A New Method of Determining XRay Intensities

N. C. Baenziger

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sistently through with small angle assumptions gives

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

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

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

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 $f(f \leqq f_c)$ 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 $n = 4$, $m_1/m_2 = \frac{3}{2}$, $l/a = 13.89$, $f_c = 0.658$, $f_c' = 0.994$.

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 $m_1/m_2 \leqq \frac{3}{2}$ and $n \leqq 4$. 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).

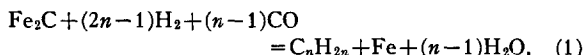## The Role of the Carbides of Iron in the Fischer-Tropsch Synthesis

S. C. SCHUMAN
Hydrocarbon Research, Inc., Trenton, New Jersey
October 14, 1948

RECENTLY Kummer, Browning, and Emmett[1] 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	K_{atmos}.
(1)	2	500	1.00
(1)	8	500	3×10^{23}
(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	6.2×10^6

$$Fe_2C + (2n-1)H_2 + (n-1)CO = C_nH_{2n} + Fe + (n-1)H_2O, \quad (1)$$

and

$$Fe_2C + 2nH_2 + (n-1)CO = C_nH_{2n+2} + Fe + (n-1)H_2O, \quad (2)$$

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).

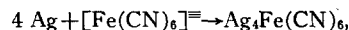## A New Method of Determining X-Ray Intensities*

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,

$$4 Ag + [Fe(CN)_6]^{\equiv} \rightarrow Ag_4Fe(CN)_6,$$

and a toning step.

$$Ag_4Fe(CN)_6 + CoX_2 \rightarrow 4 AgX + Co_2Fe(CN)_6.$$
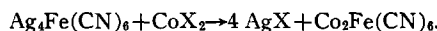
A bleach solution which has been found to be suitable is a 5 percent $K_3Fe(CN)_6$ solution with approximately ten

TABLE I. Counting rate *vs.* exposure relationship.*

Exposure	Optical density	Counting rate $(c/m \div 64)$	Linear response
Experiment 1 <space			
Background	0.10	10.00	
1		3.37	2.76
2		5.56	5.52
4		11.37	11.04
8		21.91	22.08
16		42.84	44.16
32	1.88	78.55	88.32
64	>3.0	132.44	176.6
128	>3.0	191.28	
Experiment 2 <			
Background	0.10	9.76	
1		6.10	6.72
2		13.36	13.44
4		26.99	26.88
8	1.4	53.58	53.76
16	2.38	96.34	107.5

* Each measurement is an average of two counts >10,000 counts
Counting rates have been corrected for background and dead time
Punch size =0.018 cm²; spot area =0.008 cm².

drops of concentrated NH_4OH added. The radioactive toning solution was prepared by dissolving the metallic pellets of cobalt, from the Oak Ridge National Laboratory, in nitric acid and converting to the bromide by evaporating to near dryness repeatedly with HBr. The final 100-ml solution of cobalt bromide contained 0.04 gram of cobalt and approximately 1.2 millicurie of activity.

The toning process was carried out as follows: the x-ray negative was soaked in water for 30 minutes, placed in the bleaching solution for a minimum of 30 minutes, rinsed in running water for one hour, placed in the cobalt toner for a minimum of 30 minutes, and the occluded activity on the film diluted by placing the films first in 100 ml of water for one hour, followed by another dilution in two liters of water for another hour; finally, the film was rinsed one hour in running water and dried. The toning experiments were carried out at 25° and in ordinary light, except that the bleached film was handled in subdued light before toning.

The samples were counted using a thin-window (3 mg/cm²) Victoreen Geiger-Müller counting tube and standard scaling circuit. Because of the gamma-rays, the spots were removed from the film with a punch. The punchings were mounted below the counting tube window on a lead disk. The error due to geometry was much less than the statistical counting error in all measurements.

A linear relation between optical density and exposure up to an optical density of two, reported for double-coated, non-screen x-ray film by Bell,[1] has been confirmed for Eastman non-screen film by counting the activity of eight standard spots which were printed on the film, using an eight-step sector (Table I). The deviation at the low optical density is due to the error resulting from the subtraction of a high background counting rate caused by silver deposited as chemical fog.

In order to test the method, Weissenberg diagrams of anthracene crystals were prepared, and the intensities of the $(00l)$ reflections were determined by the procedure outlined above. The results of these measurements are compared with those of Robertson[2] and Banerjee[3] in Table II.

TABLE II. Measurement of anthracene $(00l)$ intensities.*

Indices	Ionization (2)	Photometer (2)	Banerjee (3)	Observed
002	192	194	192	192
003	52	59	45	45
004	81	72	75	81
005	32	31	10	31

* One measurement of >13000 counts for each punching. Punching size =0.018 cm²; spot size =0.001 cm², counting time per punching 10–15 minutes.

The counting time and errors caused by the background can be reduced by using cobalt with higher specific activity (100 instead of 30 mc/g) and by reducing the ratio of background to spot counting rates. The latter can be accomplished using smaller punches, larger crystals, larger camera radius, or oscillating the film holder slightly during exposure.

* Work performed under Contract No. W-7405 eng-82.
[1] G. E. Bell, Brit. J. Radiol. 9, 578 (1936).
[2] J. M. Robertson, Proc. Roy. Soc. A140, 79 (1933).
[3] K. Banerjee, Ind. J. Phys. 4, 557 (1930).

Errata: On the Order-Disorder Transition in Solids. Parts I and II

Yosio Mutô
Maebashi Medical College, Maebashi, Japan

Pages	Line	Error	Correction
521 1	18	(15) and (14)	(15) into (14)
	25	$/\partial \ln G$	$/\partial \ln T$
	27	$G_{TT}' = -zw/2kT$	$G_{TT}' + G_T'' \rho_T = -zw/2kT$
521 r	26	$\lim \theta \to \rho \to 0$	$\lim \theta \to \rho - 0$
522 523		Z	z
525 1	28	in the gas phase	is the gas phase.