons for the plus-four molybdenum ion that are not a part of the valence electrons so far as the electrostatic model is concerned. On the basis of distance between pairs of molybdenum ions, Pauling has suggested that these d-electrons interact to form a covalent bond (ref. 2, p. 437). If this is true, then, since these d-electrons are not a part of the valence electrons in the electrostatic model, the energy of this covalent bond would exist independently of the electrostatic energies. It happens that the difference in measured and computed lattice energies for molybdenum dioxide is much greater than a reasonable upper limit to an estimate of this covalent bond energy. Because of this, it is worthwhile to look further to see if some unaccounted energy-producing mechanism is present.

A large difference in an ionic bond as compared with a covalent bond lies in the electron density in the region between nuclei. For a pure ionic bond, the valence electrons are virtually completely transferred from the cation to the anion and the two ions are attracted by a coulombic force. In this case, on examining the electron density along a line from the cation nucleus to the anion nucleus, there will be a point where the electron density is virtually zero. In contrast, for a covalent bond the electron density is not zero at any point between nuclei but rather it is greater than the electron density of free atoms positioned in the same locations. This implies a localization of charge between nuclei rather than charge transfer which is compatible with the conventional concept that in the covalent bond there is a sharing of electrons.

In the section entitled "Covalent Effects," it is assumed that the d-electrons in the molybdenum dioxide lattice are diffusely located between the nuclei of closely spaced molybdenum ions. A rather crude electrostatic model is then hypothesized and used to compute the coulombic energy. On comparing coulombic energy values computed with different internuclear charges with measured energy values, it can be determined that the internuclear charge which yields the correct coulombic energy is of the right order of magnitude to imply that this hypothesized model is feasible.

CRYSTAL STRUCTURE

The physical mechanisms which operate to produce the different contributions to the lattice energy and the physical properties of a crystal are closely related to the geometrical arrangement of the atoms in the crystal. It is necessary to be able to orient the crystal conceptually and to express the position of each atom in a form which may be adapted to subsequent mathematical developments.

It is difficult to form a mental image of a complex crystal. A device frequently used to facilitate description of complex crystals is to describe them in terms of polyhedra. Many crystals are made up of octahedra or tetrahedra and the description of the crystal may be simplified by expressing relationships of, say, octahedra rather than atoms. The relationship between atoms is expressed in the description of a single octahedron. In both molybdenum dioxide and molybdenum trioxide the octahedra are formed with an oxygen atom at each of the six corners and the molybdenum atom in the center. This arrangement is shown in figure 1. The octahedron shown in this figure is regular. It will be seen subsequently that the real octahedra in these oxides are distorted. The representative octahedron is shown in figure 2. In schematic sketches of crystals, corner views and edge views of the octahedra are used and these are shown in figure 3. Molybdenum trioxide is represented in figure 4 where figure 4(a) shows the top view of a single layer and figure 4(b) shows the edge view of the layers. Molybdenum dioxide is shown in figure 5. Of course, figures 4 and 5 represent only a small section of the crystal and the extension in all directions should be apparent.

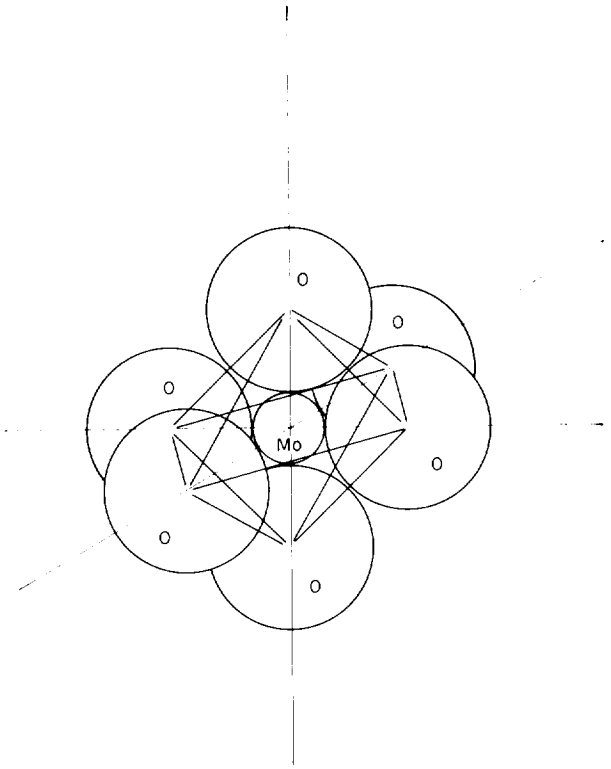


FIGURE 1.—Octahedron representing an arrangement of atoms.

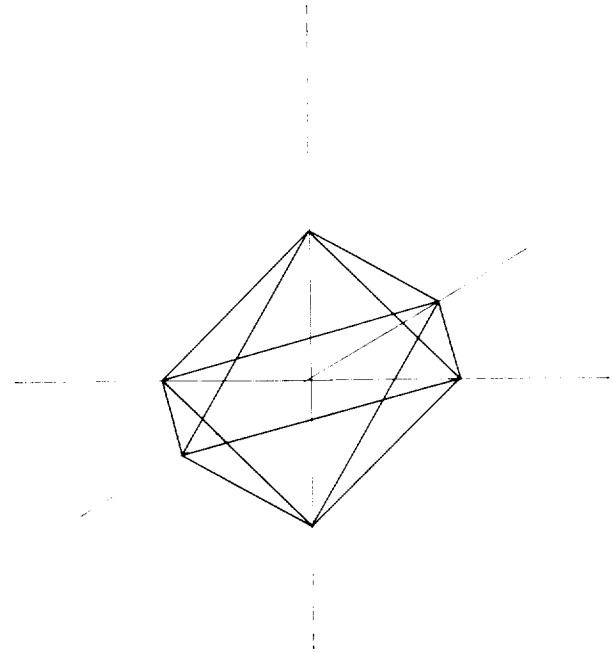
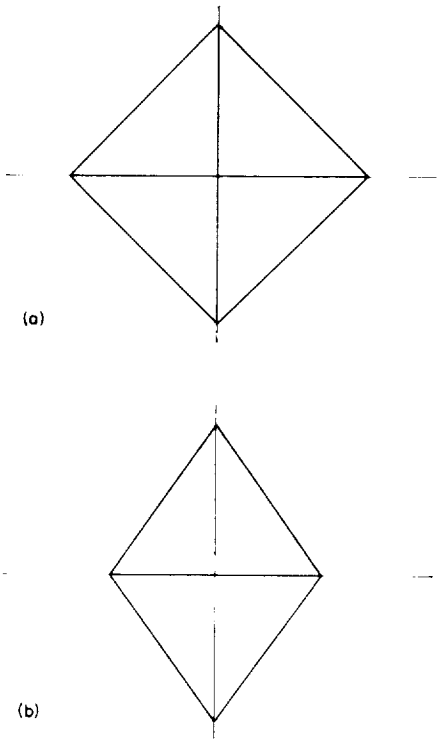


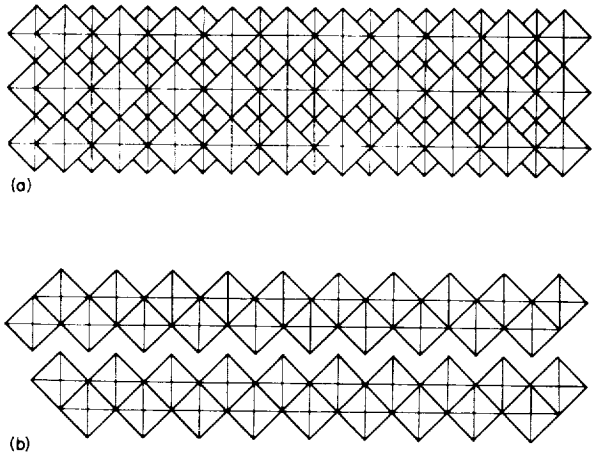
FIGURE 2.—Typical schematic drawing of octahedron used to represent atomic configuration.



(a) Corner view of an octahedron.

(b) Edge view of an octahedron.

FIGURE 3. Representative views of an octahedron.



(a) Top view of a layer.

(b) Edge view of layers.

FIGURE 4.—Schematic structure of MoO_3.

When octahedra are joined then the atoms located at such a joint are shared by the neighboring octahedra. Frequently the sharing of atoms by octahedra will define the differences in "kinds" of atoms of the same element according to environment. By inspection of figure 4, it may be seen that there are three "kinds" of oxygen atoms in molybdenum trioxide. The three "kinds" are those shared by three octahedra, those shared by two octahedra, and those that are unshared. The two "kinds" of oxygen atoms in molybdenum dioxide are not so apparent in figure 5. In this case, the distortion of the octahedra is significant in establishing environmental "kinds" of atoms.

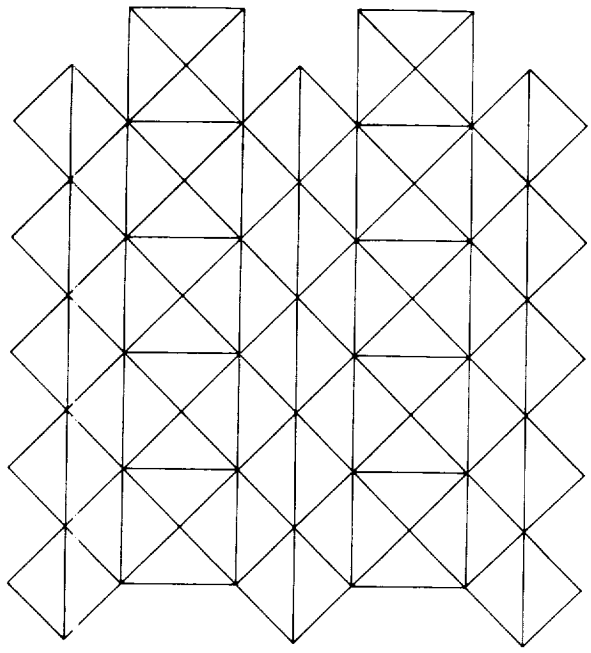


FIGURE 5.—Schematic structure of MoO_2.

The structure of crystals is established by specialists using X-ray diffraction techniques. The general subject area of crystallography and X-ray diffraction studies is somewhat complex in notation and terminology. In order to use this information it is necessary to translate the description of the crystal from the compact notation of the X-ray crystallographer into a longer form more appropriate for mathematical developments. This form may be called the "reconstructed lattice." In a practical sense, there are several features of the crystal structure that should be expressed. The size and shape of the unit cell must be known. This information is given by the type of lattice and the cell dimensions. Next, the position of each atom within the cell must be known. This is expressed by the space group and the atom position parameters. For use in subsequent

developments in this paper, it is convenient to express the position of the atoms in the cell by position vectors. The axes of the reference system for these vectors are parallel to the cell edges and the unit vectors are 1 angstrom unit long. The system is not necessarily orthogonal.

The lattices of molybdenum dioxide and trioxide are reconstructed by using the following method. The outlines of the cells and the positions of the atoms are given in figures 6 to 9. These sketches are not easy to interpret from a casual glance but rather require the coordinated study of different views, with attention directed toward atoms of particular interest. It is possible to locate and identify each atom and its neighbors and then to associate the proper position vector with each atom. A method is given for taking X-ray diffraction structural data in the form in which it is conventionally presented and from this arriving at a set of atom or ion position vectors. These position vectors are then used to reconstruct the lattice, to calculate bond lengths, and to calculate interbond angles.

Structural data from X-ray diffraction studies include the following information:

(1) Type of lattice
(2) Space group
(3) Cell dimensions
(4) Atom positions

The atom positions will be given according to the equivalent positions that are occupied and the atom position parameters to be used with the general coordinates of the equivalent positions. The general coordinates of the equivalent positions are established by the symmetry properties of the space group. This information has been assembled in the International Tables for X-ray Crystallography (ref. 3) wherein also the conventional symbols of crystallography used in this investigation are given. The information necessary for the present work is given in appendix A.

The atom position parameters may be substituted into the general coordinates of the appropriate equivalent position and the result will be the coordinates of the atoms in units of cell

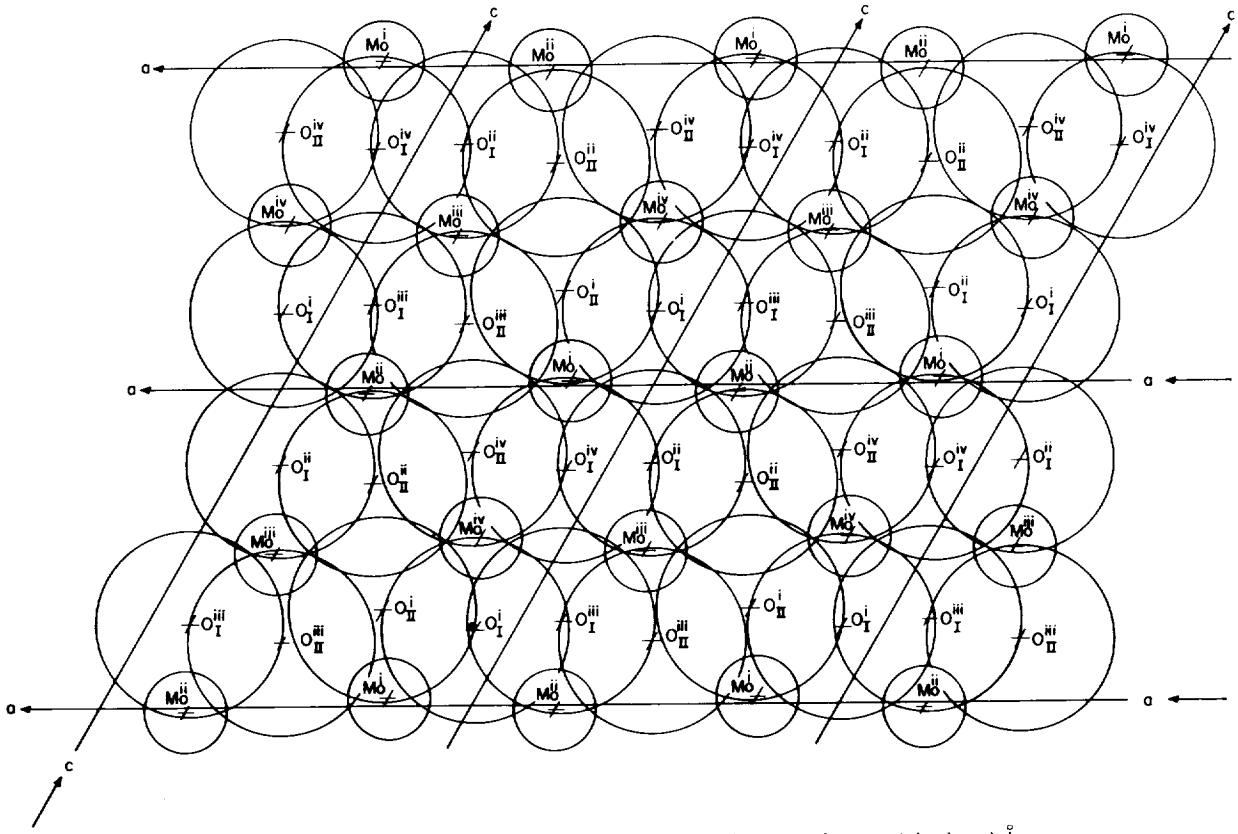


FIGURE 6.— Projection of MoO_2 model on ac-plane. 1 inch = 2 Å.

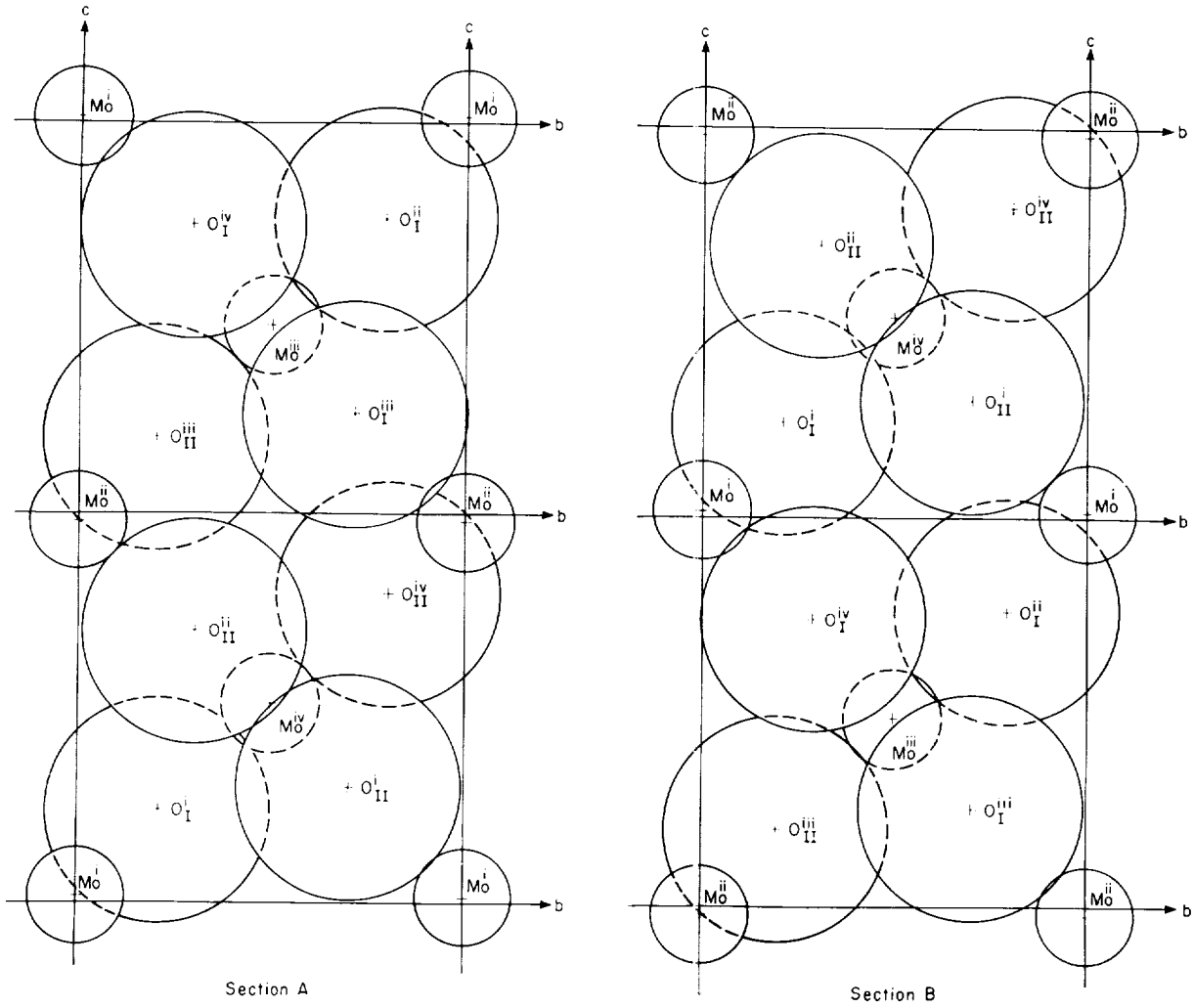


FIGURE 7.—Sectional projection of MoO_2 model on bc-plane. Sections A and B alternate along a-axis; 1 inch=2 Å.

dimensions. These coordinates may then be multiplied by the appropriate cell dimensions, expressed in angstrom units, in order to obtain the coordinates of the atoms in angstrom units. The reference system is formed by unit vectors $\hat{\alpha}$, $\hat{\beta}$, and $\hat{\gamma}$ pointing in the lattice directions a, b, and c, respectively, with interaxial angles α, β, and γ. The reference system is not necessarily orthogonal. The position vectors are readily constructed from the coordinates and unit vectors. Once the position vector of each atom is known, then the bond between two atoms is expressed by the vector difference between their two position vectors. By usual vector methods, bond lengths and interbond angles are readily determined. These methods have been applied to the lattices of MoO_2 and MoO_3.

In order to illustrate this procedure consider the case of the Mo ions in MoO_2. There are four Mo ions in the 4(e) equivalent positions. The position parameters are given as follows:

$$x=0.232 \qquad y=0.000 \qquad z=0.017$$

The general coordinates of the 4(e) positions are

$4(e)^{I}$	x, y, z
$4(e)^{II}$	$\bar{x}, \bar{y}, \bar{z}$
$4(e)^{III}$	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
$4(e)^{IV}$	$x, \frac{1}{2}-y, \frac{1}{2}+z$

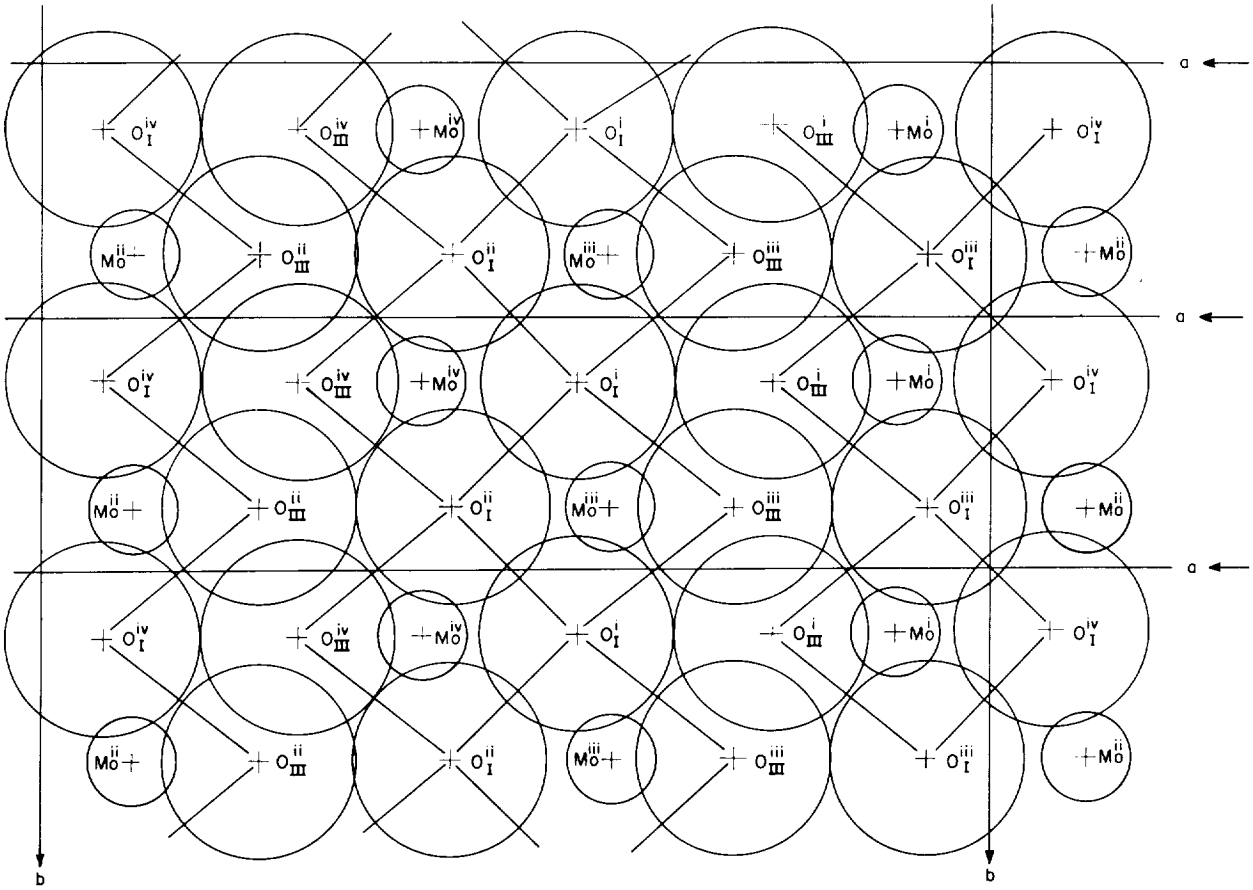


FIGURE 8.—Partial projection of MoO_3 model on ab-plane. 1 inch=2 Å.

If the position parameters are substituted in the coordinates of the (4e) positions, the coordinates of the ions are obtained. These are

0.232	0.000	0.017
−0.232	−0.000	−0.017
−0.232	0.500	0.483
0.232	0.500	0.517

These coordinates are expressed in units of cell dimensions. They may be multiplied by the cell dimensions to obtain the coordinates in angstrom units. The cell dimensions are

$$a=5.584\ \text{Å}$$
$$b=4.842\ \text{Å}$$
$$c=5.608\ \text{Å}$$
$$\beta=120.94°$$

Multiplying the coordinates by the cell dimensions gives the position vectors as follows:

$$\left.\begin{aligned}
\overrightarrow{Mo^{I}} &= 1.295\hat{\alpha}+0.000\hat{\beta}+0.0953\hat{\gamma}\\
\overrightarrow{Mo^{II}} &= -1.295\hat{\alpha}-0.000\hat{\beta}-0.0953\hat{\gamma}\\
\overrightarrow{Mo^{III}} &= -1.295\hat{\alpha}+2.421\hat{\beta}+2.709\hat{\gamma}\\
\overrightarrow{Mo^{IV}} &= 1.295\hat{\alpha}+2.421\hat{\beta}+2.899\hat{\gamma}
\end{aligned}\right\} \quad (1)$$

In the same manner, the position vectors for the ozygen ions in MoO_2 are found. The oxygen ions also occupy 4(e) positions. There are two "kinds" with position parameters as follows:
Four O_I in 4(e),

$$x=0.11 \qquad y=0.21 \qquad z=0.24$$

four O_{II} in 4(e),

$$x=0.39 \qquad y=0.70 \qquad z=0.30$$

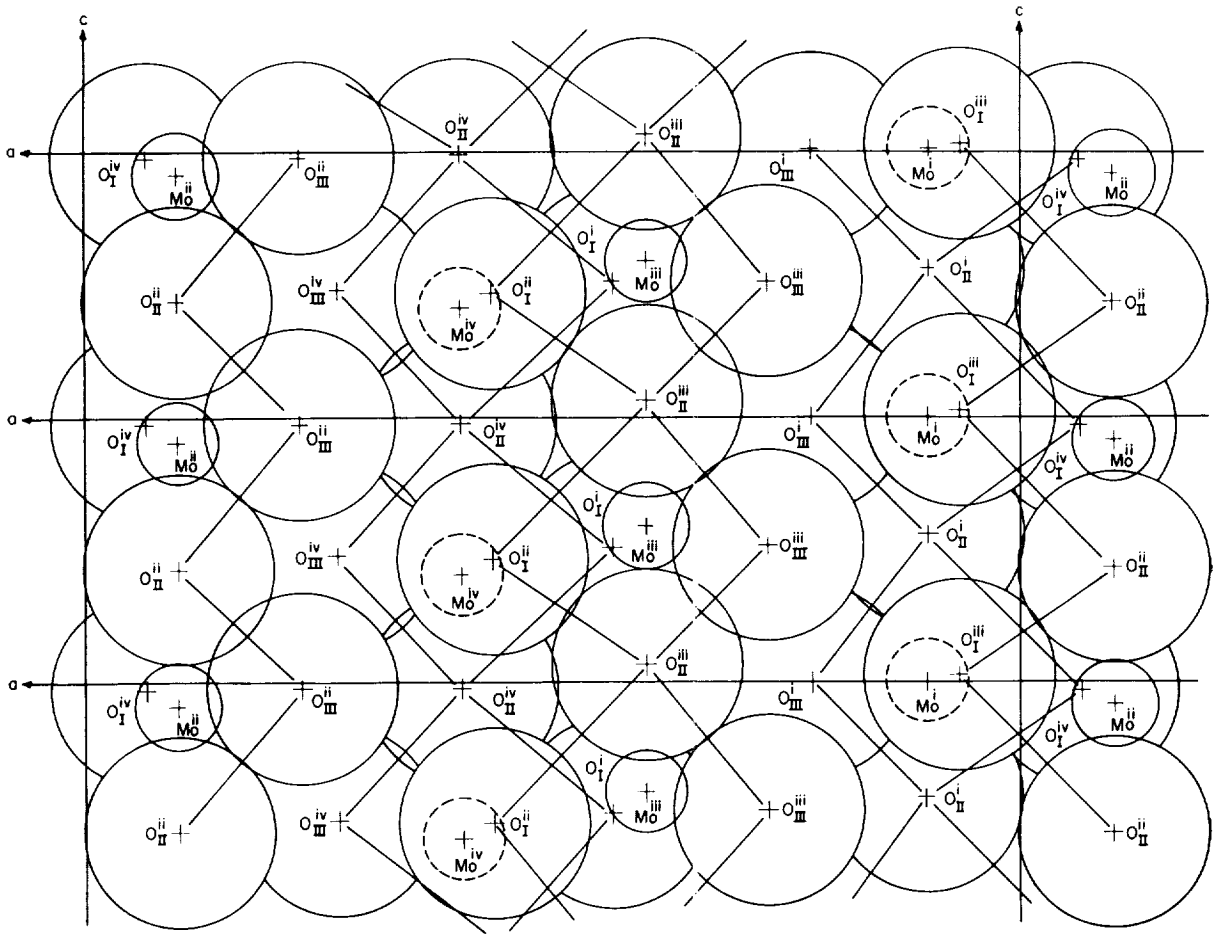


FIGURE 9.—Partial projection of MoO_3 model on ac-plane. 1 inch=2 Å.

The oxygen atom position vectors are

$$\left.\begin{aligned}
\overrightarrow{O_{I}^{i}} &= 0.614\hat{\alpha} + 1.017\hat{\beta} + 1.346\hat{\gamma} \\
\overrightarrow{O_{I}^{ii}} &= -0.614\hat{\alpha} - 1.017\hat{\beta} - 1.346\hat{\gamma} \\
\overrightarrow{O_{I}^{iii}} &= -0.614\hat{\alpha} + 3.438\hat{\beta} + 1.458\hat{\gamma} \\
\overrightarrow{O_{I}^{iv}} &= 0.614\hat{\alpha} + 1.404\hat{\beta} + 4.150\hat{\gamma} \\
\overrightarrow{O_{II}^{i}} &= 2.178\hat{\alpha} + 3.389\hat{\beta} + 1.682\hat{\gamma} \\
\overrightarrow{O_{II}^{ii}} &= -2.178\hat{\alpha} - 3.389\hat{\beta} - 1.682\hat{\gamma} \\
\overrightarrow{O_{II}^{iii}} &= -2.178\hat{\alpha} + 5.810\hat{\beta} + 1.122\hat{\gamma} \\
\overrightarrow{O_{II}^{iv}} &= 2.178\hat{\alpha} - 0.968\hat{\beta} + 4.486\hat{\gamma}
\end{aligned}\right\} \quad (2)$$

In this notation, the position vector is labeled by the atomic symbol of the element involved with a Roman numeral subscript designating a "kind" of atom and a superscript designating the particular equivalent position. The position vectors for molybdenum trioxide have been determined and are given in appendix A. A particular bond between two atoms may be expressed as a vector by taking the vector difference of the position vectors of the two atoms. The length of this bond is readily determined by using the conventional dot product.

LATTICE ENERGY

The lattice energy is the energy released when a crystal is formed from elements which are in a state of being both gaseous and ionized. To be exact, this is an enthalpy since there will be

a change in volume but the pressure-volume energy is usually very small compared with the internal energy and it is frequently ignored.

The lattice energy consists of a summation of energy contributions from several different energy-producing mechanisms. In a generalized form this summation is represented by the following equation:

$$U_t = U_c + U_p + U_{dd} + U_{dq} + U_r \tag{3}$$

where

U_t lattice energy
U_c coulombic energy
U_p polarization energy
U_{dd} dipole-dipole Van der Waals energy
U_{dq} dipole-quadrupole Van der Waals energy
U_r repulsion energy

It will be shown that the repulsion energy has the form

$$U_r = -p_r(U_c + 4U_p + 6U_{dd} + 8U_{dq}) \tag{4}$$

and each of the other energy expressions will have the following forms:

$$U_c = -\frac{A_M e^2}{\rho} \tag{5}$$

$$U_p = -\frac{C\alpha e^2}{\rho^4} \tag{6}$$

$$U_{dd} = -\frac{J}{\rho^6} \tag{7}$$

$$U_{dq} = -\frac{L}{\rho^8} \tag{8}$$

In these expressions

A_M Madelung constant
e electron charge
C constant for one type of crystal
α polarizability
J dipole-dipole coefficient
L dipole-quadrupole coefficient
ρ scaling parameter
p_r repulsion coefficient

In the following four sections these energy expressions are discussed separately and equations for computing each energy contribution to the lattice energy are derived. These equations are applied in practical calculations of the lattice energy of molybdenum dioxide and molybdenum trioxide in appendix B. In the section entitled "Summary of Energies" these contributions to the lattice energy are listed, added, and compared with the measured lattice energies.

COULOMBIC ENERGY

The coulombic energy of a crystal is the energy that is attributable to the electrostatic interaction of charged ions. In the model adopted for these calculations, it is assumed that the atoms present are ionized and that their charges are concentrated at points at the centers of the ions. The locations of these center points have been experimentally determined and are expressed by the atom or ion position vectors. Because of the distortion in the lattices of the molybdenum oxides, one of the established Madelung constants cannot be used and the usual methods of determining Madelung constants are not applicable. A general method of computing coulombic energy and the Madelung constant is developed here. This method requires the use of a digital computer but the method is simple and systematic and may be applied to any kind of crystal lattice. The coulombic energy of the dioxide and trioxide are determined.

Consider a crystal made up of positive and negative ions. There may be ions of several elements present. The position of each ion within a unit cell is known and is given by its position vector. The position of one unit cell relative to a cell selected to represent the origin is given by a vector

$$\vec{R} = n_1\hat{\alpha} + n_2\hat{\beta} + n_3\hat{\gamma} \tag{9}$$

where $\hat{\alpha}$, $\hat{\beta}$, and $\hat{\gamma}$ are unit vectors along the cell axes and n_1, n_2, and n_3 are integral multiples of the appropriate cell dimensions. Also,

$$\left.\begin{aligned} n_1 &= l_1 a \\ n_2 &= l_2 b \\ n_3 &= l_3 c \end{aligned}\right\} \tag{10}$$

where a, b, and c are cell dimensions and l_1, l_2, $l_3 = \pm 1, \pm 2, \pm 3, \ldots$. A method of assigning values to l_1, l_2, and l_3 is given subsequently.

The electrostatic potential energy, in ergs, of one ion, say the ith ion, due to another ion, the

jth ion, is given by the following expression:

$$U_{ij}=\frac{Z_iZ_je^2}{d_{ij}} \tag{11}$$

where

Z valance of the ion
e electronic charge, statcoulombs
d distance between the two ions, cm

and

$$d_{ij}=|\vec{D}_{ij}|=(\vec{D}_{ij}\cdot\vec{D}_{ij})^{1/2} \tag{12}$$

The term $\vec{D}_{ij}$ is a vector directed from the ith ion to the jth ion and is expressed as follows:

$$\vec{D}_{ij}=\vec{I}_j+\vec{R}-\vec{I}_i \tag{13}$$

The vectors $\vec{I}_i$ and $\vec{I}_j$ are the position vectors of the ith and jth ions, respectively.

The potential energy of all the ions in a given cell, the Oth cell, due to the ions in another cell, the Rth cell, is expressed as follows (here, i represents the Oth cell and j the Rth cell):

$$u_{OR}=\sum_{ij}U_{ij}=\sum_{ij}\frac{Z_iZ_je^2}{d_{ij}} \tag{14}$$

The total potential energy of the ions in the Oth cell due to all the other ions present is obtained by summing u_{OR} over all values of R from zero to infinity as

$$U_O=u_{OO}+\sum_{R=1}^{\infty}u_{OR} \tag{15}$$

The expression for R=0 is considered separately since all terms where R=0 and i=j must be discarded to avoid dividing by zero. These would represent the interaction between an ion and itself.

Since it is desirable for the energy to be expressed on a per mole basis the final energy expression becomes

$$U_e=\frac{N_{Av}U_O}{2\xi}=\frac{N_{Av}e^2}{2\xi}\left[\sum_{ij}\frac{Z_iZ_j}{d_{ij}}\right]_{R=0}+\sum_{R=1}^{\infty}\sum_{ij}\frac{Z_iZ_j}{d_{ij}} \tag{16}$$

where

N_{Av} Avogadro's number
ξ number of stoichiometric units per cell

The coefficient 1/2 compensates for double counting.

In cases where a Madelung constant is used, the energy expression is given by equation (5) which is

$$U_e=-\frac{A_Me^2}{\rho}$$

where ρ is a scaling parameter. Frequently ρ is the closest interatomic distance in the crystal. In the present development the Madelung constant is given as

$$A_M=-\frac{\rho N_{Av}}{2\xi}\left[\sum_{ij}\frac{Z_iZ_j}{d_{ij}}\right]_{R=0}+\sum_{R=1}^{\infty}\sum_{ij}\frac{Z_iZ_j}{d_{ij}} \tag{17}$$

There is no advantage in expressing a Madelung constant unless the crystal lattice is a frequently encountered type. The molybdenum oxide lattices are unique and their Madelung constants are not computed.

In expanding the coulombic energy expression, equation (16), the first summation should be made over all the ions i and j and then this rather large expression is expanded by summing over all cells. The summation over i and j is straightforward. A systematic method is needed to sum over R and extrapolate to infinity.

Consider the expressions for d_{ij} (eqs. (12) and (13), respectively)

$$d_{ij}=(\vec{D}_{ij}\cdot\vec{D}_{ij})^{1/2}$$

and

$$\vec{D}_{ij}=\vec{I}_j+\vec{R}-\vec{I}_i$$

where

$$\vec{I}_j=I_{j1}\hat{\alpha}+I_{j2}\hat{\beta}+I_{j3}\hat{\gamma} \tag{18}$$

$$\vec{I}_i=I_{i1}\hat{\alpha}+I_{i2}\hat{\beta}+I_{i3}\hat{\gamma} \tag{19}$$

In these equations the position vectors are written in terms of the unit vectors of the system and coefficients. The vector $\vec{R}$ can be written

$$\vec{R}=l_1a\hat{\alpha}+l_2b\hat{\beta}+l_3c\hat{\gamma} \tag{20}$$

Using these forms for $\vec{I}_i$, $\vec{I}_j$, and $\vec{R}$ gives

$$\vec{D}_{ij}=(I_{j1}+l_1a-I_{i1})\hat{\alpha}+(I_{j2}+l_2b-I_{i2})\hat{\beta}+(I_{j3}+l_3c-I_{i3})\hat{\gamma} \tag{21}$$

Once values for i and j have been assigned, the expansion over R involves assigning values to l_1, l_2, and l_3. Consider the Oth cell and let layers of cells be added to it layer by layer until it expands to fill all space. Let η designate a layer number starting at zero for the Oth cell only and taking values 1, 2, 3, and so forth as layers are added. The case for $\eta=0$ is a special case, as pointed out previously, and is computed separately. As values are assigned to η, the following values are taken by l (there are three groups and all combinations in each group must be taken):

(1) $l_1=\eta$ and $-\eta$ (2 values)
$l_2=-\eta$ to 0 to η, inclusive $(2\eta+1$ values)
$l_3=-\eta$ to 0 to η, inclusive $(2\eta+1$ values)

(2) $l_1=-(\eta-1)$ to 0 to $(\eta-1)$, inclusive $(2\eta-1$ values)
$l_2=\eta$ and $-\eta$ (2 values)
$l_3=-\eta$ to 0 to η, inclusive $(2\eta+1$ values)

(3) $l_1=-(\eta-1)$ to 0 to $(\eta-1)$, inclusive $(2\eta-1$ values)
$l_2=-(\eta-1)$ to 0 to $(\eta-1)$, inclusive $(2\eta-1$ values)
$l_3=\eta$ and $-\eta$ (2 values)

There are $24\eta^2+2$ possible combinations of l_1, l_2, and l_3. If there are τ ions per unit cell, there will be $\tau^2-\tau$ terms in the total summation for the case of $\eta=0$ and $\tau^2(24\eta^2+2)$ terms for each case of $\eta\neq 0$.

It is convenient to modify part of equation (16) by changing from summation over R to summation over η. The following definition may be introduced:

$$A=\sum_{\eta=0}^{\infty}\sum_{ij}\frac{Z_iZ_j}{d_{ij}} \tag{22}$$

In this equation the special provision for the $\eta=0$ case is tacitly included. A further definition may be given as

$$A_\kappa=\sum_{\eta=0}^{\kappa}\sum_{ij}\frac{Z_iZ_j}{d_{ij}} \tag{23}$$

Then, as values are assigned to κ, a value A_κ is computed. The term A_κ will converge to A as $\kappa\to\infty$. In practice, it is found that A_κ converges fairly rapidly and it is sufficient to let κ go only as high as 6 or 8. A graphical extrapolation is then used to determine the limiting value of A. Once the limiting value of A is obtained, it is substituted into equation (16) to give the coulombic energy as

$$U_c=\frac{N_{Av}e^2A}{2\xi} \tag{24}$$

The application of this method in computing the coulombic energy of the oxides of molybdenum is given in appendix B.

POLARIZATION ENERGY

The polarization energy is the energy resulting from the interaction of an electric field and a dipole induced in an ion or atom by that field.

The polarizability α of an ion or atom is defined by the equation

$$\vec{\mu}=\alpha\vec{F} \tag{25}$$

where

$\vec{\mu}$ electric dipole moment
$\vec{F}$ electric field vector

The energy is then given as (ref. 4)

$$U_p=-\frac{1}{2}\alpha\vec{F}\cdot\vec{F} \tag{26}$$

The electric field at a point in space due to a charged ion at another point in space is given by the following equation:

$$\vec{F}=\frac{Ze\vec{D}}{\left(\vec{D}\cdot\vec{D}\right)^{3/2}} \tag{27}$$

where

Z valence of the ion
e electronic charge
$\vec{D}$ vector from the ion to the point of polarization

The energy for this case is

$$U_p=-\frac{1}{2}\alpha Z^2e^2\frac{\vec{D}\cdot\vec{D}}{\left(\vec{D}\cdot\vec{D}\right)^3} \tag{28}$$

or

$$U_p=-\frac{\alpha Z^2e^2}{2\left|\vec{D}\right|^4} \tag{29}$$

Equation (29) shows the polarization energy to be proportional to the reciprocal of the fourth power

of the distance from the point in question to a charge producing the electric field. Because of this, it is not considered necessary to account for electric-field-producing ions at a great distance from the point of polarization. In computing the polarization energy of a "kind" of ion, a representative ion will be selected near the center of a cell. The electric-field vector is determined by taking a vector sum of the contributions of all ions in cases of $\eta=0$ and $\eta=1$ in a manner somewhat analogous to the coulombic-energy calculation.

Consider a polarizable ion designated by its position vector $\vec{G}_j$ as follows:

$$\vec{G}_j = g_{j1}\hat{\alpha} + g_{j2}\hat{\beta} + g_{j3}\hat{\gamma} \tag{30}$$

This ion will be selected to represent one "kind" of ion designated by j. It is selected from all the ions $\vec{I}_i$ in a cell. The polarizing ions are the remaining ions $\vec{I}_i$ as shown in the following equation:

$$\vec{I}_i = I_{i1}\hat{\alpha} + I_{i2}\hat{\beta} + I_{i3}\hat{\gamma} \tag{31}$$

The cell containing $\vec{I}_i$ is positioned relative to the cell containing $\vec{G}_j$ by the vector $\vec{R}$ as follows:

$$\vec{R} = l_1 a\hat{\alpha} + l_2 b\hat{\beta} + l_3 c\hat{\gamma} \tag{32}$$

In the subsequent summation, values of l are assigned in the same manner as for the coulombic energy and in view of the short range of the polarization effects only the cases for $\eta=0$ and $\eta=1$ are included.

The vector $\vec{D}_{ij}$ is found to be

$$\vec{D}_{ij} = \vec{G}_j - \vec{I}_i - \vec{R} \tag{33}$$

This vector is associated with an electric-field contribution $\vec{F}_{ij}$ and

$$\vec{F}_j = \sum_i \vec{F}_{ij} \tag{34}$$

or

$$\vec{F}_j = e\sum_i \frac{Z_i \vec{D}_{ij}}{\left(\vec{D}_{ij}\cdot\vec{D}_{ij}\right)^{3/2}} \tag{35}$$

If $\vec{D}_{ij}$ is written in the form

$$\vec{D}_{ij} = D_{ij1}\hat{\alpha} + D_{ij2}\hat{\beta} + D_{ij3}\hat{\gamma} \tag{36}$$

then

$$\left.\begin{aligned} D_{ij1} &= g_{j1} - I_{i1} - l_1 a \\ D_{ij2} &= g_{j2} - I_{i2} - l_2 b \\ D_{ij3} &= g_{j3} - I_{i3} - l_3 c \end{aligned}\right\} \tag{37}$$

The expanded expression for $\vec{F}_j$ is

$$\vec{F}_j = e\sum_{\eta=0}^{1}\sum_i \frac{Z_i\left(D_{ij1}\hat{\alpha} + D_{ij2}\hat{\beta} + D_{ij3}\hat{\gamma}\right)}{\left(D_{ij1}^2 + D_{ij2}^2 + D_{ij3}^2 + 2D_{ij1}D_{ij2}\cos\gamma + 2D_{ij2}D_{ij3}\cos\alpha + 2D_{ij1}D_{ij3}\cos\beta\right)^{3/2}} \tag{38}$$

There is one term in the above summation where $\vec{G}_j \equiv \vec{I}_i$ and this must be discarded. If there are τ ions per cell, then there are $(27\tau - 1)$ terms in the summation. The vector $\vec{F}_j$ comes out as a simple vector and from it and the polarizability of the polarizable ion, the energy of polarization is readily computed. The following modified expression gives the polarization energy on a per mole basis for one "kind" of ion:

$$(U_p)_j = -\frac{N_{Av}\alpha}{2}\vec{F}_j\cdot\vec{F}_j \tag{39}$$

where N_{Av} is Avogadro's number. There will be a polarization energy computed for each ion in a mole of stoichiometric unit and these must be added to obtain the total molar polarization energy.

In practice, it is convenient to define a quantity $\left(\vec{\Lambda}_p\right)_j$ as follows:

$$\left(\vec{\Lambda}_p\right)_j = \sum_i \frac{Z_i \vec{D}_{ij}}{\left(\vec{D}_{ij}\cdot\vec{D}_{ij}\right)^{3/2}} \tag{40}$$

Then,

$$\vec{F}_j = e\left(\vec{A}_p\right)_j \tag{41}$$

The term $\left(\vec{A}_p^o\right)_j$ may be obtained by modifying $\vec{D}_{ij}$ as follows:

$$\vec{D}_{ij}^o = \frac{1}{\rho}\vec{D}_{ij} \tag{42}$$

Where ρ is a scaling parameter which may be taken as the shortest distance between two ions. Then,

$$\left(\vec{A}_p^o\right)_j = \sum_i \frac{Z_i \vec{D}_{ij}^o}{\left(\vec{D}_{ij}^o \cdot \vec{D}_{ij}^o\right)^{3/2}} \tag{43}$$

This treatment gives a more general character to the $\left(\vec{A}_p\right)_j$ expression and is somewhat analogous to the Madelung constant. For computing repulsion energy subsequently it will be convenient to make the following definitions:

$$\frac{1}{2}\left(\vec{A}_p^o\right)_j \cdot \left(\vec{A}_p^o\right)_j \equiv C_j \tag{44}$$

and (eq. (6))

$$(U_p)_j = -\frac{C_j \alpha e^2}{\rho^4}$$

The following energy expression is then written for one mole of one "kind" of ion:

$$U_p = \sum_j (U_p)_j = -\frac{N_{Av}e^2}{2}\sum_j \alpha_j \left(\vec{A}_p\right)_j \cdot \left(\vec{A}_p\right)_j \tag{45}$$

or

$$U_p = -\frac{N_{Av}e^2}{2\rho^4}\sum_j \alpha_j \left(\vec{A}_p^o\right)_j \cdot \left(\vec{A}_p^o\right)_j \tag{46}$$

This treatment of polarization involves some approximations which should be pointed out. The energy of polarization calculated by the method just presented is based on the assumption that the electric field is homogeneous and that the polarizability of an ion is a constant and, in particular, not a function of the electric field. In the case of a real crystal, such as those studied herein, the electric field is not homogeneous and the polarizability depends, to some extent at least, on the environment of the ion or atom. In this investigation, an effort was made to obtain polarizabilities of the ions for conditions similar to those existing in MoO_2 and MoO_3, as discussed in appendix C. The inhomogeneity of the electric field was ignored because it is too complex a problem to be included in this work. It is implied in reference 5 that the error introduced is not large.

The application of this method in computing the polarization energy of the oxides of molybdenum is given in appendix B.

VAN DER WAALS ENERGY

The Van der Waals energy is a phenomenon of cohesion which has been explained by London (ref. 6) as the result of interaction of rapidly revolving dipoles in two atoms. The revolving dipoles are produced by the extranuclear electrons rapidly orbiting about the nucleus. When two atoms are close together, the revolving dipole in one synchronizes with the revolving dipole in the other in such a manner as to lower the total energy, and cohesion results.

The mathematical development of the Van der Waals energy equation results in a sum of decreasing terms. Only two of these energy terms are considered herein: the dipole-dipole energy (eq. (7)),

$$U_{dd} = -\frac{J}{\rho^6}$$

and the dipole-quadrupole energy (eq. (8)),

$$U_{dq} = -\frac{L}{\rho^8}$$

In these expressions, J and L are constants for a particular crystal and ρ is the scaling parameter which is usually taken as the closest interatomic distance. In order to obtain the total molar Van der Waals energy, a summation must be taken of all nearest neighbor energy contributions for each ion in a stoichiometric unit.

Consider an ion of element j and another ion of element k separated by a distance d_1. The Van der Waals energy expressions are

$$(U_{dd})_{ijk} = -\frac{J_{jk}}{d_1^6} \tag{47}$$

$$(U_{dq})_{ijk} = -\frac{L_{jk}}{d_1^8} \tag{48}$$

Then, summing over all neighbors k of ion j at distances d_1 and finally adding the contributions

of all "kinds" of ions j gives the molecular Van der Waals energy as

$$U_{dd}=-\sum_{ijk}\frac{J_{jk}}{d_i^6} \tag{49}$$

$$U_{dq}=-\sum_{ijk}\frac{L_{jk}}{d_i^8} \tag{50}$$

The scaling parameter ρ may be factored yielding final expressions (eqs. (7) and (8))

$$U_{dd}=-\frac{J}{\rho^6}$$

$$U_{dq}=-\frac{L}{\rho^8}$$

where

$$J=\sum_{ijk}\frac{J_{jk}}{(d_i^o)^6} \tag{51}$$

$$L=\sum_{ijk}\frac{L_{jk}}{(d_i^o)^8} \tag{52}$$

and

$$d_i^o=\frac{1}{\rho}d_i \tag{53}$$

The dipole-dipole coefficient has been derived by Kirkwood (ref. 7) as follows:

$$J_{jk}=\frac{3}{2}\frac{\alpha_j\alpha_k}{\sqrt{\frac{\alpha_j}{N_j}}+\sqrt{\frac{\alpha_k}{N_k}}} \tag{54}$$

In this equation,

α polarizability
N number of polarizable electrons in the ion

Equation (54) must be multiplied by $e^2a_o^{1/2}$ to convert from atomic units to centimeter-gram-second units where e is the electronic charge and a_o is the Bohr radius.

The dipole-quadrupole coefficient has been expressed in terms of the dipole-dipole coefficient by Huggins and Sakamoto (ref. 8, pp. 241–251) as follows:

$$L_{jk}=\frac{4\pi N_{Av}}{e^2}\left(\frac{J_{jj}}{N_jR_j}+\frac{J_{kk}}{N_kR_k}\right)J_{jk} \tag{55}$$

where

N_{Av} Avogadro's number
R_j ionic refraction

In order to express equation (55) in terms of polarizabilities,

$$\alpha_j=\frac{3R_j}{4\pi N_{Av}} \tag{56}$$

may be substituted for R_j and R_k is determined in a similar manner with the following result:

$$L_{jk}=\frac{3}{e^2}\left(\frac{J_{jj}}{N_j\alpha_j}+\frac{J_{kk}}{N_k\alpha_k}\right)J_{jk} \tag{57}$$

The application of these equations in computing the Van der Waals energy of the oxides of molybdenum is given in appendix B (with the data obtained being given in tables 1 and 2).

REPULSION ENERGY

The repulsion energy is the energy resulting from the displacement of two atoms or ions toward each other against an inherent force which tends to move them apart. This repelling force presumably acts in accordance with the Pauli principle. There is no general fundamental expression that expresses the energy of repulsion between two atoms. There are two empirical expressions in general use which are justified by the fact that they give good results.

Consider the case of a simple NaCl type crystal. The two repulsion energy expressions are, from the exponential law,

$$U_r=\frac{B}{e^{gd}} \tag{58}$$

and, from the inverse power law,

$$U_r=\frac{B}{d^n} \tag{59}$$

In these equations B, g, and n are unknown parameters. One of these, B, may be eliminated as follows:

If the total energy is given by

$$U=U_c+U_r \tag{60}$$

and it is assumed that, at d=R,

$$\frac{dU}{dd}=0 \tag{61}$$

where R is the equilibrium interionic distance, then by substituting equations (58) and (59) into equation (60) and applying the conditions expressed by equation (61), the energy expressions are

$$U=U_c\left(1-\frac{1}{gR}\right) \tag{62}$$

and

$$U=U_c\left(1-\frac{1}{n}\right) \tag{63}$$

TABLE 1.—VAN DER WAALS ENERGY DATA FOR MoO_2

Ion pair A	Ion pair B	M_{AB}	Bond length, R_{AB}	C_{AB}	d_{AB}
Mo^{iii}	O_I	½	1. 94	1. 23078	0. 11382
	O_I	1	1. 98		
	O_I	½	1. 98		
	O_{II}	½	2. 05		
	O_{II}	½	2. 07		
	O_{II}	1	1. 99		
O_I	O_I	½	3. 08	5. 32071	0. 721935
	O_I	½	3. 64		
	O_I	1	2. 83		
	O_I	1	2. 74		
	O_{II}	½	3. 35		
	O_{II}	1	2. 85		
	O_{II}	½	2. 77		
O_I	Mo^{iii}	½	3. 69	1. 23078	0. 11382
	Mo^{iv}	½	1. 98		
O_{II}	O_I	½	1. 49	5. 32071	0. 721935
	O_I	½	2. 91		
	O_I	½	2. 45		
	O_I	½	3. 15		
	O_{II}	1	2. 85		
	O_{II}	½	3. 48		
	O_{II}	½	2. 72		
	O_{II}	1	2. 90		
O_{II}	Mo^{i}	½	2. 05	1. 23078	0. 11382
	Mo^{ii}	½	2. 07		

$$\sum_{AB} \frac{M_{AB}C_{AB}}{R_{AB}}=0.43904 \qquad \sum_{AB} \frac{M_{AB}d_{AB}}{R_{AB}}=0.018859$$

These equations hold for the equilibrium distances only. The same approach that was used in the simple case is extended to the following complex case. The inverse power law is used because of its simplicity.

Equations of the form of (59) and (63) are used as the basis of the computations of repulsion energy for the oxides of molybdenum because they are considered accurate at the equilibrium distance and because they are rather easily applied. The structure of these oxides is considerably more complex than that of NaCl and several modifications must be made. In the NaCl type crystal, only cation-anion contacts are considered and the bond length is constant throughout the crystal. For the molybdenum oxides, both cation-anion contacts and anion-anion contacts are present. Also, the bond lengths range over several values for each type of contact. Pauling has developed an equation to compute the repulsion energy for the more complex crystals (ref. 2, p. 523).

The potential energy between the ith ion and the jth ion is given by Pauling as

$$U_{ij}=\frac{Z_iZ_je^2}{d_{ij}}+\beta_{ij}B_oe^2\frac{(r_i+r_j)^{n-1}}{d_{ij}^n} \tag{64}$$

The term on the extreme right expresses the repulsion energy as

$$U_r=\beta_{ij}B_oe^2\frac{(r_i+r_j)^{n-1}}{d^n} \tag{65}$$

TABLE 2.—VAN DER WAALS ENERGY DATA FOR MoO_3

Ion pair		M_{AB}	Bond length, R_{AB}	C_{AB}	d_{AB}
A	B				
Mo	O_I	2	1.93	0.94059	0.084511
	O_I	1	2.31		
	O_{II}	1	2.08		
	O_{II}	1	1.89		
	O_{III}	1	1.83		
O_I	O_I	1	2.58	5.32071	0.721935
	O_{II}	2	2.65		
	O_{II}	2	2.80		
	O_{II}	1	2.81		
	O_{II}	1	3.24		
	O_{III}	2	2.49		
	*$O_{III_{NL}}$	2	3.49		
O_{II}	O_{III}	1	2.56	5.32071	0.721935
	O_{III}	1	2.82		
	*$O_{III_{NL}}$	2	3.00		
	*$O_{III_{NL}}$	2	2.77		

*Next layer.

$$\sum \frac{M_{AB}C_{AB}}{R_{AB}}=0.30141 \qquad \sum \frac{M_{AB}d_{AB}}{R_{AB}}=0.0061918$$

where

B_o a constant which is not dependent on the particular ion pair

r_I, r_J ionic radii

n a constant which is dependent on the particular ion pair

Also,

$$\beta_{IJ}=1+\frac{Z_I}{P_I}+\frac{Z_J}{P_J} \tag{66}$$

where

Z valence

P number of electrons in the outermost shell for the particular ion

In order to compute repulsion energy on a per molecule basis, a summation must be taken over all bonds associated with the molecule as

$$U_r=\sum_{ij} M_{ij}\beta_{ij}B_o e^2 \frac{(r_i+r_j)^{n_{ij}-1}}{(d_{ij}^o)^{n_{ij}}} \tag{67}$$

where

M_{ij} the number of bonds of type ij in a molecule

$d_{ij}=\rho d_{ij}^o$

The constant B_o may be eliminated in a manner similar to the NaCl case except that now consideration must be given to all kinds of binding energy present in the crystal. Thus (eq. (3)),

$$U_t=U_c+U_p+U_{dd}+U_{dq}+U_r$$

or

$$U_t=-\frac{A_M e^2}{\rho}-\frac{C\alpha e^2}{\rho^4}-\frac{J}{\rho^6}-\frac{L}{\rho^8}+B_o e^2\sum_{ij}\frac{G_{ij}}{\rho^{n_{ij}}} \tag{68}$$

where

$$G_{ij}=M_{ij}\beta_{ij}\frac{(r_i+r_j)^{n_{ij}-1}}{(d_{ij}^o)^{n_{ij}}} \tag{69}$$

Now the conditions expressed by equation (61) are applied as follows:

$$\frac{dU_t}{d\rho}=\frac{A_M e^2}{\rho^2}+\frac{4C\alpha e^2}{\rho^5}+\frac{6J}{\rho^7}+\frac{8L}{\rho^9}-B_o e^2\sum_{ij}\frac{n_{ij}G_{ij}}{\rho^{n_{ij}+1}} \tag{70}$$

At equilibrium

$$\left.\begin{array}{l}\rho=R_o\\ \dfrac{dU_t}{dR_o}=0\end{array}\right\} \tag{71}$$

The constant B_o may be factored from the resulting expression to give

$$B_o=\frac{1}{\sum_{ij}\frac{n_{ij}G_{ij}}{R_o^{n_{ij}+1}}}\left(\frac{A_M}{R_o^2}+\frac{4C\alpha}{R_o^5}+\frac{6J}{e^2R_o^7}+\frac{8L}{e^2R_o^9}\right) \tag{72}$$

Then this equation may be substituted into the energy expression as follows:

$$U_t=-\frac{A_Me^2}{R_o}+e^2\frac{\sum_{ij}\frac{G_{ij}}{R_o^{n_{ij}}}}{\sum_{ij}\frac{n_{ij}G_{ij}}{R_o^{n_{ij}+1}}}\left(\frac{A_M}{R_o^2}+\frac{4C\alpha}{R_o^5}+\frac{6J}{e^2R_o^7}+\frac{8L}{e^2R_o^9}\right)-\frac{C\alpha e^2}{R_o^4}-\frac{J}{R_o^6}-\frac{L}{R_o^8} \tag{73}$$

In this equation R_o has replaced ρ.

By defining a repulsion coefficient p_r as

$$p_r\equiv\frac{\sum_{ij}M_{ij}\beta_{ij}\frac{(r_i+r_j)^{n_{ij}-1}}{d_{ij}^{n_{ij}}}}{\sum_{ij}M_{ij}n_{ij}\beta_{ij}\frac{(r_i+r_j)^{n_{ij}-1}}{d_{ij}^{n_{ij}}}} \tag{74}$$

equation (73) becomes

$$U_t=-\frac{A_Me^2}{R_o}-\frac{C\alpha e^2}{R_o^4}-\frac{J}{R_o^6}-\frac{L}{R_o^8}+p_r\left(\frac{A_Me^2}{R_o}+\frac{4C\alpha e^2}{R_o^4}+\frac{6J}{R_o^6}+\frac{8L}{R_o^8}\right) \tag{75}$$

Thus, equation (4) is obtained as

$$U_r=-p_r(U_c+4U_p+6U_{dd}+8U_{dq})$$

In computing the repulsion coefficient, it is necessary to assign a value to n_{ij}. It has been found that n may be assigned a value of 9 and for most crystals any error introduced will be small. Pauling has determined a set of values of n for ions that are isoelectronic with the inert gases (ref. 2, p. 509). For a heteronuclear bond, an average is taken to arrive at a value for n_{ij}.

The repulsion coefficient is computed for the two molybdenum oxides in appendix B and this in turn is used to compute the repulsion energy (tables 3 and 4).

SUMMARY OF ENERGIES

The contributions to the lattice energy which have been calculated in appendix B are presented as follows and are compared with the experimental lattice energy determined by means of the Born-Haber cycle. All energy units are kilocalories per mole.

	MoO_2	MoO_3
Coulombic, U_c	−2, 110. 00	−5, 850. 00
Polarization, U_p	−53. 12	−868. 46
Dipole-dipole, U_{dd}	−105. 99	−72. 76
Dipole-quadrupole, U_{dq}	−76. 57	−25. 13
Repulsion, U_r	462. 44	1, 261. 12
Calculated lattice energy	−1, 883	−5, 555
Experimental lattice energy	−2, 805	−6, 009
Difference in calculated and experimental lattice energy	−922	−454
Ratio of calculated and experimental lattice energy	0. 671	0. 924

INTERLAYER ENERGY

The bonding energy that exists between layers of a crystal is important as a factor affecting the strength and stability of the crystal. A good deal of insight as to the nature of the interlayer bond may be obtained by computing the coulombic energy of an isolated layer and comparing it with the coulombic energy of the crystal.

The layer coulombic energy may be computed in the same way that the crystal coulombic energy was computed except that the system for assigning values to l_1, l_2, and l_3 must be changed and position vectors of atoms within a single layer only must be selected. In the case of molybdenum trioxide the layers are oriented parallel to the b-c plane. If position vectors are selected to represent atoms within a single layer in the crystal cell and the crystal is expanded by adding cells in the b-c plane only, then a coulombic energy may be computed by using the method described previously and this will be the coulombic energy of an infinite single layer.

The following system of assigning values to

TABLE 3.—REPULSION ENERGY DATA FOR MoO_2

[For Mo^{4+}: r=0.68, Z=+4, P=10; for O^{2-}: r=1.40, Z=−2, P=8. Calculated ρ_r=0.1295]

Ion pair		n_{ij}	M_{ij}	d_{ij}	r_i+r_j	β_{ij}
i	j					
Mo^{iii}	O_I	8.5	½	1.939	2.08	1.15
	O_I	8.5	1	1.984	2.08	1.15
	O_I	8.5	½	1.982	2.08	1.15
	O_{II}	8.5	½	2.054	2.08	1.15
	O_{II}	8.5	½	2.073	2.08	1.15
	O_{II}	8.5	1	1.992	2.08	1.15
O_I	O_I	7	½	3.081	2.80	0.50
	O_I	7	½	3.639	2.80	.50
	O_I	7	1	2.830	2.80	.50
	O_I	7	1	2.742	2.80	.50
	O_{II}	7	½	3.347	2.80	.50
	O_{II}	7	1	2.849	2.80	.50
	O_{II}	7	½	2.765	2.80	.50
	Mo^{ii}	8.5	½	3.689	2.08	1.15
	Mo^{iv}	8.5	½	1.982	2.08	1.15
O_{II}	O_I	7	½	1.486	2.80	0.50
	O_I	7	½	2.910	2.80	.50
	O_I	7	½	2.446	2.80	.50
	O_I	7	½	3.146	2.80	.50
	O_{II}	7	1	2.845	2.80	.50
	O_{II}	7	½	3.475	2.80	.50
	O_{II}	7	½	2.717	2.80	.50
	O_{II}	7	1	2.896	2.80	.50
	Mo^{i}	8.5	½	2.054	2.08	1.15
	Mo^{ii}	8.5	½	2.074	2.08	1.15

l_1, l_2, and l_3 is applicable to layers lying parallel to the b-c plane. The value of zero is assigned to l_1 throughout the computation. The $\eta=0$ case is computed separately. For all other values assigned to η, l must take the values given as follows (all combinations of each group must be taken):

(1) $l_1=0$
$l_2=\eta$ and $-\eta$
$l_3=-\eta$ to 0 to η, inclusive

(2) $l_1=0$
$l_2=-(\eta-1)$ to 0 to $(\eta-1)$, inclusive
$l_3=-\eta$ to 0 to η

In this computation, the following position vectors were taken: $\overrightarrow{Mo^{III}}$, $\overrightarrow{Mo^{IV}}$, $\overrightarrow{O_I^i}$, $\overrightarrow{O_I^{ii}}$, $\overrightarrow{O_{II}^{iii}}$, $\overrightarrow{O_{II}^{iv}}$, $\overrightarrow{O_{III}^{iii}}$, and $\overrightarrow{O_{III}^{iv}}$. Examination of figures 8 and 9 shows that these atoms lie within a single layer and single cell.

The computation just presented has been carried out and the layer coulombic energy is given along with the crystal coulombic energy for comparison as follows:

Layer $U_c=-5{,}741$ kcal/mole
Crystal $U_c=-5{,}850$ kcal/mole

One way that the layer-structure energy relationships may be interpreted is to compare the stabilization effect of neighboring atoms on a molecular unit. For this purpose it would perhaps be better to use a molecular unit in the configuration that it would assume isolated in space. This type of information is frequently not available. Therefore, a molecular unit will be used in the configuration that the unit assumes in a crystal. For these computations the atoms

TABLE 4.—REPULSION ENERGY DATA FOR MoO_3

[For Mo^{6+}: r=0.62, Z=+6, P=8; for O^{2-}: r=1.40, Z=−2, P=8. Calculated p_r=0.1266]

Ion pair		n_{ij}	M_{ij}	d_{ij}	r_i+r_j	β_{ij}
i	j					
Mo	O_I	8. 5	2	1. 93	2. 02	1. 50
	O_I	8. 5	1	2. 31	2. 02	1. 50
	O_{II}	8. 5	1	2. 08	2. 02	1. 50
	O_{II}	8. 5	1	1. 89	2. 02	1. 50
	O_{III}	8. 5	1	1. 83	2. 02	1. 50
O_I	O_I	7	1	2. 58	2. 80	0. 50
	O_{II}	7	2	2. 65	2. 80	. 50
	O_{II}	7	2	2. 86	2. 80	. 50
	O_{II}	7	1	2. 81	2. 80	. 50
	O_{II}	7	1	3. 24	2. 80	. 50
	O_{III}	7	2	2. 49	2. 80	. 50
	O_{III}	7	2	3. 49	2. 80	. 50
O_{II}	O_{III}	7	1	2. 56	2. 80	0. 50
	O_{III}	7	1	2. 82	2. 80	. 50
	O_{III}	7	2	3. 00	2. 80	. 50
O_{III}	O_{III}	7	2	2. 77	2. 80	0. 50

$\overrightarrow{Mo^{III}}$, $\overrightarrow{O_I^i}$, $\overrightarrow{O_{II}^{iii}}$, and $\overrightarrow{O_{III}^{iii}}$ were selected and the electrostatic potential energy of this group was computed by using the position vectors to establish the configuration. The electrostatic potential energy or coulombic energy of this group was found to be −4,984 kcal/mole.

A stabilization factor may be defined as

$$\text{Stabilization factor}=\frac{\text{Crystal } U_c}{\text{Molecular } U_c} \quad (76)$$

and similarly defined for the layer coulombic energy. This stabilization factor represents the increase in the magnitude of coulombic energy gained by a molecular unit when it is located in an infinite crystal rather than when it is isolated in space. The stabilization factors for the crystal and layer are given as follows:

$$\text{Crystal stabilization factor}=\frac{-5{,}850}{-4{,}984}=1.174$$

$$\text{Layer stabilization factor}=\frac{-5{,}741}{-4{,}984}=1.152$$

On comparing these values, it can be seen that the layer stabilization factor is 98.1 percent of the crystal stabilization factor.

A different way of interpreting the layer coulombic energy is to compare differences in energy rather than ratios of energy. Stabilization energy may be defined as

$$\text{Crystal } U_s=\text{Crystal } U_c-\text{Molecular } U_c \quad (77)$$

and similarly defined for the layer stabilization energy. Values obtained with this method are

Layer U_s=−757 kcal/mole

Crystal U_s=−866 kcal/mole

From these values it can be observed that the layer contains 87.4 percent of the crystal stabilization energy.

The difference between the crystal coulombic energy and the layer coulombic energy is −109 kcal/mole. This value represents the coulombic energy that a molecular unit gains when an infinite crystal is placed (with the right orientation) against each surface of the layer. Since two surfaces are involved, half the difference between the energies may be considered to represent an

average interlayer coulombic energy. Thus, the average interlayer coulombic energy is −54.5 kcal/mole.

From table 2, it may be seen that there are two $O_{III}-O_{III}$ and two $O_{II}-O_{III}$ next-neighbor type interlayer bonds per molecular unit. From these data, the interlayer Van der Waals energy may be computed and the values obtained are given with the average interlayer coulombic energy for comparison as follows:

Average interlayer $U_c = -54.5$ kcal/mole
Average interlayer $U_{dd} = -9.2$ kcal/mole
Average interlayer $U_{dq} = -2.6$ kcal/mole

These values indicate that the interlayer bonding mechanism is not predominantly Van der Waals type but that the bonding energy is small nevertheless.

COVALENT EFFECTS

In reviewing the summary of energies, it is readily apparent that the electrostatic model of a crystal is capable of accounting for the total lattice energy of molybdenum trioxide although it is entirely possible that there is cancellation of errors in summing the different energy contributions. It is also apparent that this model does not account for the total lattice energy of molybdenum dioxide. A quantitative estimate of covalent energy contributions will not be undertaken herein but it is worthwhile to examine possible evidence of covalent effects. Consider first the dioxide of molybdenum. According to Pauling (ref. 2, p. 437) the two d-electrons on the Mo^{4+} ion interact between pairs of molybdenum ions and form a bond of bond number 1.47. The alternate close and far spacing of the molybdenum ions in MoO_2 plus the close bond distance of 2.49 Å as compared with the metallic bond distance of 2.72 Å tends to support this hypothesis. It is difficult to estimate accurately an energy contribution from this source. The energy of atomization of molybdenum is 155.5 kcal/mole. If molybdenum is considered to have a metallic valence of 6, then there are three single bonds per atom and the single bond energy would be 51.8 kcal/bond mole. In the MoO_2 crystal there is one half-bond of bond number 1.47 per mole. A reasonable estimate of an upper limit to this energy contribution would be 100 kcal/mole and this value is far short of the 922 kcal/mole of energy which is as yet unaccounted for. Other bond distances in MoO_2 may be examined and compared with the following covalent bond distances:

From the Shomaker-Stevenson relationship discussed in reference 9,

Bond Mo—O, 188 Å

and from the O_2 molecule, reference 10,

Bond O—O, 1.207 Å

The ionic bond distances (based on 0.68 Å as Mo^{4+} radius) are 2.08 Å and 2.80 Å for Mo—O and O—O, respectively. In the octahedron, the Mo—O bond distances are as follows: 1.94, 1.98, 1.98, 1.99, 2.06, and 2.08 Å. The O—O distances vary from 2.68 to 4.00 Å. These distances do not give a conclusive indication of the covalent or ionic nature of the bonds, especially when allowance is made for distortion of the lattice and polarization.

A possible mechanism which could account for the energy in MoO_2 would be an electrostatic energy contribution induced by a covalent bond between the two close molybdenum ions. If a covalent bond is present between these two ions as Pauling suggests, then the electron density will be increased between the two ions and decreased at the ends of this ion pair as compared with the case of two individual ions. A crude model was set up by placing a charge −q midway between every close pair of molybdenum ions in the MoO_2 lattice and a charge ½q was added at the position of every molybdenum ion. The quantity A from equation (22)

$$A = \sum_{\eta=0}^{\infty} \sum_{ij} \frac{Z_i Z_j}{d_{ij}}$$

and from

$$U_c = -\frac{165.9A}{\xi} \qquad (78)$$

was computed for the cases of q=1, 2, and 4. The results of this work are shown in figure 10.

On the basis of coulombic energy alone, with 100 kcal/mole being allowed for the Mo—Mo bond, a value of A=70.7 is needed to account for all the energy in the MoO_2 lattice. This value of A is equivalent to q=0.4. From a qualitative concept of a covalent bond of bond number 1.47 and in consideration of the crude nature of this model, this seems to be a reasonable value for q.

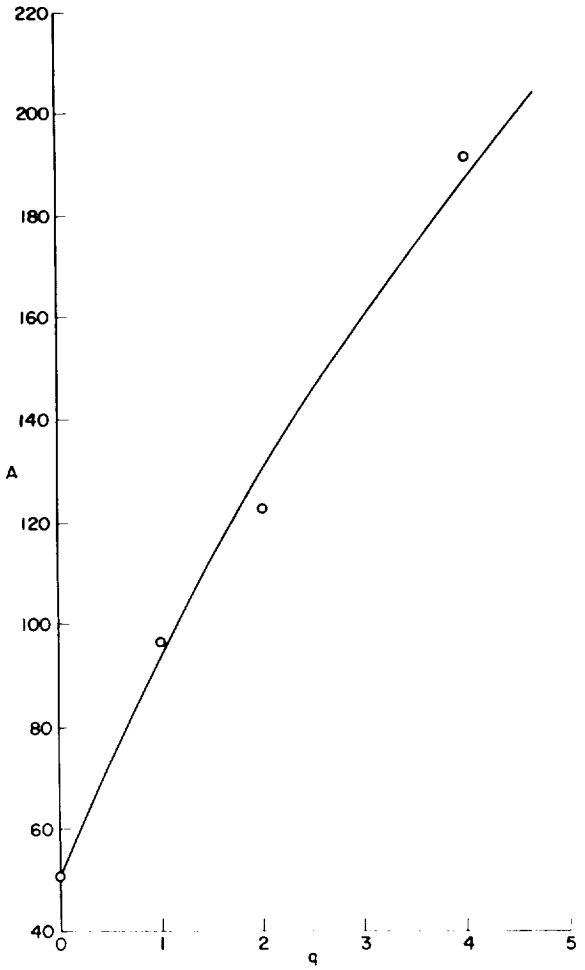


FIGURE 10.—Covalently induced electrostatic effects on A.

Summarizing the consideration of the MoO_2 lattice shows that the evidence for a covalent bond between the close pairs of molybdenum ions is good. There is probably some covalent contribution to the energies of the Mo—O bonds but there is no conclusive evidence that this contribution is large.

In the case of the trioxide of molybdenum, there is no evidence, other than possibly a bond distance, of an appreciable covalent contribution to the bond energies. A comparison of bond distances shows some Mo—O bonds to be at the right distance to be covalent. However, the large amount of polarization present in this lattice makes it possible for some ionic bonds to exist at distances other than the sum of ionic radii. This possibility tends to reduce the implication that these bonds must be considered covalent on the basis of distance alone.

DISCUSSION

MODEL

The model used in these calculations has already been described; however, there are several comments concerning the use of this model as applied to the more complex crystals studied here in contrast to the simple crystals studied prior to this investigation.

The idea that the net charge of an ion can be considered to be located at a point in the center of the ion comes from the approximation that the electronic charge in an ion has a spherically symmetrical distribution about the nucleus either in a series of thin shells or a solid distribution with perhaps some radial variation in density. It can be shown in classical electrostatic computations that the electric field generated by this model of an ion will be the same as that generated by a point charge located at the center of the ion. The requisite key to this concept lies in the spherical symmetry of the charge distribution, and the electric field resulting from the net ionic charge is considered only at points outside the ion.

The electrostatic model has been applied to many crystals with great accuracy. The crystals that have been amenable to methods of calculation based on this model have a number of unique features in common. The geometry of the crystals was simple and highly symmetric. The ions were isoelectronic with the inert gases. The positive ions were highly electropositive and the negative ions, highly electronegative. The polarizabilities of the ions were relatively low. Although these features appear to be desirable for accurate use of the electrostatic model, it is apparent that there can be appreciable deviation from these features and still obtain calculated energies that are within 90 percent of the experimental energies. This value may be compared with about 98 percent for the more ideal crystals.

If the concepts of electron charge distribution that are derived from quantum chemistry are representative of a true physical situation, then the real atom does not possess the kind of charge distribution needed in the electrostatic model in an exact sense, although the approximation must be very good. The features of the ideal ionic crystal appear to be such that they accomplish

one basic act. They tend to preserve the symmetry of charge distribution of an ion about the nucleus. The large difference in electronegativity of the cations and anions assures complete charge transfer leaving the ions isoelectronic with inert gases. The symmetry of the crystal provides that the electric field at the position of each ion is zero and the distribution of charge in an ion is then not altered by polarization.

The application of this model to a distorted crystal like molybdenum trioxide incurs several effects worth observation. In this work it was assumed that the position vector of an ion established the position of the nucleus of the ion and that this was the center of net charge. If this assumption is true the electric field which has been shown to exist at the nuclei would cause a polarization that would destroy the symmetry of the ion charge distribution. This polarization would induce two effects: (1) there would be established a polarization energy such as that computed in this work and (2) the symmetry of charge distribution would be changed and the center of positive charge would no longer coincide with the center of negative charge. In order for the model used in this investigation to approach the real physical situation more exactly, each ion should be considered not as a point charge but rather as two point charges representing the centers of positive and negative charge. This representation is still an approximation and is perhaps a less accurate approximation to a real polarized ion than the point charge approximation to a nonpolarized ion. It is probably true that the separation of centers of charge is very small because the inner electrons of an ion are so tightly bound although the orbitals representing the outer electrons may be quite distorted. The position vectors probably do locate the positions of the nuclei with good accuracy, as far as the model is concerned, since the position vectors are established by X-ray diffraction maximums which are a function of electron density. Even for polarized ions, the electron density should be greatest near the nucleus. The distortion of the outer orbitals should have some influence in the measurement of atom positions in a crystal and this is possibly an important factor in barring great accuracy in this type of work.

A distortion of the outer orbitals of an ion would be expected to have an effect on the computation of Van der Waals energy and repulsion energy. The polarizability of a distorted ion would be expected to be nonisotropic. Also, the compressibility of a distorted ion would be expected to be nonisotropic. The Van der Waals energy and the repulsion energy of individual bonds are probably not as accurately computed in these crystals as they would have been had the crystals been symmetric and without distortion of the ions. Since there are bonds in all directions about a distorted ion, it is perhaps reasonable to assume that the effects of this nonisotropy on calculations involving the whole crystal will cancel in an averaging process.

In many studies of bond types, much emphasis is placed on the bond length or distance. Atoms and ions have been assigned various radii, that is, covalent, ionic, metallic, Van der Waals, and so forth, and these are used with the assumption that a bond distance should be equal to the sum of the appropriate type of radii. In this sense distance establishes bond type. These radii are determined from measurements made on crystals or molecules known to possess certain types of bonds. The distance relationships appear to work out very well on many substances and the bond types determined by this method correspond qualitatively with other features of the substance. It is to be expected that these relationships will not be valid for substances containing distorted ions although, with some allowance for the distortion, bond distances may be compared with sums of radii to provide a rough indication of bond type.

When the types of bonds in a crystal are being considered, comparisons with radii sums should be made with some allowance for the direction and magnitude of the electric field at each ion, the polarizability of the ion, and the expected shape of the ion. An analysis of bond distances is made in the section entitled "Covalent Effects" where the bond distances in MoO_2 are used to obtain some insight as to bond type. On the basis of polarization energy, MoO_2 is considerably less distorted than MoO_3 and the bond-distance criteria is useful to some extent. The bond distances in MoO_3 do not appear to be very meaningful as to bond type. Of course, in considering bond distances in crystals, it is necessary to be certain that the geometry of the crystal

permits ion contact at the point that the bond is under consideration.

EXPERIMENTAL WORK

Since the energy computations are based on the relative positions of the atoms or ions and these positions have been experimentally established, the importance of the accuracy of these measurements is worth consideration.

In X-ray diffraction work, the size and shape of the crystal cell may be determined with great accuracy, that is, five or six significant figures. The positions of the atoms in the cell are determined with less accuracy, perhaps three to five significant figures. The data used in this investigation were obtained by a highly experienced group of specialists using single-crystal methods. In general, the positions of the molybdenum atoms are believed to be established with accuracy at least as good as three significant figures. The positions of the oxygen atoms are considered to be established with only fair accuracy. Although three significant figures were assumed in establishing the positions of the oxygen atoms, the data in the original reports (refs. 11 and 12) imply that this is perhaps a bit optimistic for some of the oxygen positions.

No effort was made to determine the effect of atom position accuracy on the energy computations. The displacement of an ion from its true equilibrium position in a crystal would have the effect of increasing the lattice energy. The extent of the increase would depend upon the displacement, or error in position, and the shape of the potential energy "well." It is not necessarily true, however, that a real crystal exists in an idealized state of lowest potential energy especially at moderately high temperatures and it is possible that the displacement of an ion could lower the lattice energy. It is not known what effect an error in an atom position vector would have on the lattice energy. This effect could be determined but it would involve much computational work. The experimental work on which these computations were based has been accepted in this investigation as being accurate.

TEMPERATURE

There are temperature effects present in the energies discussed herein which have been ignored in this work but are sometimes considered in other studies of this kind. The lattice energy of a crystal should properly be the electrostatic potential energy of the ions in a crystal at 0° K. In some work, even the zero-point vibrational energy is removed. The error involved in ignoring room-temperature effects is of the order of magnitude of 5 kcal/mole.

The Born-Haber cycle calculations are effectively isothermal at 298.15° K. It would be possible to determine the measured lattice energies of 0° K but there are other considerations which make this hardly worthwhile.

The calculated lattice energy determined in this work is the electrostatic potential energy of the ions in a crystal without any temperature-induced kinetic energy effects. Even the zero-point vibrational energy has been omitted. The crystal lattice is not that which would naturally occur at 0° K but it is a lattice whose configuration is established at, presumably, room temperature and the atom positions are mean positions.

These temperature corrections would appear in this work in comparing the calculated lattice energy with the measured lattice energy. It was felt that the magnitude of the correction was trivial; the effect is compensated somewhat by the omission of the ΔnRT term which was also ignored in the Born-Haber cycle calculations.

CONCLUDING REMARKS

A method has been developed which makes possible the calculation of the components of the lattice energy of an ionic crystal; this method has been applied to molybdenum dioxide and molybdenum trioxide. The method is unique in that it may be applied to complex and distorted crystals. It may also be used to study perturbations in a crystal lattice. Essentially all that is necessary for this method to be applied is that the crystal be ionic and possess periodicity from cell to cell. The main contribution from this research is the development of means of computing coulombic energy and polarization energy. In addition, established techniques for computing Van der Waals energy and repulsion energy have been modified and extended to provide a complete method for studying ionic crystals.

This method was applied to two oxides of molybdenum which are highly distorted structures. The trioxide of molybdenum was found to be amenable to this method of study. The

calculated lattice energy was 92.4 percent of the measured lattice energy. Molybdenum trioxide is known to have a layer structure and, as would be expected for this type of structure, it was found to have a relatively high polarization energy. The interlayer bonding energy was studied and the interlayer bonding was found to be relatively weak. This weakness would account for the high vapor pressure of molybdenum trioxide. Although the interlayer bonding is weak, Van der Waals bonding is not predominant as might be expected; rather there is a coulombic contribution which predominates.

The dioxide of molybdenum was found not to be amenable to this method of study. Only 67.1 percent of the measured lattice energy was given by the energy calculations. A metal-to-metal bond involving d-electrons in pairs of molybdenum atoms was investigated by a simple model which contains a hypothesized induced electrostatic effect. This model is very crude but the calculations imply that the metal-to-metal bond exists, and the induced electrostatic effect will account for the energy discrepancy.

The relationships between energy-producing mechanisms and the crystal structure of these oxides appear to be feasible according to general concepts of structural chemistry. Much doubt has existed as to the nature of the bonds in oxides like molybdenum trioxide. Some investigators have expressed the opinion that these compounds are covalent. This research indicates molybdenum trioxide to be an ionic compound. The nature of the bonds in the dioxide of molybdenum is not clearly established in this investigation. The evidence is moderately strong for ionic bonds plus the special atom-pair metal bond. It may be speculated that many of the distorted metal oxides will be found to be of an ionic nature with perhaps additional anomalous mechanisms responsible for their unique character.

LANGLEY RESEARCH CENTER,
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION,
LANGLEY AIR FORCE BASE, VA., *March 7, 1961.*

APPENDIX A

CRYSTAL-STRUCTURE CALCULATIONS

For a number of years X-ray diffraction techniques have been employed by specialists to determine the structure of crystals. By means of these measurements the type of crystal, the space group, cell dimensions, atom position parameters, and other features may be determined. With modern equipment and techniques these measurements may be made with great accuracy especially where single-crystal measurements are made. In the following section on structural data the experimental crystallographic data on molybdenum dioxide and molybdenum trioxide are given. These data are taken from the original papers and compendiums on the structure of crystals. The section entitled "Atom Positions and Bonds" gives computed data in the form of position vectors, bond vectors, bond length, and bond angles. This is the detailed numerical information derived from the X-ray diffraction measurements which establishes the structure of these crystals, implies the nature of the chemical bonds, and forms the basis of the energy computations.

CRYSTAL-STRUCTURE DATA

Molybdenum dioxide:

The X-ray diffraction data for molybdenum dioxide (ref. 11) are presented as follows. The notation is that used in reference 3.

Crystal type	Monoclinic
Space group	$C_2^2-P2_1$
Cell content	4 units MoO_2
Cell dimensions:	
a, Å	5.584
b, Å	4.842
c, Å	5.608
β, deg	120.94
Cell volume, Å^3	120.3
Density, g/cm^3	7.02
Coordinates of equivalent positions:	
4(e) positions	x, y, z $\overline{x}$, $\overline{y}$, $\overline{z}$ $\overline{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$ x, $\frac{1}{2}-y$, $\frac{1}{2}+z$

The atom position parameters are:

For four Mo in 4(e),

$$x=0.232, \qquad y=0.000, \qquad z=0.017$$

for four O_I in 4(e),

$$x=0.11, \qquad y=0.21, \qquad z=0.24$$

and for four O_{II} in 4(e),

$$x=0.39, \qquad y=0.70, \qquad z=0.30$$

Molybdenum trioxide:

The X-ray diffraction data for molybdenum trioxide (ref. 12) are presented as follows:

Crystal type	Orthorhombic
Space group	$D_{2h}^{16}-P_{nma}$
Cell content	4 units MoO_3
Cell dimensions:	
a, Å	13.85
b, Å	3.696
c, Å	3.966
Cell volume, Å^3	203.0
Density, g/cm^3	4.50
Coordinates of equivalent positions:	
4(c) positions	x, $\frac{1}{4}$, z $\overline{x}$, $\frac{3}{4}$, $\overline{z}$ $\frac{1}{2}-x$, $\frac{3}{4}$, $\frac{1}{2}+z$ $\frac{1}{2}+x$, $\frac{1}{4}$, $\frac{1}{2}-z$

The atom position parameters are:

For four Mo in 4(c),

$$x=0.0998, \qquad z=0.084$$

for four O_I in 4(c),

$$x=0.435, \qquad z=0.525$$

for four O_{II} in 4(c),

$$x=0.100, \qquad z=0.56$$

and for four O_{III} in 4(c),

$$x=0.230, \qquad z=0.015$$

ATOM POSITIONS AND BONDS

The X-ray crystallographer presents structural data in the concise form given in the previous section. These data have been converted to a more usable form by the method described in the section entitled "Crystal-Structure Calculation." By this method the position of each atom in a crystal can be expressed by a position vector $\vec{I}$. The bond between two atoms $\vec{I}_i$ and $\vec{I}_j$ may be expressed by a vector as follows:

$$\overrightarrow{I_iI_j}=\vec{I}_j-\vec{I}_i$$

The bond distances L are determined by the dot-product relationship

$$L_{ij}=\left(\overrightarrow{I_iI_j}\cdot\overrightarrow{I_iI_j}\right)^{1/2}$$

The interbond angles are also determined by the dot-product relationship; for example, in the case of $\overrightarrow{I_iI_j}$ and $\overrightarrow{I_iI_l}$,

$$\angle I_jI_iI_l=\theta_{jil}$$

$$=\cos^{-1}\frac{\left(\overrightarrow{I_iI_j}\cdot\overrightarrow{I_iI_l}\right)}{L_{ij}L_{il}}$$

The notation used is keyed to the figures and the particular atoms may be located by referring to the vectors identified by element symbol, subscripts, and superscripts.

Molybdenum dioxide:

The atom position vectors for molybdenum dioxide have been computed as an example to illustrate the method in the section entitled "Crystal-Structure Calculations." There are four equivalent positions, one "kind" of molybdenum atom, and two "kinds" of oxygen atom. The reference system is nonorthogonal. The atom position vectors are as follows:

$$\overrightarrow{Mo^{I}}=1.295\hat{\alpha}+0.000\hat{\beta}+0.0953\hat{\gamma}$$
$$\overrightarrow{Mo^{II}}=-1.295\hat{\alpha}-0.000\hat{\beta}-0.0953\hat{\gamma}$$
$$\overrightarrow{Mo^{III}}=-1.295\hat{\alpha}+2.421\hat{\beta}+2.709\hat{\gamma}$$
$$\overrightarrow{Mo^{IV}}=1.295\hat{\alpha}+2.421\hat{\beta}+2.899\hat{\gamma}$$

$$\overrightarrow{O_I^{i}}=0.614\hat{\alpha}+1.017\hat{\beta}+1.346\hat{\gamma}$$
$$\overrightarrow{O_I^{ii}}=-0.614\hat{\alpha}-1.017\hat{\beta}-1.346\hat{\gamma}$$
$$\overrightarrow{O_I^{iii}}=-0.614\hat{\alpha}+3.438\hat{\beta}+1.458\hat{\gamma}$$
$$\overrightarrow{O_I^{iv}}=0.614\hat{\alpha}+1.404\hat{\beta}+4.150\hat{\gamma}$$

$$\overrightarrow{O_{II}^{i}}=2.178\hat{\alpha}+3.389\hat{\beta}+1.682\hat{\gamma}$$
$$\overrightarrow{O_{II}^{ii}}=-2.178\hat{\alpha}-3.389\hat{\beta}-1.682\hat{\gamma}$$
$$\overrightarrow{O_{II}^{iii}}=-2.178\hat{\alpha}+5.810\hat{\beta}+1.122\hat{\gamma}$$
$$\overrightarrow{O_{II}^{iv}}=2.178\hat{\alpha}-0.968\hat{\beta}+4.486\hat{\gamma}$$

These position vectors have been used to sketch projections of the lattice. The projections are shown in figures 6 and 7. It may be observed that if the c-axis in figure 6 is drawn perpendicular to the a-axis, there will be only slight deviation from true periodicity due to the distortion of the lattice and from this viewpoint the lattice is very similar to the rutile lattice.

The bond vectors have been computed and are listed with the bond distances. These vectors have been computed in an orthogonal reference system for convenience. The transformation used is

$$\hat{\alpha}=\hat{\imath}$$
$$\hat{\beta}=\hat{\jmath}$$
$$\hat{\gamma}=-(\cos 59.06^\circ)\hat{\imath}+(\sin 59.06^\circ)\hat{k}$$

The transformed vectors may be used as long as the bounds of a single crystal cell are not exceeded. Periodicity cannot be carried over in the transformation. Along the a-axis the alternating Mo—Mo distances are 2.497 Å and 3.096 Å. These distances are important in postulating a unique Mo—Mo bond. With appropriate vector subtraction, vectors to represent bonds are obtained as follows:

$$\overrightarrow{Mo^{iii}O_I^{iv}}=1.17\hat{\imath}-1.02\hat{\jmath}+1.24\hat{k}\qquad(L=1.98\text{ Å})$$
$$\overrightarrow{Mo^{iii}O_I^{iii}}=1.32\hat{\imath}+1.02\hat{\jmath}-1.07\hat{k}\qquad(L=1.98\text{ Å})$$
$$\overrightarrow{Mo^{iii}O_I^{ii}}=-0.118\hat{\imath}+1.40\hat{\jmath}+1.33\hat{k}\qquad(L=1.94\text{ Å})$$
$$\overrightarrow{Mo^{iii}O_{II}^{i}}=-1.58\hat{\imath}+0.968\hat{\jmath}-0.881\hat{k}\qquad(L=2.06\text{ Å})$$
$$\overrightarrow{Mo^{iii}O_{II}^{ii}}=-1.51\hat{\imath}-0.968\hat{\jmath}+1.045\hat{k}\qquad(L=2.08\text{ Å})$$
$$\overrightarrow{Mo^{iii}O_{II}^{iii}}=-0.068\hat{\imath}-1.45\hat{\jmath}-1.36\hat{k}\qquad(L=1.99\text{ Å})$$

$\vec{O_I^{iii}O_I^{iv}} = -0.156\hat{i} - 2.034\hat{j} + 2.31\hat{k}$ (L=3.082 Å)

$\vec{O^{ii}O_I^{iv}} = 1.29\hat{i} - 2.42\hat{j} - 0.096\hat{k}$ (L=2.74 Å)

$\vec{O_{II}^{i}O_I^{iv}} = 2.75\hat{i} - 1.98\hat{j} + 2.12\hat{k}$ (L=4.00 Å)

$\vec{O_{II}^{ii}O_I^{iv}} = 2.68\hat{i} - 0.049\hat{j} + 0.192\hat{k}$ (L=2.68 Å)

$\vec{O_{II}^{iii}O_I^{iv}} = 1.24\hat{i} + 0.436\hat{j} + 2.60\hat{k}$ (L=2.91 Å)

$\vec{O_I^{ii}O_I^{iii}} = 1.44\hat{i} - 0.387\hat{j} - 2.41\hat{k}$ (L=2.82 Å)

$\vec{O_{II}^{i}O_I^{iii}} = 2.91\hat{i} + 0.049\hat{j} - 0.192\hat{k}$ (L=2.92 Å)

$\vec{O_{II}^{ii}O_I^{iii}} = 2.83\hat{i} + 1.99\hat{j} - 2.12\hat{k}$ (L=4.06 Å)

$\vec{O_{II}^{iii}O_I^{iii}} = 1.39\hat{i} + 2.47\hat{j} + 2.88\hat{k}$ (L=2.85 Å)

$\vec{O_{II}^{i}O_I^{ii}} = 1.47\hat{i} + 0.436\hat{j} + 2.21\hat{k}$ (L=2.69 Å)

$\vec{O_{II}^{ii}O_I^{ii}} = 1.39\hat{i} + 2.37\hat{j} + 0.288\hat{k}$ (L=2.77 Å)

$\vec{O_{II}^{iii}O_I^{ii}} = -0.050\hat{i} + 2.86\hat{j} + 2.69\hat{k}$ (L=3.93 Å)

$\vec{O_{II}^{ii}O_{II}^{i}} = -0.075\hat{i} + 1.94\hat{j} - 1.93\hat{k}$ (L=2.73 Å)

$\vec{O_{II}^{iii}O_{II}^{i}} = -1.52\hat{i} + 2.42\hat{j} + 0.480\hat{k}$ (L=2.90 Å)

$\vec{O_{II}^{iii}O_{II}^{ii}} = -1.44\hat{i} + 0.485\hat{j} + 2.41\hat{k}$ (L=2.85 Å)

The bond length in each case is shown on the right. The bond vectors may point toward either end of the bond but the direction must be considered in computing the interbond angles. The bond vectors given here point from the atom on the left toward the atom on the right.

The interbond angles are computed using the dot-product relationship. The angles with apexes at the Mo^{iii} atom have been computed and are tabulated as follows:

$\angle O_I^{iv}Mo^{iii}O_I^{ii} = 88.76°$

$\angle O_I^{ii}Mo^{iii}O_{II}^{i} = 84.65°$

$\angle O_{II}^{i}Mo^{iii}O_{II}^{iii} = 91.38°$

$\angle O_{III}^{iii}Mo^{iii}O_I^{iv} = 94.17°$

$\angle O_{II}^{ii}Mo^{iii}O_I^{ii} = 86.96°$

$\angle O_I^{ii}Mo^{iii}O_I^{iii} = 92.25°$

$\angle O_I^{iii}Mo^{iii}O_{II}^{iii} = 91.65°$

$\angle O_{II}^{iii}Mo^{iii}O_{II}^{ii} = 88.82°$

$\angle O_{II}^{ii}Mo^{iii}O_I^{iv} = 82.81°$

$\angle O_I^{iv}Mo^{iii}O_I^{iii} = 92.06°$

$\angle O_I^{iii}Mo^{iii}O_{II}^{i} = 92.19°$

$\angle O_{II}^{i}Mo^{iii}O_{II}^{ii} = 82.87°$

Molybdenum trioxide:

The atom position vectors for molybdenum trioxide are determined by using the method described for molybdenum dioxide. There are four equivalent positions, one "kind" of molybdenum atom, and three "kinds" of oxygen atoms. The reference system is orthogonal. The atom position vectors are as follows:

$\vec{Mo^{i}} = 1.38\hat{i} + 0.924\hat{j} + 0.333\hat{k}$

$\vec{Mo^{ii}} = -1.38\hat{i} + 2.77\hat{j} - 0.333\hat{k}$

$\vec{Mo^{iii}} = 5.54\hat{i} + 2.77\hat{j} + 2.32\hat{k}$

$\vec{Mo^{iv}} = 8.30\hat{i} + 0.924\hat{j} + 1.65\hat{k}$

$\vec{O_I^{i}} = 6.03\hat{i} + 0.924\hat{j} + 2.08\hat{k}$

$\vec{O_I^{ii}} = -6.03\hat{i} + 2.77\hat{j} - 2.08\hat{k}$

$\vec{O_I^{iii}} = 0.900\hat{i} + 2.77\hat{j} + 4.07\hat{k}$

$\vec{O_I^{iv}} = 12.95\hat{i} + 0.924\hat{j} - 0.099\hat{k}$

$\vec{O_{II}^{i}} = 1.38\hat{i} + 0.924\hat{j} + 2.22\hat{k}$

$\vec{O_{II}^{ii}} = -1.38\hat{i} + 2.77\hat{j} - 2.22\hat{k}$

$\vec{O_{II}^{iii}} = 5.54\hat{i} + 2.77\hat{j} + 4.20\hat{k}$

$\vec{O_{II}^{iv}} = 8.30\hat{i} + 0.924\hat{j} - 0.024\hat{k}$

$\vec{O_{III}^{i}} = 3.19\hat{i} + 0.924\hat{j} + 0.0595\hat{k}$

$\vec{O_{III}^{ii}} = -3.19\hat{i} + 2.77\hat{j} - 0.0595\hat{k}$

$\vec{O_{III}^{iii}} = 3.74\hat{i} + 2.77\hat{j} + 2.04\hat{k}$

$\vec{O_{III}^{iv}} = 10.11\hat{i} + 0.924\hat{j} + 1.92\hat{k}$

By using these atom position vectors, the lattice of MoO_3 can be reconstructed. Projections of this lattice are shown in figures 8 and 9. In these figures the cell boundaries are shown and the centers of the oxygen atoms are connected to outline the octahedra. It is readily apparent that MoO_3 has a layer structure. The layers are formed from one kind of octahedron and alternate octahedra are oriented differently. The layers are staggered to form a semi-interlocking joint. The three "kinds" of oxygen atoms result from the particular way that the octahedra are joined in this structure. The O_I atoms are common to three octahedra and are a part of an edge joint. The O_{II} atoms are common to two octahedra and form a corner joint. The O_{III} atoms belong only to one octahedron and are unshared. Presumably, however, the

O_{III} atoms play the dominant role in the interlayer bonding.

The bond vectors have been computed and are given as follows. As in the case of MoO_2, one octahedron is singled out to illustrate bonds and interbond angles. The bond vectors point from the molybdenum atom at the center of the octahedron to the oxygen atoms at the corners.

In the +a direction,

$$\overrightarrow{Mo^{iv}O^{iv}_{III}} = 1.81\hat{i} + 0.270\hat{k} \qquad (L = 1.83\ \text{Å})$$

in the −a direction,

$$\overrightarrow{Mo^{iv}O^{i}_{I}} = -2.27\hat{i} + 0.430\hat{k} \qquad (L = 2.31\ \text{Å})$$

in the +b direction,

$$\overrightarrow{Mo^{iv}O^{ii}_{I}} = -0.480\hat{i} + 1.85\hat{j} + 0.240\hat{k} \qquad (L = 1.93\ \text{Å})$$

in the −b direction,

$$\overrightarrow{Mo^{iv}O^{ii}_{I}} = -0.480\hat{i} - 1.85\hat{j} + 0.240\hat{k} \qquad (L = 1.93\ \text{Å})$$

in the +c direction,

$$\overrightarrow{Mo^{iv}O^{iv}_{II}} = 2.08\hat{k} \qquad (L = 2.08\ \text{Å})$$

and in the −c direction,

$$\overrightarrow{Mo^{iv}O^{iv}_{II}} = -1.89\hat{k} \qquad (L = 1.89\ \text{Å})$$

Vectors for the Mo—Mo bonds are directed from the nearest neighbor Mo atoms to the Mo^{iv} atom at the center of this octahedron and are given as follows (the subscript NC indicates next cell):

In the −a+b direction,

$$\overrightarrow{Mo^{iv}Mo^{iii}} = -2.76\hat{i} + 1.85\hat{j} + 0.670\hat{k} \qquad (L = 3.38\ \text{Å})$$

in the −a−b direction,

$$\overrightarrow{Mo^{iv}Mo^{iii}_{NC}} = -2.76\hat{i} - 1.85\hat{j} + 0.670\hat{k} \qquad (L = 3.38\ \text{Å})$$

in the +a+b direction,

$$\overrightarrow{Mo^{iv}Mo^{ii}} = 4.17\hat{i} + 1.85\hat{j} - 1.32\hat{k} \qquad (L = 4.75\ \text{Å})$$

in the +a−b direction,

$$\overrightarrow{Mo^{iv}Mo^{ii}_{Sc}} = 4.17\hat{i} - 1.85\hat{j} - 1.32\hat{k} \qquad (L = 4.75\ \text{Å})$$

in the +c direction,

$$\overrightarrow{Mo^{iv}Mo^{iv}_{NC}} = 3.97\hat{k} \qquad (L = 3.97\ \text{Å})$$

and in the −c direction,

$$\overrightarrow{Mo^{iv}Mo^{iv}_{NC}} = -3.97\hat{k} \qquad (L = 3.97\ \text{Å})$$

The O—O bond vectors are given for the bonds within an octahedron. The interlayer O—O bonds will be considered subsequently. The selection of positive direction for these vectors is arbitrary and not of any significance. The O—O bond vectors were chosen positive toward O_{III} as much as possible and positive toward O_{II} otherwise. These vectors were obtained by determining the vector difference between the appropriate two Mo—O bond vectors as follows (the subscripts A, B, L, and R designate, respectively, atoms above, below, left, and right with respect to the chosen orientation):

$$\overrightarrow{O^{i}_{I}O^{ii}_{IL}} = 1.79\hat{i} - 1.85\hat{j} - 0.19\hat{k} \qquad (L = 2.58\ \text{A})$$

$$\overrightarrow{O^{i}_{I}O^{ii}_{R}} = 1.79\hat{i} + 1.85\hat{j} - 0.19\hat{k} \qquad (L = 2.58\ \text{Å})$$

$$\overrightarrow{O^{i}_{I}O^{iv}_{IIA}} = 2.27\hat{i} + 1.65\hat{k} \qquad (L = 2.81\ \text{Å})$$

$$\overrightarrow{O^{i}_{I}O^{iv}_{IIB}} = 2.27\hat{i} - 2.32\hat{k} \qquad (L = 3.24\ \text{Å})$$

$$\overrightarrow{O^{ii}_{IL}O^{iv}_{III}} = 2.29\hat{i} + 1.85\hat{j} + 0.03\hat{k} \qquad (L = 2.94\ \text{Å})$$

$$\overrightarrow{O^{ii}_{IR}O^{iv}_{III}} = 2.29\hat{i} - 1.85\hat{j} + 0.03\hat{k} \qquad (L = 2.94\ \text{Å})$$

$$\overrightarrow{O^{iv}_{IIA}O^{iv}_{III}} = 1.81\hat{i} - 1.81\hat{k} \qquad (L = 2.56\ \text{A})$$

$$\overrightarrow{O^{iv}_{IIB}O^{iv}_{III}} = 1.81\hat{i} + 2.16\hat{k} \qquad (L = 2.82\ \text{Å})$$

$$\overrightarrow{O^{ii}_{IL}O^{iv}_{IIA}} = 0.48\hat{i} + 1.85\hat{j} + 1.84\hat{k} \qquad (L = 2.65\ \text{Å})$$

$$\overrightarrow{O^{ii}_{IR}O^{iv}_{IIA}} = 0.48\hat{i} - 1.85\hat{j} + 1.84\hat{k} \qquad (L = 2.65\ \text{Å})$$

$$\overrightarrow{O^{ii}_{IL}O^{iv}_{IIB}} = 0.48\hat{i} + 1.85\hat{j} - 2.13\hat{k} \qquad (L = 2.86\ \text{Å})$$

$$\overrightarrow{O^{ii}_{IR}O^{iv}_{IIB}} = 0.48\hat{i} - 1.85\hat{j} - 2.13\hat{k} \qquad (L = 2.86\ \text{Å})$$

The interbond-angle relationships are perhaps more clearly demonstrated by establishing a system of polar angles. This system shows the nature of the distortion of the octahedron better than using the angles between bonds. There is a plane of symmetry containing the Mo^{iv}, two O^{iv}_{II}, O^{iv}_{III}, and O^{i}_{I} atoms which provides for easy orientation of the octahedron.

A unique and important feature of the MoO_3 lattice is the layer structure. The O_{III} atoms are unshared by octahedra. If the nearest neighbor relationships only are considered, the $O_{III}-O_{III}$

bonds make up the interlayer bonding. The O^{iii}_{III} atom has been arbitrarily selected as a representative atom and the bond vectors to O_{III} atoms in the next layers have been determined as follows:

$$\overrightarrow{O^{iii}_{III}O^{i}_{IIIA}} = -0.55\hat{i} - 1.85\hat{j} + 1.99\hat{k} \quad (L = 2.77\ \text{Å})$$

$$\overrightarrow{O^{iii}_{III}O^{i}_{IIIB}} = -0.55\hat{i} - 1.85\hat{j} - 1.98\hat{k} \quad (L = 2.76\ \text{Å})$$

$$\overrightarrow{O^{iii}_{III}O^{i}_{IIIA}} = -0.55\hat{i} + 1.85\hat{j} + 1.99\hat{k} \quad (L = 2.77\ \text{Å})$$

$$\overrightarrow{O^{iii}_{III}O_{IIIB}} = -0.55\hat{i} + 1.85\hat{j} - 1.98\hat{k} \quad (L = 2.76\ \text{Å})$$

$$\overrightarrow{O^{iii}_{III}O^{iii}_{I}} = -2.84\hat{i} + 2.03\hat{k} \quad (L = 3.49\ \text{Å})$$

The last bond vector represents the bond between a layer surface atom and the nearest nonsurface atom in the next layer.

APPENDIX B

METHODS OF ENERGY CALCULATIONS

There are four sections in this appendix which are devoted to the numerical work involved in the calculation of the contributions to the lattice energy. The theory which forms the basis for the practical calculations discussed herein has been introduced in a general way in the section entitled "Introductory Discussion of Theoretical Concepts" and the particular development of the equations has been given in the section entitled "Lattice Energy." These equations are used in this appendix to calculate the lattice energy of molybdenum dioxide and molybdenum trioxide. There are four sections in which coulombic energy, polarization energy, Van der Waals energy, and repulsion energy are discussed.

CALCULATION OF COULOMBIC ENERGY

The coulombic energy of a crystal is given by equation (24) as follows:

$$U_c = \frac{N_{Av} e^2 A}{2\xi}$$

In order to have the coulombic energy expressed in kilocalories per mole, this equation is modified as follows:

$$U_c = \frac{c}{10^{-8}} \frac{N_{Av} e^2 A}{2\xi} \qquad (79)$$

where

N_{Av} Avogadro's number, 6.024×10^{23} molecules/mole
c conversion factor, 2.3889×10^{-11} kcal/erg
ξ molecules per cell
e electronic charge, 4.802×10^{-10} esu

The constants may be combined to give a working formula (eq. (78)):

$$U_c = -\frac{165.9A}{\xi} \text{ kcal/mole}$$

The factor A is determined by equation (22) as follows:

$$A = \sum_{\eta=0}^{\infty} \sum_{ij} \frac{Z_i Z_j}{d_{ij}}$$

The limiting value of this equation is obtained by taking finite sums as follows (eq. (23)):

$$A_\kappa = \sum_{\eta=0}^{\kappa} \sum_{ij} \frac{Z_i Z_j}{d_{ij}}$$

The quantity A_κ is determined on a computer for values of κ from 0 to 6 or 8 where the convergence should be very good; then, graphical means are used to get the limiting value A at κ equal to infinity. Two systems of graphical extrapolation were used in this work. One system was to plot A_κ as ordinate and $A_\kappa - A_{\kappa-1}$ or ΔA_κ as abscissa then extrapolate to A at ΔA_κ equal to zero.

The other system was to select a convenient value of A_κ at a point where the sum was converging uniformly. This starting point may be designated A_b. The following quantities are then determined and plotted:

$\log_e (A_\kappa - A_b)$ is plotted on the ordinate

$1/\kappa$ is plotted on the abscissa

The extrapolation to $1/\kappa$ equal to zero, or κ equal infinity is made and the limiting value $(A_\kappa - A_b)_{\text{limit}}$ is obtained. Then,

$$A = A_b + (A_\kappa - A_b)_{\text{limit}}$$

Both methods were used and the two extrapolations were adjusted to give values of A that agreed and at the same time conformed to reasonable curvature of the extrapolation curves.

The most complicated part of the work in computing the coulombic energy is the computation of A which, in turn, requires computation of a sequence of values A_κ. This work must be done on a computer and the following comments are

offered to aid in the programing of the problem. The input data are as follows:

(1) Position vectors of all ions in a unit cell. The form of these vectors is (eq. (31))

$$\vec{I}_j = I_{j1}\hat{\alpha} + I_{j2}\hat{\beta} + I_{j3}\hat{\gamma}$$

(2) The angles α, β, and γ between the axes of the reference system

(3) The cell dimensions a, b, and c in angstrom units

(4) The values for l_1, l_2, and l_3 determined from values assigned to η

(5) The values Z_j which represent the number of charges on the jth ion and the sign of the charge

Equation (23) which is

$$A_\kappa = \sum_{\eta=0}^{\kappa} \sum_{ij} \frac{Z_i Z_j}{d_{ij}}$$

represents interaction between all the ions, designated by i, in the cell at the origin and all the ions, designated by j, in a cell located by R where (eq. (32))

$$\vec{R} = l_1 a\hat{\alpha} + l_2 b\hat{\beta} + l_3 c\hat{\gamma}$$

Then, if $\vec{I}_i$ and $\vec{I}_j$ are the position vectors of the ith ion and jth ion in their respective cells, the relative positions of these two ions is expressed by the vector (eq. (36))

$$\vec{D}_{ij} = D_{ij1}\hat{\alpha} + D_{ij2}\hat{\beta} + D_{ij3}\hat{\gamma}$$

The coefficients of the unit vectors are (eq. (37))

$$D_{ij1} = I_{j1} + l_1 a - I_{i1}$$

$$D_{ij2} = I_{j2} + l_2 b - I_{i2}$$

$$D_{ij3} = I_{j3} + l_3 c - I_{i3}$$

From this, d_{ij} may be obtained as the magnitude of the vector $\vec{D}_{ij}$ as follows:

$$\begin{aligned} d_{ij} &= (\vec{D}_{ij} \cdot \vec{D}_{ij})^{1/2} \\ &= (D_{ij1}^2 + D_{ij2}^2 + D_{ij3}^2 + 2D_{ij1}D_{ij2}\cos\gamma \\ &\quad + 2D_{ij1}D_{ij3}\cos\beta + 2D_{ij2}D_{ij3}\cos\alpha)^{1/2} \end{aligned} \quad (80)$$

It is convenient to form a matrix

$$\begin{array}{c} \\ I_1 \\ I_2 \\ I_3 \\ \cdot \\ \cdot \\ \cdot \\ I_i \end{array} \begin{array}{c} \begin{array}{cccccc} I_1 & I_2 & I_3 & . & . & I_j \end{array} \\ \begin{bmatrix} I_{11} & I_{12} & I_{13} & . & . & I_{1j} \\ I_{21} & I_{22} & I_{23} & . & . & I_{2j} \\ I_{33} & I_{32} & I_{33} & . & . & I_{3j} \\ . & . & . & & & . \\ . & . & . & & & . \\ . & . & . & & & . \\ I_{i1} & I_{i2} & I_{i3} & . & . & I_{ij} \end{bmatrix} \end{array}$$

where the jth ions are arranged across the top and the ith ions down the side. Each position in the matrix may be designated by the symbol I_{ij}. Then, this symbol may be assigned to represent the following operation:

$$I_{ij} \equiv \frac{Z_i Z_j}{d_{ij}} \quad (81)$$

Terms from all positions in the matrix are added and this large expression is then expanded by permitting η to increase from zero up to the point where the series converges. It is important to note that when $R=0$ and $\eta=0$ then all terms on the diagonal must be discarded. Thus,

$$A_\kappa = \sum_{\eta=0}^{\kappa} \sum_{ij} I_{ij} = \sum_{\eta=0}^{\kappa} \sum_{ij} \frac{Z_i Z_j}{d_{ij}} \quad (82)$$

and the special provision for $\eta=0$ must be tacitly understood.

These methods were applied to two oxides of molybdenum. The convergence of A_κ is shown in figures 11 and 12 for MoO_2 and MoO_3,

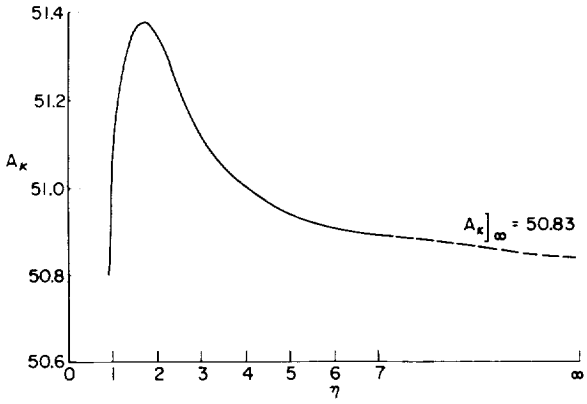


FIGURE 11.—Convergence of A_κ for MoO_2.

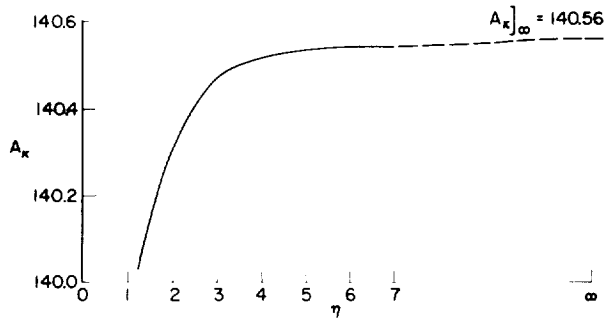


FIGURE 12.—Convergence of A_κ for MoO_3.

respectively. The limiting values were found to be:

For MoO_2,

$$A=50.8, \qquad \xi=4$$

and for MoO_3,

$$A=141, \qquad \xi=4$$

These values were substituted into the formula (eq. (78))

$$U_c=-\frac{165.9A}{\xi}$$

to obtain coulombic energies as follows:

For MoO_2,

$$U_c=-2{,}110 \text{ kcal/mole}$$

and for MoO_3,

$$U_c=-5{,}850 \text{ kcal/mole}$$

These computations required about 30 minutes each on an IBM 704 electronic data processing machine.

CALCULATION OF POLARIZATION ENERGY

The polarization energy of a crystal is given as follows:

$$U_p=-\sum_j \frac{N_{Av}e\alpha_j e^2}{2}\left(\vec{A}_p\right)_j\cdot\left(\vec{A}_p\right)_j \qquad (83)$$

where

N_{Av} Avogadro's number, 6.024×10^{23}, molecules/mole
e conversion factor, 2.3889×10^{-11}, kcal/erg
α_j polarizability of jth ion, cm^3
e electronic charge, 4.802×10^{-10}, esu

and the index j represents the jth polarizable ion or atom in a molecule and the summation is over all ions or atoms in the molecule. The constants may be combined to give a working formula, in kcal/mole,

$$U_p=-165.92\sum_j \alpha_j'\left(\vec{A}_p\right)_j\cdot\left(\vec{A}_p\right)_j \qquad (84)$$

where the prime indicates that the polarizability is in $Å^3$ units. The evaluation of the vector $\left(\vec{A}_p\right)_j$ must be made on a computer. The following comments are offered to aid in the programing of the problem. The input data are as follows:

(1) Position vectors of all ions in a unit cell; the form of these vectors is (eq. (31))

$$\vec{I}_i=I_{i1}\hat{\alpha}+I_{i2}\hat{\beta}+I_{i3}\hat{\gamma}$$

(2) Position vectors of the selected representative polarizable ions. These will be designated $\vec{G}_j$. One ion of each kind j will be selected from ions $\vec{I}_i$. All the ions j will constitute a molecular unit. The form of these vectors is

$$\vec{G}_j=g_{j1}\hat{\alpha}+g_{j2}\hat{\beta}+g_{j3}\hat{\gamma} \qquad (85)$$

(3) The angles α, β, and γ between the axes of the reference system

(4) The cell dimensions a, b, and c in angstrom units

(5) The values for l_1, l_2, and l_3 determined from values assigned to η (in this work only values 0 and 1 are assigned to η)

(6) The values Z_i which represent the number of charges on the ith ion and the sign of the charge

The vector $\left(\vec{A}_p\right)_j$ is computed from equation (40) which is

$$\left(\vec{A}_p\right)_j=\sum_i \frac{Z_i\vec{D}_{ij}}{\left(\vec{D}_{ij}\cdot\vec{D}_{ij}\right)^{3/2}}$$

where (eq. (36))

$$\vec{D}_{ij}=D_{ij1}\hat{\alpha}+D_{ij2}\hat{\beta}+D_{ij3}\hat{\gamma}$$

and (eqs. (37))

$$D_{ij1}=g_{j1}-I_{i1}-l_1a$$

$$D_{ij2}=g_{j2}-I_{i2}-l_2b$$

$$D_{ij3}=g_{j3}-I_{i3}-l_3c$$

The expanded expression for $\left(\vec{A}_p\right)_j$ is

$$\left(\vec{A}_p\right)_j=\sum_{\eta=0}^{1}\sum_{i}\frac{Z_i\left(D_{ij1}\hat{\alpha}+D_{ij2}\hat{\beta}+D_{ij3}\hat{\gamma}\right)}{\left(D_{ij1}^2+D_{ij2}^2+D_{ij3}^2+2D_{ij1}D_{ij2}\cos\gamma+2D_{ij2}D_{ij3}\cos\alpha+2D_{ij1}D_{ij3}\cos\beta\right)^{3/2}} \tag{86}$$

In this expression for $\eta=0$, there will be terms where $\vec{G}_j=\vec{I}_i$ and these must be discarded to avoid dividing by zero. They would represent the interaction of an ion with itself.

In computing the polarization energies of the two oxides of molybdenum, the polarizable ions were selected as follows:

For MoO_2,

$$\vec{G}_1=\overrightarrow{Mo^{IV}}=1.295\hat{\alpha}+2.421\hat{\beta}+2.899\hat{\gamma}$$

$$\vec{G}_2=\vec{O}_I=0.614\hat{\alpha}+1.017\hat{\beta}+1.346\hat{\gamma}$$

$$\vec{G}_3=\overrightarrow{O_{II}}=2.178\hat{\alpha}+3.389\hat{\beta}+1.682\hat{\gamma}$$

and for MoO_3,

$$\vec{G}_1=\overrightarrow{Mo^{VI}}=5.54\hat{\alpha}+2.77\hat{\beta}+2.32\hat{\gamma}$$

$$\vec{G}_2=\vec{O}_I=6.03\hat{\alpha}+0.924\hat{\beta}+2.08\hat{\gamma}$$

$$\vec{G}_3=\overrightarrow{O_{II}^{III}}=5.54\hat{\alpha}+2.77\hat{\beta}+4.20\hat{\gamma}$$

$$\vec{G}_4=\overrightarrow{O_{III}^{III}}=3.74\hat{\alpha}+2.77\hat{\beta}+2.04\hat{\gamma}$$

The computed $\left(\vec{A}_p\right)_j$ vectors were as follows:

For MoO_2,

$$\left(\vec{A}_p\right)_1=0.304\hat{\alpha}-0.0473\hat{\beta}+0.0599\hat{\gamma}$$

$$\left(\vec{A}_p\right)_2=0.242\hat{\alpha}+0.173\hat{\beta}+0.353\hat{\gamma}$$

$$\left(\vec{A}_p\right)_3=0.0713\hat{\alpha}-0.0342\hat{\beta}-0.00262\hat{\gamma}$$

and

$$\left(\vec{A}_p\right)_1\cdot\left(\vec{A}_p\right)_1=0.9795 \qquad (Mo^{4+})$$

$$\left.\begin{aligned}\left(\vec{A}_p\right)_2\cdot\left(\vec{A}_p\right)_2&=0.1253\\ \left(\vec{A}_p\right)_3\cdot\left(\vec{A}_p\right)_3&=0.00645\end{aligned}\right\} \qquad (O^{2-})$$

and for MoO_3,

$$\left(\vec{A}_p\right)_1=-0.680\hat{\alpha}-0.00686\hat{\beta}-0.0719\hat{\gamma}$$

$$\left(\vec{A}_p\right)_2=-0.333\hat{\alpha}-0.0625\hat{\beta}-0.282\hat{\gamma}$$

$$\left(\vec{A}_p\right)_3=-0.853\hat{\alpha}-0.00311\hat{\beta}+0.289\hat{\gamma}$$

$$\left(\vec{A}_p\right)_4=-1.295\hat{\alpha}-0.00362\hat{\beta}-0.0905\hat{\gamma}$$

and

$$\left(\vec{A}_p\right)_1\cdot\left(\vec{A}_p\right)_1=0.4676 \qquad (Mo^{6+})$$

$$\left.\begin{aligned}\left(\vec{A}_p\right)_2\cdot\left(\vec{A}_p\right)_2&=0.1943\\ \left(\vec{A}_p\right)_3\cdot\left(\vec{A}_p\right)_3&=0.8111\\ \left(\vec{A}_p\right)_4\cdot\left(\vec{A}_p\right)_4&=1.298\end{aligned}\right\} \qquad (O^{2-})$$

The polarizabilities used were as follows:

For Mo^{4+},

$$\alpha'=0.35\ \text{Å}^3$$

for Mo^{6+},

$$\alpha'=0.26\ \text{Å}^3$$

and for O^{2-}

$$\alpha'=2.22\ \text{Å}^3$$

These quantities may be substituted into the working formula (eq. (84))

$$U_p=-165.92\sum_j\alpha_j'\left(\vec{A}_p\right)_j\cdot\left(\vec{A}_p\right)_j$$

to yield polarization energy. The results are

for MoO_2,

$$U_p=53.12\ \text{kcal/mole}$$

and for MoO_3,

$$U_p=868.46\ \text{kcal/mole}$$

Approximately 10 minutes on the IBM 704 computer were required to compute a set of electric-field vectors for either oxide.

CALCULATION OF VAN DER WAALS ENERGY

The Van der Waals forces are very short-order forces and consequently, the computation of the Van der Waals energies may be limited to consideration of nearest neighbor interactions only. In computing the Van der Waals energies on a per-mole basis, it is necessary to sum the contributions of all bonds associated with one molecular unit and multiply this by Avogadro's number. For one bond, the dipole-dipole and dipole-quadrupole energies are given by the following expressions:

For dipole-dipole energy (eq. (62)),

$$(U_{dd})_{ijk} = -\frac{J_{jk}}{d_i^6}$$

and for dipole-quadrupole energy (eq. (64)),

$$(U_{dq})_{ijk} = -\frac{L_{jk}}{d_i^8}$$

In these expressions the indices j and k refer to interaction between an ion of element j and an ion of element k. The index i refers to bond distance i for those two elements. In the distorted structures there are several bond distances for each pair of elements rather than a single distance found in more symmetrical structures. The coefficients J_{jk} and L_{jk} are determined as follows. The dipole-dipole coefficient is computed by using equation (54) which is

$$J_{jk} = \frac{3}{2}\frac{\alpha_j \alpha_k}{\sqrt{\frac{\alpha_j}{N_j}} + \sqrt{\frac{\alpha_k}{N_k}}}$$

where

α polarizability

N number of polarizable electrons in the ion

For ions with closed-shell structures, the value for N is that computed for the isoelectronic inert gas. These values were computed by Herzfeld and Wolf (ref. 13) as follows:

For argon,

$$N = 4.6$$

for krypton,

$$N = 5.1 \text{ (interpolated)}$$

and for xenon,

$$N = 5.6$$

On this basis, the value of N for Mo^{6+} is 5.1 and for O^{2-} is 4.6. The value of N for the Mo^{4+} ion must be estimated since it does not have a closed-shell structure. It is assumed that the two d-electrons will cause an increase in N for Mo^{4+} over that for Mo^{6+} and a value $N = 5.5$ is estimated for Mo^{4+}.

In order to establish a working formula for the dipole-dipole energy, equation (54) must be multiplied by $e^2 a_o^{1/2}$ which converts from atomic to cgs units and where

e electronic charge, 4.802×10^{-10} esu

a_o Bohr radius, 0.529×10^{-8} cm

The following constants must also be applied in order to give a final expression in the units kcal/mole:

c 2.3889×10^{-11} kcal/erg

N_{Av} Avogadro's number, 6.024×10^{23} molecules/mole

These constants are combined to give the formula, in kcal/mole,

$$(U_{dd})_{ijk} = -241.41\left(\frac{3}{2}\frac{\alpha'_j \alpha'_k}{\sqrt{\frac{\alpha'_j}{N_j}} + \sqrt{\frac{\alpha'_k}{N_k}}}\right)\frac{1}{R_i^6} \quad (87)$$

It is convenient to use the form, in kcal/mole,

$$(U_{dd})_{ijk} = -241.41\frac{C_{jk}}{R_i^6} \quad (88)$$

where

$$C_{jk} = \frac{3}{2}\frac{\alpha'_j \alpha'_k}{\sqrt{\frac{\alpha'_j}{N_j}} + \sqrt{\frac{\alpha'_k}{N_k}}} \quad (89)$$

The polarizabilities α are in $Å^3$ units and R_i is in Å units. The dipole-quadrupole coefficient is computed by using equation (57) which is

$$L_{jk} = \frac{3}{e^2}\left(\frac{J_{jj}}{N_j \alpha_j} + \frac{J_{kk}}{N_k \alpha_k}\right)J_{jk}$$

The unit conversion factors are combined to give the following formula, in kcal/mole,

$$(U_{dq})_{ijk} = -4{,}060\frac{d_{jk}}{R_i^8} \quad (90)$$

where

$$d_{jk} = \frac{3}{4.80^2}\left(\frac{C_{jj}}{N_j \alpha_j} + \frac{C_{kk}}{N_k \alpha_k}\right)C_{jk} \quad (91)$$

The final formulas for computing the Van der

Waals energies, in kcal/mole, are as follows:

$$U_{dd} = -241.41 \sum_{ijk} \frac{M_{ijk} C_{jk}}{R_i^6} \quad (92)$$

$$U_{dq} = -4{,}060 \sum_{ijk} \frac{M_{ijk} d_{jk}}{R_i^8} \quad (93)$$

where M_{ijk} is the number of bonds present between ions j and k with a distance R_i. The terms in the summations of equations (92) and (93) are tabulated in tables 1 and 2. These values are substituted into equations (92) and (93) to yield the following Van der Waals energies, in kcal/mole:

For MoO_2,

$$U_{dd} = -105.99$$
$$U_{dq} = -76.57$$

and for MoO_3,

$$U_{dd} = -72.76$$
$$U_{dq} = -25.13$$

CALCULATION OF REPULSION ENERGY

The repulsion energy U_r is given by equation (4) which is

$$U_r = -p_r(U_c + 4U_p + 6U_{dd} + 8U_{dq})$$

where the U terms are the different kinds of attractive energy and p_r is a repulsion coefficient. The repulsion coefficient is given by equation (74) which is

$$p_r = \frac{\sum_{ij} M_{ij}\beta_{ij} \frac{(r_i + r_j)^{n_{ij}-1}}{d_{ij}^{n_{ij}}}}{\sum_{ij} M_{ij} n_{ij} \beta_{ij} \frac{(r_i + r_j)^{n_{ij}-1}}{d_{ij}^{n_{ij}}}}$$

where (eq. (66))

$$\beta_{ij} = 1 + \frac{Z_i}{P_i} + \frac{Z_j}{P_j}$$

and

M_{ij} number of bonds per mole between ions i and j at a distance d_{ij}
r ionic radius
d_{ij} bond distance between ions i and j
Z valence of the ion
P number of outer electrons for the ion
n_{ij} a constant dependent on the particular ion pair

The value of n_{ij} is obtained by using the method of Pauling (ref. 2, p. 509). The quantities used in the calculations of p_r are given in tables 3 and 4. The calculated values of p_r are as follows:

For MoO_2,

$$p_r = 0.1295$$

and for MoO_3,

$$p_r = 0.1266$$

Substituting these values in equation (20) gives the repulsion energies as follows:

For MoO_2,

$$U_r = 462.44 \text{ kcal/mole}$$

and for MoO_3,

$$U_r = 1{,}261.12 \text{ kcal/mole}$$

APPENDIX C

METHOD OF OBTAINING POLARIZABILITIES OF IONS

The polarizabilities of the ions assumed to exist in the oxides of molybdenum must be known in order to compute lattice energy. Since some of these data were not found in the literature it was necessary to search for an empirical relationship that would be capable of providing reasonably accurate values of the polarizabilities. A method frequently employed is the use of the cube of the ionic radius as the polarizability. This value is generally recognized as a rough estimate; however, it does not agree with the method established in this investigation. The empirical relationship presented here is believed to be a new and more accurate method of obtaining polarizabilities of positively charged ions.

The polarizabilities of O^{2-}, Mo^{4+}, and Mo^{6+} ions are needed to compute the polarization energy and the Van der Waals energy. The polarizability of an ion is sometimes regarded as a constant. Actually, the polarizability of an ion varies over a small range of values according to the environment. Ionic polarizabilities have been calculated and measured by many investigators. A small part of this work is described in references 14 to 16.

According to reference 15 the polarizability of O^{2-} varies according to crystal type. Of the available data, it appears that TiO_2 provides an ion environment most like that in the oxides of molybdenum for the O^{2-} ion. Measurements on TiO_2 yield a value of 2.22 Å^3 for the polarizability of the O^{2-} ion. Fajans and Joos (ref. 16) found a value of 2.75 Å^3 for the O^{2-} ion in solution. Polarizability calculations for the O^{2-} ion in a free or gaseous environment yield values near 3.8 Å^3. Polarizability measurements on several crystals yield values ranging from 2.0 to 2.5 Å^3 for the O^{2-} ion. The value of 2.22 Å^3 as the polarizability of the O^{2-} ion has been adopted for the computations in this paper.

The polarizabilities of Mo^{4+} and Mo^{6+} ions were not found to be reported in the literature and presumably have not been determined. An empirical relationship was determined to predict the polarizability of ions having the inert-gas-type closed-outer-shell structure. It is found that the following relationship holds for ions having the same charge and closed-shell structure:

$$\alpha' = k \frac{r^3}{E_I} \tag{94}$$

where

α'	polarizability in Å^3
r	ionic radius in Å
E_I	ionization potential in electron volts
k	a constant for ions of the same charge

Polarizabilities of ions in solution measured by Fajans and Joos (ref. 16) are plotted against r^3/E_I in figures 13 to 16 with a separate plot for ions of different charge. The slope of each straight line produced yields a value of k for the particular ionic charge. Values of k corresponding to charges of +1 to +4 were determined. A plot of k against charge (fig. 17) was then made and k was extrapolated to give a value for ions of charge +6. By this means it was possible to arrive at a value for the polarizability of the Mo^{6+} ion. The values of k were determined as follows:

Charge	k	
+1	12.5	
+2	24	
+3	44	
+4	70	
+5	100	By extrapolation
+6	134	By extrapolation

For Mo^{6+}, $\frac{r^3}{E_I} = 0.00192$ which yields polarizability α' equal to 0.26.

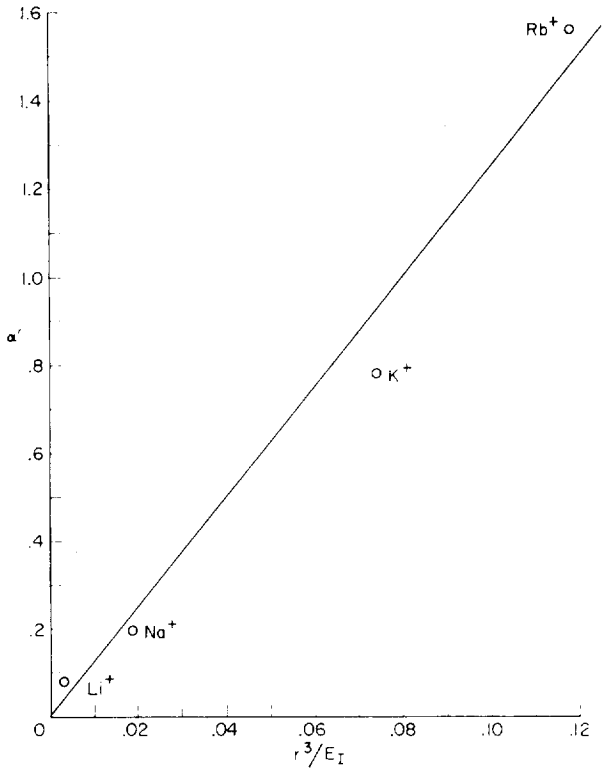


FIGURE 13.—Polarizability relationships of +1 ions. Polarizability taken from reference 16.

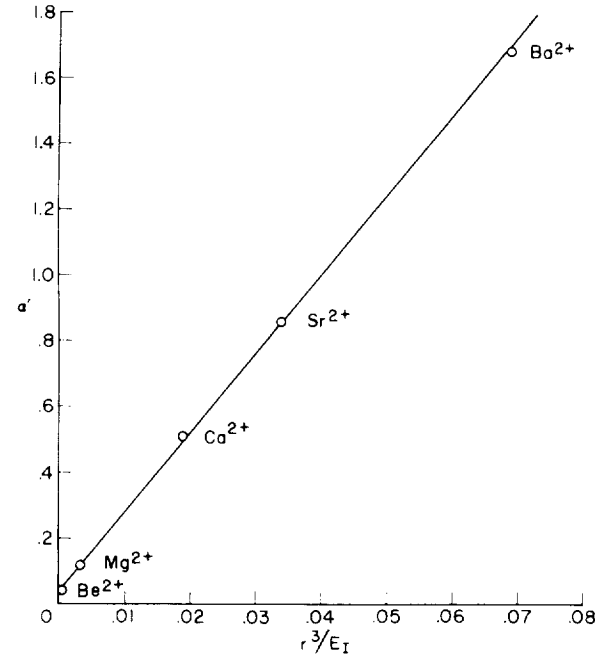


FIGURE 14.—Polarizability relationships of +2 ions. Polarizability taken from reference 16.

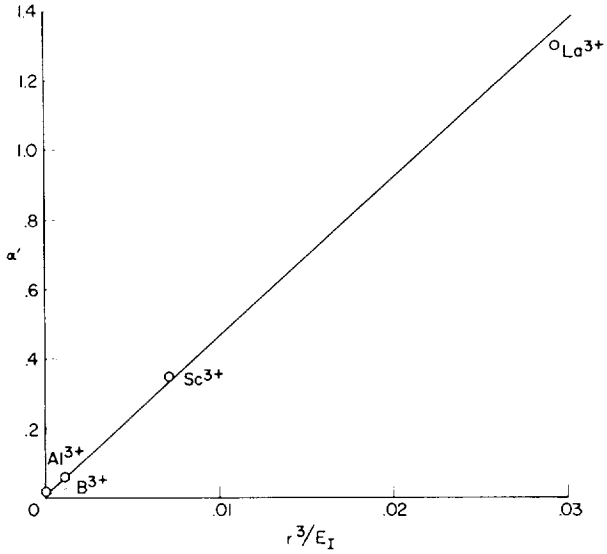


FIGURE 15.—Polarizability relationships of +3 ions. Polarizability taken from reference 16.

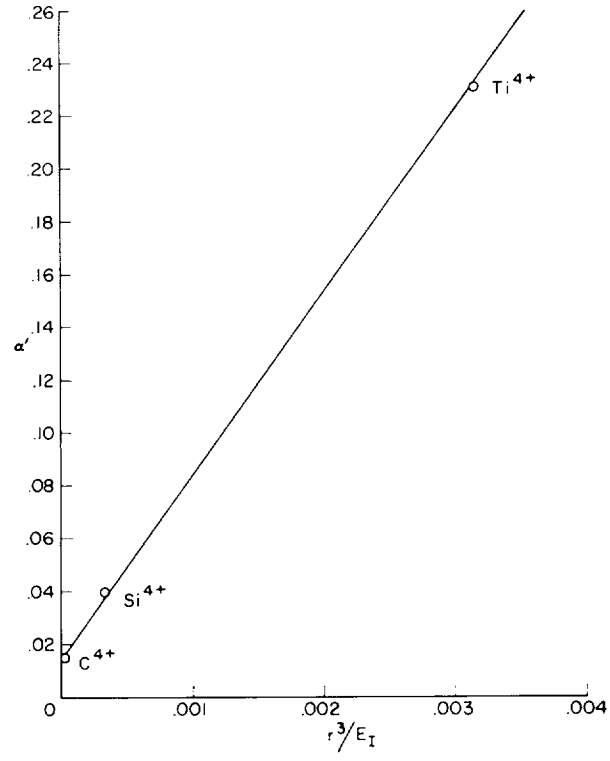


FIGURE 16.—Polarizability relationships of +4 ions. Polarizability taken from reference 16.

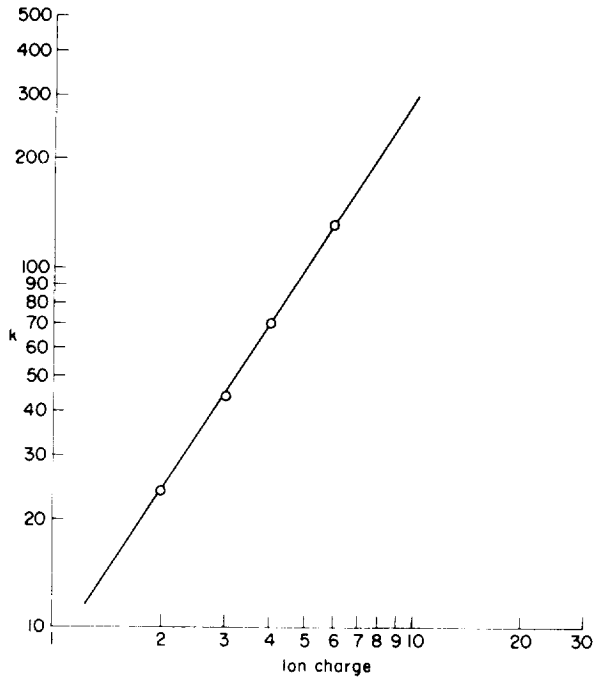


FIGURE 17.—Polarizability constant for cations.

Presumably, the polarizability for the Mo^{4+} ion can be obtained only by estimation. There are some factors to serve as a qualitative guide in such estimation, however. The polarizability of the Mo^{4+} ion must be larger than that of the Mo^{6+} ion. The Mo^{6+} ion has eight electrons in an outer-closed-shell configuration which is inherently stable. The Mo^{4+} ion has the eight electrons in the closed shell plus two additional electrons. The additional two electrons are in larger orbitals and are less firmly bound. They would tend to cause increased polarizability. However, the presence of the two outer electrons would inhibit somewhat the deformability of the eight electron orbitals in the next inner shell and reduce the polarizability slightly. In consideration of these relationships, the polarizability of the Mo^{4+} ion is estimated to be 0.35 Å^3. No doubt there is a good possibility of error in arriving at a value of the polarizability of Mo^{4+} ion by this means. There was no other apparent recourse and it is felt that the error introduced is less than that which would result from assigning a zero value to the polarizability of the Mo^{4+} ion, that is, from ignoring it altogether.

In summary, the polarizabilities used in computations in this paper are as follows:

For O^{2-},

$$\alpha' = 2.22 \text{ Å}^3$$

for Mo^{6+},

$$\alpha' = 0.26 \text{ Å}^3$$

and for Mo^{4+},

$$\alpha' = 0.35 \text{ Å}^3$$

APPENDIX D

THERMOCHEMICAL DATA AND THE BORN-HABER CYCLE

The values which have been obtained for the lattice energies of the oxides of molybdenum by theoretical methods may be compared with experimental measurements. Thermochemical measurements are made of the heats of formation of compounds. These data are transformed into lattice energy by the Born-Haber cycle. The thermochemical data are given in the first section of this appendix and these are applied in the second section which describes the Born-Haber cycle calculations.

THERMOCHEMICAL DATA

The heats of formation of MoO_2 and MoO_3 have been measured (refs. 17 and 18). The recommended mean values are given as follows (at 298.15° C):

$Mo(c)+O_2(g) \rightarrow MoO_2(c)$	$\Delta H=-140.8$ kcal/mole
$Mo(c)+1\frac{1}{2}O_2(g) \rightarrow MoO_3(c)$	$\Delta H=-178.1$ kcal/mole

Other thermochemical data from reference 19 are

$Mo(c) \rightarrow Mo(g)$	$\Delta H=155.5$
$O_2 \rightarrow 2O$	$\Delta H=116.8$

Electron Affinity:

The electron affinity of O^{2-} has been recently determined by Huggins and Sakamoto (ref. 8, p. 241) as follows:

Electron affinity O^{2-} 162 ± 15 kcal/mole

Ionization Potential:

The energies required to remove the first six electrons from molybdenum are given as follows (ref. 20):

For Mo,

I	7.18 electron volts	IV	40.5 electron volts
II	15.2 electron volts	V	56 electron volts
III	27.0 electron volts	VI	72 electron volts

for Mo^{4+},

89.88 electron volts or 2,068 kcal/mole

and for Mo^{6+},

217.88 electron volts or 5,014 kcal/mole

LATTICE-ENERGY CALCULATIONS BY BORN-HABER CYCLE

The Born-Haber cycle is expressed by the following equation:

$$\Delta H_L=\Delta H_f-\Delta H_g-\Delta H_d-E_A-E_I \qquad (95)$$

where

ΔH_L	lattice enthalpy ($\approx$lattice energy)
ΔH_g	heat of atomization (molybdenum)
ΔH_d	heat of dissociation (oxygen)
E_A	electron affinity (oxygen)
E_I	ionization potential (molybdenum)
ΔH_f	heat of formation

Also,

$$\Delta H_L=\Delta E_L+\Delta nRT \qquad (96)$$

The term ΔnRT is relatively small and is neglected; therefore, $\Delta H_L\approx\Delta E_L$.

For MoO_2,

$$\Delta H_L=-140.8-155.5-116.8-324-2{,}068$$
$$=2{,}805 \text{ kcal/mole}$$

For MoO_3,

$$\Delta H_L=-178.1-155.5-175.2-486-5{,}014$$
$$=-6{,}009 \text{ kcal/mole}$$

REFERENCES

1. Kubaschewski, O., and Hopkins, B. E.: Oxidation of Metals and Alloys. Butterworths Scientific Pub. (London), 1953, p. 130.
2. Pauling, Linus: The Nature of the Chemical Bond. Third ed., Cornell Univ. Press (Ithaca, N.Y.), 1960.
3. Henry, Norman F. M., and Lonsdale, Kathleen, eds.: International Tables for X-Ray Crystallography. Vol. I Symmetry Groups. The Kynoch Press (Birmingham, England), 1952.
4. Van Arkal, A. E.: Molecules and Crystals. Butterworths Scientific Pub. (London), 1956, p. 257.
5. Garrick, F. J.: Studies in Coordination.—Pt. IV. Some Fluorides and Chlorides and Their Complex Ions. Phil. Mag., ser. 7, vol. 14, no. 94, Nov. (Supplement) 1932, pp. 914–937.
6. London, F.: Zur Theorie und Systematik der Molekularkräfte. Z. Physik, vol. 63, nos. 3–4, July 1930, pp. 245–279.
7. Kirkwood, John G.: Polarisierbarkeiten, Suszeplibilitäten und van der Waalssche Kräfte der Atome mit mehreren Elektronen. Phys. Z., Jahrg. 33, Nr. 2, Jan. 15, 1932, pp. 57–60.
8. Huggins, Maurice L., and Sakamoto, Yosio: Lattice Energies and Other Properties of Crystals of Alkaline Earth Chalcogenides. Jour. Phys. Soc. of Japan, vol. 12, no. 3, Mar. 1957, pp. 241–251.
9. Gould, Edwin S.: Inorganic Reactions and Structure. Henry Holt and Co., c.1955, p. 143.
10. Bowen, H. J. M., and Donohue, J., et al. (compilers): Tables of Interatomic Distances and Configuration in Molecules and Ions. Special Pub. No. 11, The Chem. Soc. (London), 1958.
11. Magnéli, Arne, and Andersson, Georg: On the MoO_2 Structure Type. Acta Chemica Scandinavica, vol. 9, no. 8, 1955, pp. 1378–1381.
12. Bijvoet, J. M., ed.: Inorganic Compounds. Sec. II of Structure Reports for 1950, vol. 13, N.V. A. Oosthoek's Uitgevers Mij (Utrecht, The Netherlands), c.1954, pp. 219–221.
13. Herzfeld, K. F., and Wolf, K. L.: Prüfung der klassischen Dispersionsformel an einatomigen Gasen und Dämpfen. Ann. Phys., 4th Folge, Bd. 76, Heft 1, 1925, pp. 71–105.
14. Weislinger, Edmond: Contribution au Calcul Variationnel des Polarisabilités Ioniques. Jour. Chimie Physique, t. 55, no. 7–8, July-Aug. 1958, pp. 528–539.
15. Tessman, Jack R., Kahn, A. H., and Shockley, William: Electronic Polarizabilities of Ions in Crystals. Phys. Rev., vol. 92, no. 4, Second ser., Nov. 15, 1953, pp. 890–895.
16. Fajans, K., and Joos, G.: Molrefraktion von Ionen und Molekülen im Lichte der Atomstruktur. Z. Physik, Bd. XXIII, Nrs. 1–2, Jan. 1924, pp. 1–46.
17. Mah, Alla D.: Heats of Formation of Alumina, Molybdenum Trioxide and Molybdenum Dioxide. Jour. Phys. Chem., vol. 61, no. 11, Nov. 18, 1957, pp. 1572–1573.
18. Staskiewicz, Bernard A., Tucker, James R., and Snyder, Paul E.: The Heat of Formation of Molybdenum Dioxide and Molybdenum Trioxide. Jour. American Chem. Soc., vol. 77, no. 11, June 5, 1955, pp. 2987–2989.
19. Rossini, Frederick D., Wagman, Donald D., et al.: Selected Values of Chemical Thermodynamic Properties. NBS Circular 500, U.S. Dept. Commerce, Feb. 1, 1952.
20. Allen, C. W.: Astrophysical Quantities. The Athlone Press (London), 1955, p. 35.

U.S. GOVERNMENT PRINTING OFFICE: 1962