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Hugh S. Taylor, Henry Eyring, and Albert Sherman

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Binding Energies in the Growth of Crystal Nuclei from Metallic Atoms

HUGH S. TAYLOR, HENRY EYRING AND ALBERT SHERMAN, *Frick Chemical Laboratory, Princeton University*

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First order perturbation theory has been employed to compute the binding energies of various geometrical configurations of three to eight atoms of sodium. It has been assumed that in the metal lattice the binding is essentially homopolar. It has been shown that the growth of a unit cell probably proceeds via the diatomic molecule to a square, a fifth atom adding along a cube edge, a sixth at the body center and the cell completed by location of atoms at the remaining cube corners. The unit cell is still a very unstable unit, a result in agreement with high vapor pressures and solubility of finely divided particles, and with the concept of active centers on reaction surfaces. The fifth order secular equation employed to determine the energies of configurations of five and six atoms has

been made more amenable to use in calculations. A fourteenth order secular equation, with similar characteristics, has been employed for the cases of seven and eight atoms. Approximate calculations with copper atoms instead of sodium give similar results but indicate that higher activation energies of nuclei formation may obtain in this case. The percentage of the total binding assigned to interchange is shown to be an important factor. The calculations indicate that the net effect of interchange forces in homopolar crystals is to increase the potential energy. The crystal structure is stable only because of the coulombic and van der Waals' forces. When applied to hydrogen (90 percent interchange) it is shown that a metallic lattice is utterly unstable.

THE recent development in the application of quantum mechanics to problems of chemical reaction, with the exhibition in terms of modern theory of the well-known chemical concept of activation energy has prompted the present inquiry into the problem of the association of metallic atoms to form a lattice structure. Numerous data drawn from the fields of electrode phenomena and surface reactions indicate that many of the properties of metallic surfaces are a function of the position of the atoms in the surface layer. It is also known that the surface structure is sensitive to the influence of temperature, that, therefore, the concept of activation energy is applicable to processes operative during changes of surface structure. The sintering of catalysts is one piece of experimental evidence. The concept of centers of abnormal activity on such surfaces is also indicative of positions in the surface of high potential energy. The type of adsorption, whether van der Waals' or activated adsorption, which occurs on these surfaces is governed in part by the arrangement of atoms in the surface layers as is evident from recent quantum mechanical examination of this phenomenon.¹ It was, therefore, of interest to examine how far the application of first order per-

turbation theory could be utilized to exhibit such characteristics of a metallic surface.

In addition, also, to the subjects already mentioned the properties of small particles have a quite general physico-chemical interest. We need only recall, for example, in this connection, the extensive work on the increased solubility of fine particles, first emphasized by the researches of Hulett² on the solubility of barium sulphate. Such increased solubility is paralleled by the high values found for the vapor pressures of condensed films of metals on surfaces such as glass, with correspondingly small heats of vaporization of such films. These latter data are more pertinent to the problem which we have had under consideration. As was shown by Estermann³ the condensation of cadmium vapor on glass, copper and silver gave films whose heats of vaporization (3000–5000 calories) represent only 1/5 to 1/7 that of bulk crystalline cadmium. Frenkel⁴ has pointed out that such films are to be regarded as composed of "twins" and that the first nuclei of such film growth are diatomic aggregates. Our calculations should serve to show something of the transition states from such twins to the macroscopic crystals.

¹ (a) M. Polanyi, *Zeits. f. Elektrochemie* **35**, 561 (1929). (b) J. E. Lennard-Jones, *Trans. Faraday Soc.* **28**, 333 (1932). (c) A. Sherman and H. Eyring, *J. Am. Chem. Soc.* **54**, 2661 (1932).

² G. A. Hulett, *Zeits. f. physik. Chemie* **37**, 385 (1901); **47**, 357 (1904).

³ I. Estermann, *Zeits. f. Elektrochemie* **31**, 441 (1925).

⁴ J. Frenkel, *Zeits. f. Physik* **26**, 117 (1924).

Slater⁵ has already discussed the problem of the properties of the metallic lattice of sodium. He has thus shown that the perturbation method is capable of yielding an approximation to actual observed properties, so that the method of treatment inspires some confidence that a more detailed examination from a somewhat different standpoint might produce other fruitful results. Slater treated in particular detail the problem of many atoms in a linear assembly or filament. To do this it was necessary to neglect terms which arise from atoms more distant than neighbors. By restricting attention to fewer atoms it is possible to consider all interactions and to treat in the same detail configurations other than filaments. The method used is that employed by Slater⁶ for three and four atoms and since extended⁷ to as many as eight atoms, which represents the maximum number here considered. Our study differs from recent investigations of Kossel⁸ and Stranski⁹ on crystal growth in that their work deals principally with ionic lattices and actual crystals. We have confined our attention to metal atoms and the initial stages of formation of a crystal unit. Our limitation of the problem to that of a few atoms is dictated mainly by the inherent difficulty of the many-atom problem, but also because, with more atoms, terms other than the coulombic and interchange become increasingly important. Such terms may be thought of as involving the simultaneous interchange of more than two electrons.

It was not expected that such calculations would yield information concerning crystallization of metals in bulk at high temperatures. Rather we have sought to examine theoretically the phenomena occurring with films of metallic atoms laid down at low temperatures and which show processes of incipient crystallization on raising to moderate temperatures; for example, phenomena such as those of Estermann already mentioned and those studied by Langmuir in the change of properties of molybdenum films de-

posited on glass at liquid air temperatures, the characteristics of which are in part destroyed by raising the film to room temperature.¹⁰ Films of iron behave similarly.¹¹ The processes known as "sintering" in the study of catalysts have certain analogies to such changes in films. In each case the experimental evidence points to the existence of definite, if small, activation energies.

PROCEDURE

At the outset we shall present the procedure which we have followed with reference to the element sodium. We shall do so because it is a case already considered by Slater for material in bulk. Also, for this element, the data for the binding energies of the sodium molecule and the ratio of interchange to coulombic binding as deduced by Rosen¹² represent, at the present time, the most trustworthy data for any metallic vapor with the possible exception of lithium. We have calculated the total binding energy of systems composed in the main of 3, 4, 5 and 6 metal atoms and have explored the additional possibilities obtaining with 8 atoms. We have examined the binding energies of these systems for a variety of geometric configurations chosen to exhibit the stages in which the formation of a metallic lattice might be achieved.

For the simpler systems we have made use of the roots of the secular equations for three atoms, E_3 , and four atoms, E_4 ,

$$E_3 = A + B + C + \left[\frac{1}{2} ((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2) \right]^{1/2}, \quad (1)$$

$$E_4 = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \left[\frac{1}{2} ((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2) \right]^{1/2}, \quad (2)$$

which have already been employed by one of us¹³ in the computation of activation energies of reaction between atoms and molecules as well as between two diatomic molecules. Additional evi-

⁵ J. C. Slater, Phys. Rev. [2], **35**, 509 (1930).

⁶ J. C. Slater, Phys. Rev. [2], **38**, 1109 (1931).

⁷ Reference 1(c) and forthcoming publications.

⁸ W. Kossel, *Machr. Ges. Wiss. Gottingen*, 1927, p. 135; *Leipziger Vortrage*, 1928, p. 1.

⁹ I. N. Stranski, *Zeits. f. physik. Chemie* **136**, 259 (1928); **17B**, 127 (1932).

¹⁰ I. Langmuir, *J. Am. Chem. Soc.* **41**, 167 (1919).

¹¹ W. Frankenburger and K. Mayrhofer, *Zeits. f. Elektrochemie* **35**, 590 (1929); **37**, 473 (1931).

¹² N. Rosen, Phys. Rev. [2], **38**, 255 (1931).

¹³ H. Eyring and M. Polanyi, *Zeits. f. physik. Chemie* **12B**, 279 (1931). H. Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931).

dence of the applicability of such formulae is furnished by the recent calculations of Pelzer and Wigner¹⁴ concerning the ortho-para hydrogen conversion, from which not only the activation energy but also the actual rate of reaction has been successfully derived.

For five and six atoms the more complex fifth order secular equation recently published¹⁵ has been rendered more amenable to calculation by employing eigenfunctions which are orthogonal to the degree of approximation used in the 3-4 atom calculations. The first eigenfunction of the earlier work was retained here and the subsequent functions were each in turn made orthogonal to those which preceded it, according to the well-known method of Schmidt.¹⁶ This yielded a

fifth order determinant, $|H_{ij} - d_{ij}E| = 0$, with the elements given in Table I.

The use of Table I is at once apparent from the following single example: $H_{11} = 4C + 4ab - 2ac - 2ad - 2ae - 2bc - 2bd - 2be + 4cd - 2ce - 2de - 2af - 2bf - 2cf - 2df + 4ef$. Here, C is the total coulombic binding of six atoms situated in any configuration $abcdef$ under study; ab, ac, ad , etc., represent the interchange integrals between the two atoms so designated, and determined by the energy of binding of the two atoms at the given distance as derived from a Morse potential energy curve for a diatomic molecule. This table determines all the elements when it is remembered that $H_{ji} = H_{ij}$. The values of d_{ij} in the determinant have the same values as the coefficients of C in the corre-

TABLE I.

	H_{11}	H_{22}	H_{33}	H_{44}	H_{55}	H_{12}	H_{13}	H_{14}	H_{15}	H_{23}	H_{24}	H_{25}	H_{34}	H_{35}	H_{45}
C	+4	+3	+3	+2.25	+2	0	0	0	0	0	0	0	0	0	0
ab	+4	+3	-3	-2.25	-2	0	0	0	0	0	0	0	0	0	0
ac	-2	-1.5	+1.5	$+1\frac{1}{8}$	-2	0	-3	0	0	0	$-2\frac{1}{4}$	0	0	0	0
ad	-2	-1.5	+1.5	$-1\frac{1}{8}$	$+\frac{2}{3}$	0	+3	0	0	0	$-\frac{3}{4}$	+2	0	0	-1
ae	-2	-1.5	-1.5	$+\frac{3}{8}$	$+\frac{2}{3}$	0	0	$-\frac{3}{2}$	-2	$-\frac{3}{2}$	$+\frac{3}{2}$	-1	$-\frac{3}{2}$	+1	$+\frac{1}{2}$
bc	-2	-1.5	+1.5	$+1\frac{1}{8}$	-2	0	+3	0	0	0	$+2\frac{1}{4}$	0	0	0	0
bd	-2	-1.5	+1.5	$-1\frac{1}{8}$	$+\frac{2}{3}$	0	-3	0	0	0	$+\frac{3}{4}$	-2	0	0	-1
be	-2	-1.5	-1.5	$+\frac{3}{8}$	$+\frac{2}{3}$	0	0	$+\frac{3}{2}$	+2	$+\frac{3}{2}$	$-\frac{3}{2}$	+1	$-\frac{3}{2}$	+1	$+\frac{1}{2}$
cd	+4	-3	-3	$-\frac{3}{4}$	$+\frac{2}{3}$	0	0	0	0	0	0	0	0	0	+2
ce	-2	+1.5	-1.5	$-1\frac{1}{8}$	$+\frac{2}{3}$	-3	0	0	0	0	0	0	$+\frac{3}{4}$	-2	-1
de	-2	+1.5	-1.5	$+1\frac{1}{8}$	-2	+3	0	0	0	0	0	0	$+\frac{3}{4}$	0	0
af	-2	-1.5	-1.5	$+\frac{3}{8}$	$+\frac{2}{3}$	0	0	$+\frac{3}{2}$	+2	$+\frac{3}{2}$	$+\frac{3}{2}$	-1	$+\frac{3}{2}$	-1	$+\frac{1}{2}$
bf	-2	-1.5	-1.5	$+\frac{3}{8}$	$+\frac{2}{3}$	0	0	$-\frac{3}{2}$	-2	$-\frac{3}{2}$	$-\frac{3}{2}$	+1	$+\frac{3}{2}$	-1	$+\frac{1}{2}$
cf	-2	+1.5	-1.5	$+\frac{3}{8}$	$+\frac{2}{3}$	+3	0	0	0	0	0	0	$-\frac{3}{4}$	+2	-1
df	-2	+1.5	-1.5	$+1\frac{1}{8}$	-2	-3	0	0	0	0	0	0	$-2\frac{1}{4}$	0	0
ef	+4	-3	+3	$-2\frac{1}{4}$	-2	0	0	0	0	0	0	0	0	0	0

sponding H_{ij} ; thus, $d_{11} = 4$, $d_{22} = 3$ and so on. It will be noted that $d_{ij} = 0$ (for $i \neq j$) because of the orthogonality of our eigenfunctions. Inspection of Table I will further reveal that with systems possessing a reasonable degree of symmetry, by suitable assignment of letters to particular positions in the configuration, many of the non-diagonal elements may become zero. Thus, for example, in a configuration composed of four atoms $abcd$ forming a square with a fifth atom, e , at the face center and the sixth atom, f , at infinity, thus reducing it essentially to a five atom problem, the symmetry is such that the

fifth order determinant reduces at once to a quadratic expression, the roots of which are $C - 2ac$ and $C - 2ab$, the other three roots of the quintic being $\frac{1}{4}H_{11}$, $\frac{1}{3}H_{22}$, and $\frac{1}{3}H_{33}$. Since the coulombic and interchange integrals are negative the lowest root is obviously $C - 2ab$ if ab is a diagonal of the square configuration, ac a side of the same. Additional examples of such simplification will be noted in the presentation of results.

For seven and eight atoms the procedure is to be detailed elsewhere. It is essentially similar to the cases already discussed, but, even with the simplifications noted, the determinant received is of the fourteenth order, the roots of which are the energies of the fourteen singlet states of the seven or eight atoms in the given configuration. It is obvious that the computations involved severely restrict the number of such examples

¹⁴ H. Pelzer and E. Wigner, Zeits. f. physik. Chemie **15B**, 445 (1932).

¹⁵ Reference 1(c).

¹⁶ Courant-Hilbert, *Methoden der Mathematischen Physik*, 2d edition, p. 41, Springer.

studied. In all cases, the lowest root, algebraically, corresponds to the lowest energy of such a configuration and, therefore, the most favored energy level of the system. Where necessary, graphical representation of the value of the determinant with arbitrarily assigned values for the energy permits the finding of the lowest energy value at which the determinant becomes zero.

In addition to sodium, we have attempted also to apply the procedure to copper. We are aware of the arbitrary nature of some of our assumptions in this case, but wished to explore a metal, possessing different lattice features (face centered cubic) from those of sodium, and of which, from the data of surface catalysis, we know something concerning surface changes on sintering. We have also examined the case of hydrogen in a similar manner for the purpose of exhibiting the properties of a substance which definitely forms molecular rather than atomic lattice structure.

We have neglected the influence of van der Waals' forces, in the calculations up to eight atoms. The additive nature of both the van der Waals' and the coulombic forces implies that both are in principle involved in that portion, C , of our total energies normally assigned to coulombic forces. In the case of copper it was necessary, in the absence of definite data, to assign an arbitrary fraction of the total to the coulombic portion. We have, however, in this case, traced the influence of changes in this fraction on the values of energies obtained for various configurations. These will be presented in the subsequent sections.

RESULTS

I. Sodium

The binding energies of two atoms at any distance have been derived from a Morse curve set up from the following data, $D_{Na_2} = 17.5$ k.cals., $\omega_0 = 159$ cm⁻¹ and $r_0 = 3.15$ Å. For the coulombic binding C we have used Rosen's value¹² of 28.3 percent of the total binding and have indicated it by a subscript, $C_{28.3}$. The interchange factor is then 0.717 giving the interchange energy, $I_{71.7}$. With this material the following results were obtained for various possible configurations.

1. *Three atoms. (a) Linear configuration:* With the aid of Eq. (1) which reduces to $E_a = 2A + B + \alpha - \beta$, the following data were obtained:

r	2.6	3.15	3.25	3.43	3.7	4.25	4.8
$C_{28.3}$	-8.2	-10.7	—	-10.1	-8.9	-6.5	-4.4
$I_{71.7}$	-4.2	-10.9	—	-11.0	-10.2	-7.8	-5.5
E	-12.4	-21.6	-21.8	-21.1	-19.1	-14.3	-9.9

2. *Four atoms. (a) Linear configuration:* The energy of a system of four atoms in a line, equally spaced, was determined, by means of Eq. (2), which reduces to

$$E_a = 3A + 2B + C + [\frac{1}{2}((\alpha - \gamma)^2 + (\alpha - \beta)^2 + (\alpha + \gamma - 2\beta)^2)]^{1/2}$$

as a function of increasing interatomic distance, r . The data so obtained were:

r	2.6	3.15	3.25	3.43	3.70	4.25	4.80
$C_{28.3}$	-13.4	-16.45	—	-15.3	-13.6	-9.85	-6.7
$I_{71.7}$	-8.1	-18.9	—	-19.2	-17.7	-13.5	-9.5
E	-21.5	-35.4	-35.7	-34.5	-31.3	-23.4	-16.2

The lowest figure in the preceding data for E and in all subsequent tabulations represents the value obtained by interpolation from a graph of the other calculated data.

(b) *Square configuration:* The equation in this case simplifies to:

$$E_b = 2[2A + C + 0.717(A + \alpha - (C + \gamma))],$$

from which the following data are derived:

r	2.6	3.15	3.3	3.43	3.7	4.25	4.8
$C_{28.3}$	-22.0	-25.6	—	-23.4	-20.5	-14.6	-9.7
$I_{71.7}$	+5.5	-11.2	—	-13.6	-13.7	-11.7	-8.8
E	-16.5	-36.8	-37.7	-37.0	-34.2	-26.3	-18.5

(c) *Cubic arrangement:* The atoms occupy four adjacent corners of a cube of side r . The equation simplifies so far that all interchange energy is absent. $E_c = 3(A + B)$, and yields the values:

r	2.6	2.9	3.15	3.43	3.7	4.25	4.8
$E = C_{28.3}$	-23.0	-24.9	-23.5	-20.8	-17.8	-12.3	-8.0

(d) *Regular tetrahedral configuration:* The tetrahedron of side r also gives an equation from which the interchange energy is absent, $E_d = 6A$. The values can obviously be derived immediately from a Morse curve by multiplication with the factor 1.7 ($= 6 \times 0.283$).

r	2.6	3.15	3.43	3.7	4.25	4.8
$E = C_{28.3}$	-19.8	-30.1	-28.8	-26.0	-19.2	-13.2

(e) *Linear configuration, abc, with d at right angles to abc at a:* This configuration calculated by means of Eq. (2) gives:

r	2.6	3.15	3.43	3.7	4.25	4.8
$C_{28.3}$	-16.9	-18.9	-17.2	-15.0	-10.6	-7.1
$I_{71.7}$	-5.2	-14.7	-15.7	-15.0	-11.9	-8.55
E	-22.1	-33.6	-32.9	-30.0	-22.5	-15.7

(f) *Linear configuration, abc, with d at right angles to abc at b*: This configuration gives similarly: $E_f = 3A + 2B + C + \alpha - \gamma$.

r	2.6	3.15	3.43	3.7	4.25	4.8
$C_{28.3}$	-20.3	-21.3	-19.1	-15.5	-11.5	-6.1
$I_{71.7}$	-4.2	-10.9	-11.1	-10.2	-7.8	-4.5
E	-24.5	-32.2	-30.2	-25.7	-19.3	-10.6

3. *Five atoms. (a) Face centered square*: The fifth atom e is at the center of a square $abcd$. The symmetry of this configuration is such that $I_{71.7} = -0.717 (2ab)$. In this and succeeding tables r refers to the length of side of the square in angstroms.

r	3.68	3.8	4.0	4.2	4.4	4.95
$C_{28.3}$	-33.9	-36.0	—	-34.5	-33.1	-27.4
$I_{71.7}$	+8.3	+7.3	—	+4.7	+3.8	+2.0
E	-25.6	-28.7	-30.6	-29.8	-29.3	-25.4

(b) *Five atoms at face and center of body centered cube*: The equation is identical with that of the preceding example. The dimensions, however, at the minimum may be especially noticed.

r	3.3	3.60	3.68	4.0	4.53	4.95
$C_{28.3}$	-43.3	—	-40.8	-36.8	-27.5	-21.5
$I_{71.7}$	+12.3	—	+8.3	+5.8	+3.2	+2.0
E	-31.1	-32.6	-32.5	-31.0	-24.3	-19.5

(c) *Five atoms at cube corners, with four on one face*: The best arrangement of letters for the solution of the determinant calls for $acbd$ as the face, with a diagonal to b , and e symmetrical to a and b . This symmetry yields a fifth order determinant which factors into a quadratic and a cubic equation of which the lowest root is found in the cubic.

r	2.8	3.0	3.2	3.4	3.7	4.0
$C_{28.3}$	-40.3	-39.0	-36.9	-33.8	-29.1	-24.4
$I_{71.7}$	+13.4	+6.5	+1.2	-2.7	-5.5	-7.7
E	-26.9	-32.5	-35.5	-36.5	-34.6	-32.1

(d) *Four atoms, on square, fifth on diagonal extension at distance $0.707r$* : The best arrangement of letters calls for $acbe$ as the face, a diagonal to b , d on the extension of ce . This also yields a determinant which factors into a quadratic and a cubic equation.

r	3.43	4.0	4.25	4.53	4.80
$C_{28.3}$	-27.1	-23.6	-20.6	-17.7	-15.1
$I_{71.7}$	+6.3	-10.1	-11.0	-11.9	-11.6
E	-20.8	-33.7	-31.6	-29.6	-26.7

4. *Six atoms. (a) Five atoms at cube corners, sixth at body center*: The configuration employed showed $afbd$ as the atoms on the cube face, atom

e was at the fifth cube corner and adjacent to d ; the body centered atom was c .

r	3.0	3.2	3.4	3.7	4.95
$C_{28.3}$	-55.2	-59.4	-58.0	-54.0	-27.1
$I_{71.7}$	+14.8	+12.5	+9.5	+7.2	+2.0
E	-40.4	-46.9	-48.5	-46.8	-25.1

(b) *Six atoms at cube corners forming two faces*: The two cube faces were labeled $afbe$ and $fbcd$. In this way maximum simplification was obtained but the resultant determinant was still fifth order.

r	2.5	2.8	3.0	3.2	3.7	4.0
$C_{28.3}$	-46.6	-59.2	-56.8	-53.6	-41.8	-34.9
$I_{71.7}$	+10.3	+22.0	+20.8	+19.1	+14.4	+12.0
E	-36.3	-37.2	-36.0	-34.5	-27.4	-22.9

5. *Eight atoms. (a) Seven atoms at cube corners, eighth at the body center*: For this configuration four solutions were obtained each involving a 14th order determinant. The data gave a minimum at 3.4A.

r	3.15	3.4	3.7	4.3
$C_{28.3}$	-104.9	-99.7	-90.1	-65.8
$I_{71.7}$	+38.9	+31.5	+24.7	+16.8
E	-66.0	-68.2	-65.4	-49.0

(b) *Eight atoms at cube corners*: Four solutions of this configuration were obtained. It is evident that the increased symmetry of the complete cube gives the configuration a greater stability than that possessed by system 4b of six atoms at cube corners.

r	2.9	3.0	3.15	3.25
$C_{28.3}$	-106.9	-104.0	-99.3	-94.4
$I_{71.7}$	+53.8	+42.5	+31.2	+27.4
E	-53.1	-61.5	-68.1	-66.9

We present a graphical summary of some of these calculations in Figs. 1, 2, 3 and 4.

II. Copper

For this element we have constructed a Morse curve using the following estimated data $D_{Cu_2} = 56$ k.cals., $\omega_0 = 248$ cm⁻¹ and $r_0 = 2.18$ A. The heat of dissociation of the molecule was assumed to be the same fraction of the heat of sublimation ($\lambda = 82.06$ k.cals.)¹⁷ that the dissociation energy of the sodium molecule is of the heat of sublimation of sodium. The equilibrium distance, r_0 , was deduced from those of copper

¹⁷ H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. [2], 30, 201 (1927).

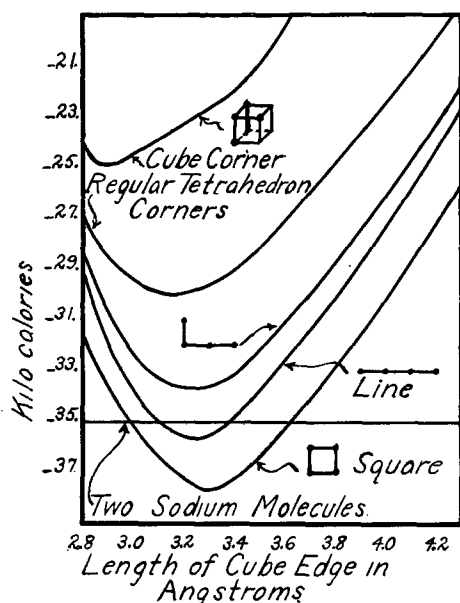


FIG. 1. Binding energies of four atom configurations.

hydride and hydrogen ($2r_{\text{CuH}} - r_{\text{H}_2}$). For the value of ω for copper, it was assumed that it bore the same ratio to that of sodium that the characteristic temperatures of the two elements possess in the evaluation of the specific heat data.

We present graphically in Figs. 5a and 5b the data for a 4 atom linear configuration, a square and a 5 atom face centered square with two assumptions as to the fraction of coulombic binding. In Fig. 5a this is assumed to be 20 percent;

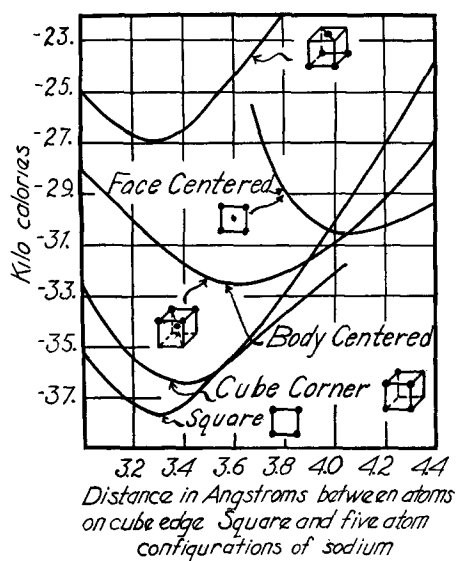


FIG. 2. Binding energies of five atom configurations.

in Fig. 5b the fraction is 30 percent. It will readily be seen that the general nature of the results is the same as in the case of sodium. The actual magnitudes of the energy differences at the minima are in each case much greater than with sodium and are very much larger with the assumption of 20 percent coulombic binding.

III. Hydrogen

To illustrate the fundamental importance of the coulombic : interchange ratio thus evident we have made calculations of the binding energies of various configurations of 4 and 6 atoms of

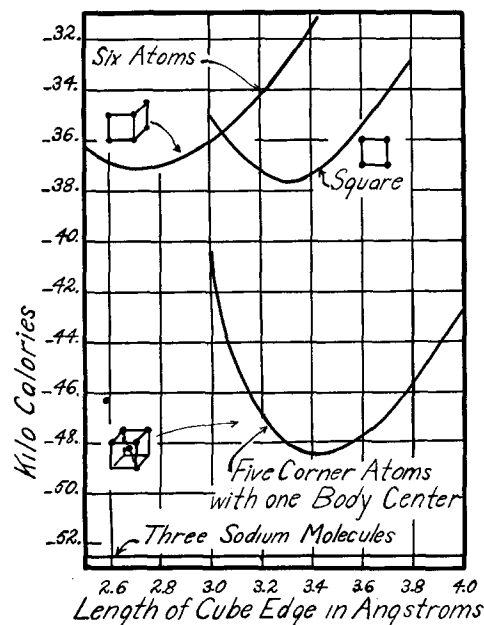


FIG. 3. Binding energies of six atom configurations.

hydrogen, using the 10 : 90 ratio that has been assumed in earlier work on the homogeneous reactions involving hydrogen.¹³ The Morse curve data in this case were $D_{\text{H}_2} = 101.5$ k.cals., $\omega_0 = 4262$ cm⁻¹; $r_0 = 0.76$ Å.¹³ Table II summarizes the data.

TABLE II.

Configuration	r_0	$E_{\text{min.}}$
Molecule	0.76	-101.5
Three atoms in line	0.93	-90.0
Square	1.0	-117.0
Five atoms at cube corner, sixth at body center	1.3	-35.7

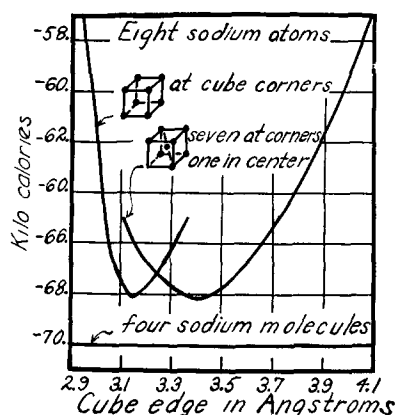


FIG. 4. Binding energies of eight atom configurations.

DISCUSSION

The data presented indicate the manner in which a unit cell would grow from the vapor phase away from surfaces. Fig. 1 shows that, of the possible configurations of four atoms there evaluated, the square configuration is the most stable. This may arise either from four atoms or two molecules, the relative frequency of the two modes of formation being, of course, determined by the pressure-temperature relations. It will also be seen that this configuration of four atoms is more stable than that of two sodium molecules by about 2 kilo.cals. Its concentration, however, under normal conditions, will be vanishingly small. This plane configuration is more stable than any of the possible three-dimensional con-

figurations, as has already been emphasized in another connection by Eyring.¹³ Further, as shown by the curves in Fig. 1 for the linear and right-angle configurations, should a linear aggregate of four atoms arise, an activation energy would be required if the mechanism of square formation passed through the right angle configuration shown.

For five atom configurations, Fig. 2, it is noteworthy that all the cases investigated show an inferior degree of stability to the square configuration. In contrast to the case of four atoms, the cube corner configuration is, in this group, the most stable. It is evident, therefore, that, in the cases considered, the approach of a fifth atom to a square can be accomplished with the mini-

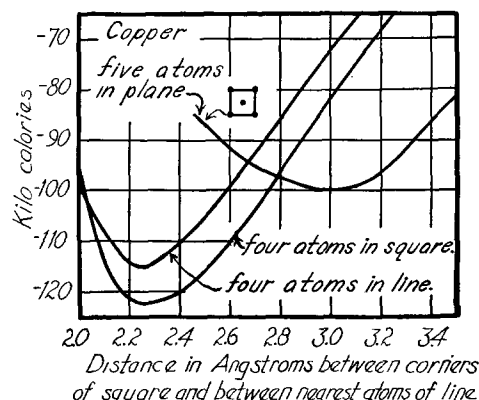


FIG. 5b. Four and five atom configurations of copper, coulombic binding 30 percent of total binding.

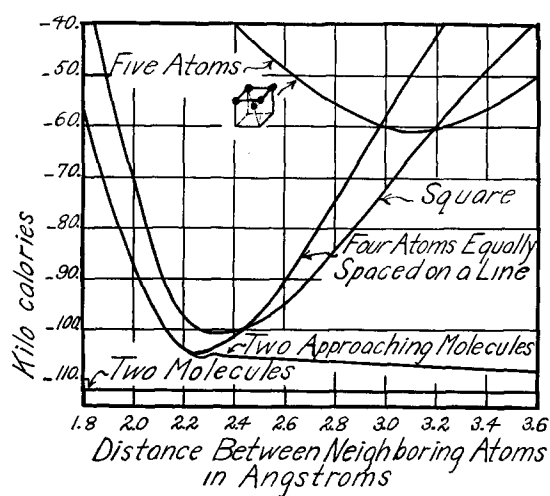


FIG. 5a. Potential energy for configurations of copper atoms when the coulombic is taken as 20 percent of the total binding.

imum activation energy when the approach is along the cube edge. The approach of a fifth atom produces, in general, an increase in the edge dimension at the position of maximum stability, most pronounced in the face centered configuration, where the edge is now 4Å. It should be noted, however, that, even in this case, the distance of nearest atoms is 2.83Å, hence less than that in the diatomic molecule.

In the case of six atoms, Fig. 3, the striking fact emerges that the cube corner configuration is still less stable than the square configuration. Here, however, the stabilizing influence of the body center atom makes itself very evident. The body center configuration of six atoms is some 10.5 kilo.cals. more stable than the square. Three molecules of sodium are, however, the more stable system by about 4 kilo.cals.

The increased stability obtaining with the body centered configuration is even more pronounced in the case of the eight atom configuration. Here, the addition of two more sodium atoms to the six atom body-centered system decreases the potential energy of the system by a further 20 kilo.cals., a decrease which is greater than the binding energy of the molecule. It will be seen that the binding energy is practically equal to that of four molecules. Fig. 4 shows, however, that this configuration has practically the same binding energy as that of a cube with edge equal to 3.15Å units. There is, therefore, the possibility that the body center atom may pass to the eighth cube corner, with an accompanying shrinkage of the lattice dimension. Presumably, a ninth atom would stabilize the body centered configuration. We hope, at a later date, to examine this possibility as an extension of this work.

Summarizing the data on all the configurations concerned, it would seem that the formation of a unit cell would proceed from the atoms, via the diatomic molecule to a square. A fifth atom would add along the cube edge. The sixth would enter the lattice at the body center and the cell would be completed by location of atoms at the remaining cube corners. It may further be emphasized that these several stages will involve definite, if small, activation energies of the order of 2 or 3 large calories at certain points in the synthesis.

We desire next to draw attention to the instability of such a unit cell. As we have seen, the binding energy of the unit cell is approximately equivalent to that of four molecules of sodium. Bulk crystalline sodium is formed from molecular sodium with the evolution of 17.25 kilo.cals. per gram atom (heat of sublimation, $\lambda_{Na} = 26$ kilo.cals.; $D_{Na_2} = 17.5$ kilo.cals.). One must conclude that, until one reaches structures more complex than the unit cell, the aggregates differ energetically but little from the "twins" visualized by Frenkel¹⁴ as the units of deposited films of the metals, and, statistically, the twin structures would be favored. Our conclusion as to the unit cell is in best agreement with our knowledge of the high vapor pressures, solubility, and the like, of finely divided particles. It also confirms our present concepts of the abnormal activity, energetically, of incompletely crystallized units on

surfaces such as are assumed to be of importance in the phenomena of adsorption and surface reactions. It also indicates a possible reason for the marked supersaturation effects shown by certain metallic vapors.

It will be noted that the edge dimension of our best unit cell (cube edge = 3.4Å) is still far from the distance required in the crystal lattice (cube edge = 4.3Å). The nearest atom distance is 2.95Å as compared with 3.15Å in the diatomic molecule and 3.7Å in the bulk crystal. That expansion, to distances greater than that of the atoms in a diatomic molecule, may occur with arrays of many unit cells is indicated by our data for three and four atom linear configurations which shows a definite expansion of the interatomic distance in the most stable state.

Since the coulombic binding is independent of electron spin it is additive, to the approximation here considered, for a large crystal. We determined the value of these bonds from a central atom outwards over the 82 nearest neighbors and this amounted to -36.7 kilo.cals. An integration to infinity beyond this gave a total coulombic binding of -37.8 kilo.cals. per gram atom. In addition to the attraction due to coulomb forces there is also that due to van der Waals' forces. This we have estimated from the polarizability of sodium atoms. For sodium practically the entire light absorption is that due to the *D*-lines so that to estimate the van der Waals' forces between atoms, $E = \frac{3}{4}(\alpha^2 h \nu / R^6)$, we may use¹⁸ the polarizability α and the frequency ν corresponding to the *D*-lines. The second order Stark effect ΔE may be written

$$\Delta E = \sum_i \frac{|X_{0i}|^2}{E_i - E_0} e^2 F^2 = \frac{1}{2} \alpha F^2,$$

where F is the field strength, X_{0i} is the corresponding matrix component for the x coordinate of the electron. But, $\sum_i (E_i - E_0) |X_{0i}|^2 = \hbar^2 / 8\pi^2 m$ as one sees immediately by using the commutation rule $\sum_i (P_{0i} X_{i0} - X_{0i} P_{i0}) = \hbar / 2\pi i$ and from the fact that $P_{ij} = dX_{ij}/dt = 2\pi i m (E_i - E_j) X_{ij}$. For the *D*-lines, we may neglect the difference in the values of E_i for the different final levels, so that we may write,

¹⁸ F. London, Zeits. f. physik. Chemie 11B, 222 (1930).

$$E = h^2 e^2 F^2 / (8 \pi^2 m (E_i - E_0)^2) = \frac{1}{2} \alpha F^2,$$

whence,

$$\alpha = e^2 h^2 / (4 \pi^2 m (E_i - E_0)^2) = 24.7 \times 10^{-24} \text{ cc},$$

a rather large polarizability. As has already been emphasized for hydrogen atoms by Eisenschitz and London¹⁹ such a value for the polarizability only has significance when applied at distances of the order of kinetic theory diameters or larger. Over such distances the value for the van der Waals' potential between sodium atoms amounts to -1.5 kilo.cals. per gram atom. The combined van der Waals' and coulombic bindings thus amount to $-37.8 - 1.5 = -39.3$ kilo.cals. Since the heat of sublimation of sodium is 26 kilo.cals. per gram atom it would seem that the interchange energy in the large crystal must be about $+13.3$ kilo.cals. This represents a positive interchange energy equal numerically to about 36 percent of the coulombic binding. It is of interest to note that in our progression from four atoms to eight the interchange binding has become progressively more positive and in the eight atom case has reached numerically 32 percent of the coulombic binding.

The calculation given refers to van der Waals' forces operative at or beyond distances of 9.37\AA , and implies a zero value for the binding at lesser distances. If one assumes the van der Waals' attraction operating between atoms at distances less than 9.37\AA is equal to that at 9.37\AA , then the total van der Waals' binding amounts to -2.41 kilo.cals. Had the limit of the calculation been set, not at 9.37\AA but at 4.8\AA , the van der Waals' energy would amount to -15.2 kilo.cals. With such values for the van der Waals' energy,

the interchange energy of a large crystal would be a correspondingly larger numerical fraction of the coulombic-van der Waals' attraction.

With respect to copper, our calculations assume that only one valence electron is operative. The data accumulated add nothing in principle to the conclusions already stated with reference to sodium. The outstanding divergence is in the magnitude of the energy differences between minima. With an assumed 20 percent coulombic binding the energy difference between the square and five atom face center is as much as 40 kilo.cals. With an assumed 30 percent coulombic binding the energy difference is 25 kilo.cals. In either case the contrast with sodium is marked. The crystallization of small aggregates should, therefore, require a higher temperature with copper than with sodium, a quite reasonable conclusion. Fig. 5a shows, in addition, the activation energy of the formation of a linear aggregate of four atoms from a pair of molecules.

The influence exerted by the actual magnitude of the coulombic-interchange ratio is best exhibited by a consideration of the data for hydrogen with a 10 percent coulombic binding. In this case, the square configuration, having a potential energy of -117 kilo.cals., or 86 kilo.cals. greater than that for two hydrogen molecules would require an activation energy of at least 86 kilo.cals. for its formation, obviously impossible of attainment. With larger aggregates of atoms the situation is still more impossible. The binding energy of the six atoms in the body centered configuration is but one-third that of a single hydrogen molecule. The enormous expansion of the lattice caused by the high interchange energy ratio is also to be noted. The data show conclusively why hydrogen cannot form a metallic lattice.

¹⁹ R. Eisenschitz and F. London, *Zeits. f. Physik* **60**, 491 (1930).