

The Calculation of Interaction Potentials from Collision CrossSection Measurements

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lattice, and this number determines the most important term in the contribution to the van der Waals-London energy. For a given value of the valence angles, covalent, and van der Waals radii, the zigzag chain lattice is thus the more stable of the two. To explain why, nevertheless, the spiral chain lattice is found actually, one has to assume that the abnormal radius of 1.74 Å could not exist in the zigzag chain lattice. The decrease of the "van der Waals" radius from 2.0 Å to 1.74 Å would thus be caused by the metallic forces and the existence of these forces in the trigonal form of selenium would make the spiral chain lattice the more stable of the two. From this point of view the peculiar structure of trigonal selenium and tellurium as well as the abnormal value of the van der Waals radius are indications that a simple picture for the lattice forces is not sufficient to describe the situation in these lattices, and a contribution of forces of the metallic type must be taken into account.

¹ A. von Hippel, *J. Chem. Phys.* **16**, 372 (1948).

² F. de Boer, *Rec. Trav. Chim.* **62**, 151 (1943).

³ Linus Carl Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940), p. 176.

⁴ W. Beamer and C. R. Maxwell, *J. Chem. Phys.* **14**, 569 (1946).

⁵ Maurice L. Huggins, *J. Chem. Phys.* **23**, 37 (1945).

The Calculation of Interaction Potentials from Collision Cross-Section Measurements

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October 8, 1948

A METHOD for calculating interaction potentials from collision cross-section measurements has been presented by J. H. Simons, C. M. Fontana, E. E. Muschlitz, Jr., and S. R. Jackson,¹ and J. H. Simons, E. E. Muschlitz, Jr., and L. G. Unger.² Their method consists essentially of using classical theory and of integrating the collision cross section along the scattering path. They have developed the theory for an interaction potential of the form $V(r) = -K/r^n$, where r is the distance of separation of the centers of mass of the interacting particles. In the present article their method for calculating a correct value of K is shown to be unnecessary; a consistent approximate treatment presented here is entirely satisfactory for the determination of K .

The symbols which will be used are defined as follows:

l = length of the scattering path,

a = radius of the receiver,

b = perpendicular distance from the scattering molecule to the original line of approach of the beam particle,

x = a variable representing distance measured along the scattering path,

TABLE I. The correction factors f'_e and f_e .

m_1/m_2		$\frac{1}{2}$					1				
l/a	5	10	13.89	21.11	63.53		5	10	13.89	28.12	84.71
f'_e	1.000	0.988	0.988	0.994	0.997		1.039	1.003	0.997	0.995	0.997
f_e	0.624	0.697	0.764	0.836	0.939		0.456	0.637	0.712	0.837	0.940

r_0 = distance of closest approach of the interacting particles,

m_1 = mass of the beam particle,

m_2 = mass of the scattering particle,

W = kinetic energy of the beam particle,

$\mu = m_1 m_2 / (m_1 + m_2)$,

ϕ = scattering angle in apparatus coordinates,

K_e = potential constant K obtained from an exact treatment,

K_a = potential constant K obtained from the above authors' approximate treatment,

K_a' = potential constant K obtained by consistent use of small angle assumptions,

$C = \pi^{1/2} \Gamma(\frac{1}{2}n + \frac{1}{2}) / \Gamma(\frac{1}{2}n)$,

$f_e = K_e / K_a$ = the factor by which K_a (determined graphically from the experimental measurements by using the method of the above authors) is multiplied to obtain the correct value of $K = K_e$,

$f'_e = K_e / K_a'$ = the correction factor for obtaining K_e from K_a' which may be determined graphically in the same manner as K_a .

The values of $f_e = K_e / K_a$ reported by the above authors are valid only for a value of l/a of 13.89 which corresponds to the geometry of their particular apparatus.³ The factor f_e is obtained from the appropriate integrals in the manner shown below.

The classical treatment of the scattering problem for two point masses, involving conservation of angular momentum and total energy, yields the following general relation:

$$\int_0^l b^2 dx = \int_0^l r_0^2 dx + (K/W)(m_1/\mu) \int_0^l r_0^{2-n} dx. \quad (1)$$

The exact treatment for the case $n=4$ (the deviation of f_e from unity increases for a given m_1/m_2 and l/a as n increases, and $n=4$ is the largest n value investigated by the above authors) then gives, with $dx = -ad \cot \phi$ and S_n defined as $S_n = (K/W)(m_1/\mu r_0^n)$:

$$\begin{aligned} \int_0^l b^2 dx &= a(K_e m_1 / W \mu)^{1/2} \\ &\times \left[\int_0^{l/a} S_4^{-1/2} d \cot \phi + \int_0^{l/a} S_4^{1/2} d \cot \phi \right] \\ &= a(K_e m_1 / W \mu)^{1/2} (A + B). \end{aligned} \quad (2)$$

The integrals A and B are evaluated graphically.

The above authors' approximate treatment overlooks the r_0^{2-n} integral of Eq. (1) and assumes all collisions to result in small angle scattering. This gives for the case $n=4$

$$\int_0^l b^2 dx = \int_0^l r_0^2 dx = l^3 (\pi K_a / 3aW)^{1/2}. \quad (3)$$

Then by equating the values of the integral, $\int_0^l b^2 dx$, from Eqs. (2) and (3), the above authors' factor f_e is obtained in the form

$$f_e = K_e / K_a = [\pi/3] [(l/a)^3] [\mu/m_1] [(A+B)^{-2}]. \quad (4)$$

However, if the r_0^{2-n} integral is not omitted in an approximate treatment, a completely satisfactory value of K , determined graphically from the experimental data, may be obtained directly. The approximate treatment carried con-

sistently through with small angle assumptions gives

$$\int_0^l b^2 dx = [n/(n+2)]^{1+2/n} (K_a' C/aW)^{2/n} + [anm_1/2\mu] C^{(2/n)-1} (K_a' l/Wa)^{2/n}. \quad (5)$$

For $n=4$ the factor f_c' is then obtained in the form

$$f_c' = K_a/K_a' = [\pi/3][l/a]^3[\mu/m_1] + [8/3][l/a]^2 + [16/3\pi][m_1/\mu][l/a](A+B)^{-2}. \quad (6)$$

The dependence of f_c' and f_c on l/a was investigated for the cases $m_1/m_2 = \frac{1}{2}$ and $m_1/m_2 = 1$. In Table I the results are shown.

It is of interest to note that f_c' is within about one percent of unity for l/a greater than about 10. In general, as l/a increases above the values shown, the deviation of f_c' and f_c from unity will decrease.

For the case $n=2$ the above authors' values are used for $f(f \cong f_c)$ and f_c' is calculated from the relation

$$f_c' \cong f + (1/D)(\mu/m_1)(l/a), \quad (7)$$

where D corresponds to $A+B$ with one small angle approximation. The D values are obtained from the factor f since

$$f = [\pi/4D][(\mu/m_1)(l/a)]^2. \quad (8)$$

For $m_1/m_2 = \frac{1}{2}$, $l/a = 13.89$, $f = 0.882$, $f_c' = 1.003$, for $m_1/m_2 = 1$, $l/a = 13.89$, $f = 0.843$, $f_c' = 0.998$, and for $m_1/m_2 = \frac{3}{2}$, $l/a = 13.89$, $f = 0.806$, $f_c' = 0.991$. In a similar manner for $n=4$, $m_1/m_2 = \frac{1}{2}$, $l/a = 13.89$, $f_c = 0.658$, $f_c' = 0.994$.

For values of l/a greater than about 10 then the small angle assumption treatment will give values of K accurate to within present experimental error for $m_1/m_2 \leq \frac{3}{2}$ and $n \leq 4$. For sufficiently large values of l/a , accurate values of K may undoubtedly be attained by the small angle treatment for values of $m_1/m_2 > \frac{3}{2}$ and $n > 4$.

¹ Simons, Fontana, Muschlitz, Jr., and Jackson, J. Chem. Phys. 11, 307 (1943).

² Simons, Muschlitz, Jr., and Unger, J. Chem. Phys. 11, 322 (1943).

³ Simons, Francis, Fontana, and Jackson, Rev. Sci. Inst. 13, 419 (1942).

The Role of the Carbides of Iron in the Fischer-Tropsch Synthesis

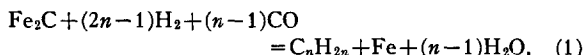
S. C. SCHUMAN

Hydrocarbon Research, Inc., Trenton, New Jersey
October 14, 1948

RECENTLY Kummer, Browning, and Emmett¹ have indicated from thermodynamic considerations that "the direct reduction by hydrogen of either form of Fe_2C cannot account for the synthesis of normal 1-monoolefins or of higher paraffins from carbon monoxide and hydrogen over the temperature and pressure range commonly employed in the Fischer-Tropsch synthesis." However, it should not be implied that this conclusion represents conclusive or even substantial evidence that thermodynamic data preclude the carbide being intermediate in the synthesis. For example, we have calculated the equilibrium constants for the reactions

TABLE I. Equilibrium constants for formation of hydrocarbons from Fe_2C , CO, and H_2 .

Reaction	n	Temp. °K	Katmos.
(1)	2	500	1.00
(1)	8	500	3×10^{22}
(1)	2	600	9.1×10^{-3}
(1)	8	600	6.6×10^4
(2)	2	500	8.3×10^7
(2)	8	500	6×10^{29}
(2)	2	600	2.6×10^3
(2)	8	600	6.2×10^8



and



by which hydrocarbons are produced with each hydrocarbon molecule containing one carbon atom derived from an Fe_2C intermediate, using the free energy data for Fe_2C given by Kummer, Browning, and Emmett, and the data for CO, H_2O , and hydrocarbons of Rossini.² Table I gives the equilibrium constants for both reactions at 227°C and 327°C for $n=2$ and $n=8$. These data indicate that the formation of hydrocarbons from Fe_2C is thermodynamically possible under the conditions employed in the Fischer-Tropsch synthesis. While no claim is being made here that reactions (1) and (2) represent the chemical process responsible for the formation of Fischer-Tropsch hydrocarbons, they are at least as compatible with the experimental synthesis data as the reactions considered by Kummer, Browning, and Emmett.

¹ Kummer, Browning, and Emmett, J. Chem. Phys. 16, 739 (1948).
² Rossini *et al.*, J. Research Nat. Bur. of Stand. 34, 143, 403 (1945); 36, 559 (1946).

A New Method of Determining X-Ray Intensities*

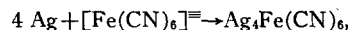
N. C. BAENZIGER

Institute for Atomic Research, Iowa State College, Ames, Iowa
October 12, 1948

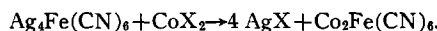
A NEW solution to the problem of determining integrated intensities of x-ray reflections recorded on film has been found which involves the radioactive toning of the photographic film. Because of the presently available radioactive isotopes suitable for this purpose, the best reagents are the mercuric chloride intensifier and the cobalt ferrocyanide toner. Only the latter has been examined.

The cobalt isotope, Co^{60} (half-life = 5.3 years, 1.1- and 1.3-Mev γ , and 0.31-Mev β), may be obtained in specific activities up to 100 millicuries per gram.

The toning process takes place in a bleaching,



and a toning step.



A bleach solution which has been found to be suitable is a 5 percent $\text{K}_3\text{Fe}(\text{CN})_6$ solution with approximately ten