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THE GASEOUS EQUILIBRIA IN THE CARBON-SILICON BINARY SYSTEM

J. SMILTENS

Graphite and Carbon

JULY 1958

ELECTRONICS
RESEARCH
DIRECTORATE

conference on SILICON CARBIDE
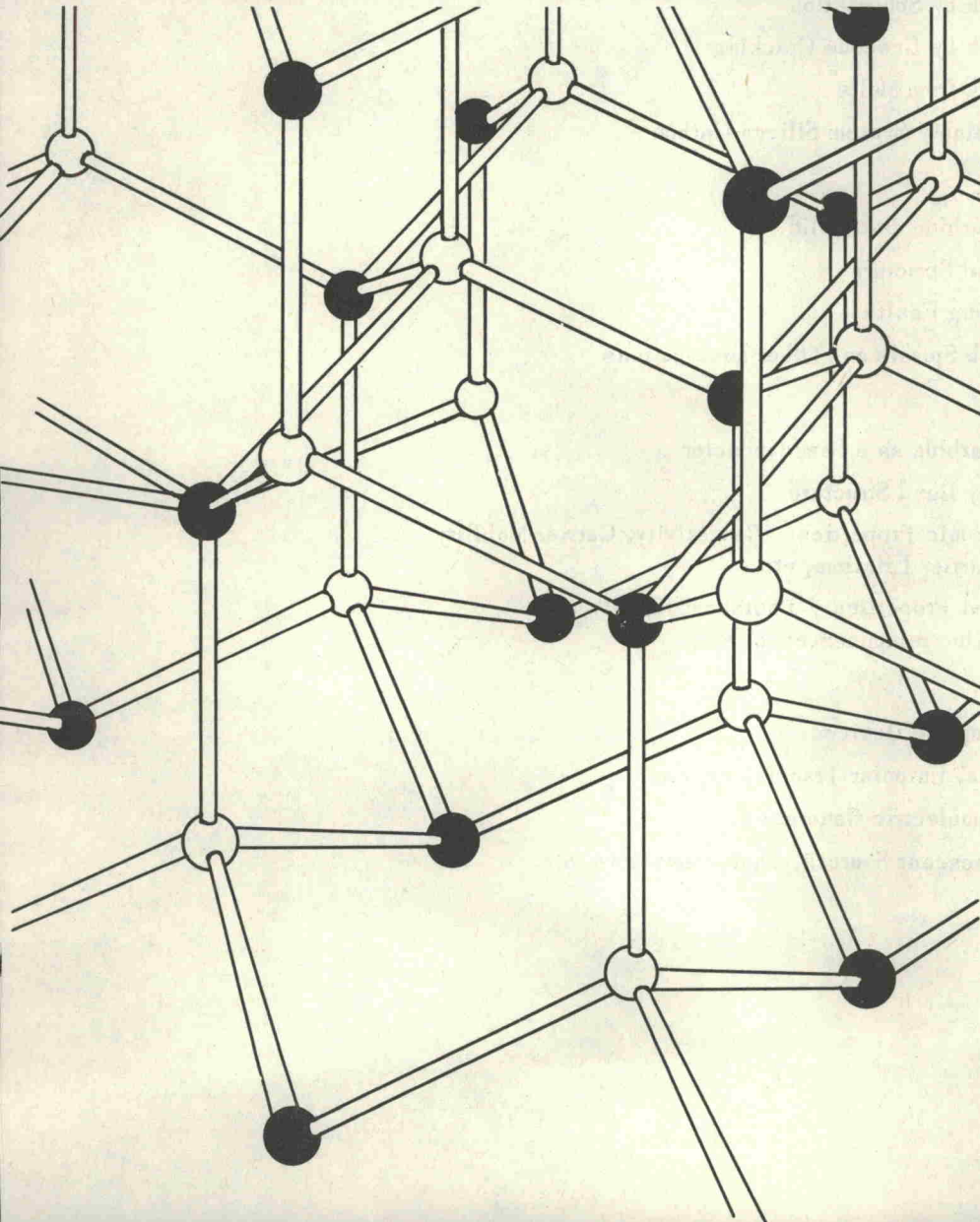
AIR FORCE
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CONFERENCE ON SILICON CARBIDE

AIR FORCE CAMBRIDGE RESEARCH CENTER
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TENTATIVE PROGRAM

I. Growing of Silicon Carbide Single Crystals

  A. Growth by Sublimation

  B. Growth by Gaseous Cracking

  C. Growth from Melts

  D. The Binary System Silicon-Carbon

II. Silicon Carbide as a Solid

  A. Crystal Structure

  B. Stacking Faults

  C. Growth Spirals and Other Dislocations

III. Silicon Carbide as a Semiconductor

  A. Energy Band Structure

  B. Electronic Properties: Resistivity, Carrier Mobility, Carrier Lifetime, etc.

  C. Optical Properties: Photoconductivity, Electroluminescence, etc.

IV. Silicon Carbide Devices

  A. Diodes, Unipolar Transistors, etc.

  B. Thermoelectric Generators

  C. Luminescent Sources, Photoconductors, etc.

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Date _____

To assist in Conference planning, it is requested that you furnish information in the following categories:

1. Name(s) of those planning to attend.

2. Topics of interest in addition to those listed in the tentative program.

3. Papers, if any, to be presented.

Title   Author, Organization, Address

Please return this participation notice to:
Mr. J. R. O'Connor, CRRCSS
Electronics Research Directorate
Air Force Cambridge Research Center
L. G. Hanscom Field
Bedford, Massachusetts

CONFERENCE ON SILICON CARBIDE

AIR FORCE CAMBRIDGE RESEARCH CENTER
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2 - 3 APRIL 1959

The Electronics Research Directorate of the Air Force Cambridge Research Center will sponsor a Conference on the new high temperature semiconductor, silicon carbide. This Conference will be held in Boston, Massachusetts, on 2 - 3 April 1959.

The purpose of this Conference is to further the exchange of information among scientists interested in research and development of silicon carbide. Emphasis will be placed upon theoretical and experimental aspects of this material as well as its various applications. It is hoped that the Conference will provide a focal point for all scientific work carried out on this relatively new semiconductor. To help achieve such a goal many leading workers on silicon carbide in this country and abroad have been invited.

As a group or individual actively interested in silicon carbide you are invited to attend or to send technical representatives to this Conference. It is requested that you complete and return the enclosed participation notice by 1 November 1958.

A tentative agenda illustrates the range of material to be covered. The chairman will welcome suggestions for additional topics and comments on the overall program; suggestions may be made on the participation notice.

Papers on one or more of the topics of interest are invited. These papers will be limited to approximately 30 minutes, including discussion period. An abstract of about 200 words should be submitted to the chairman before 1 January 1959. The Conference also encourages presentation of shorter "recent news" type papers of about ten minutes in length; abstracts of these should be submitted not later than 1 March 1959.

Although this announcement is being distributed as widely as possible, some workers in the field of silicon carbide may have been unintentionally overlooked. Please feel free to circulate this invitation to others having an interest, or potential interest, in this new semiconductor material.

THE GASEOUS EQUILIBRIA IN THE CARBON-SILICON BINARY SYSTEM

J. SMILTENS

JULY 1958

ABSTRACT

A method is presented for calculating the pressure and composition of the vapor phase in the carbon-silicon binary system. The following quantities are necessary: partition functions of the various molecular species present in the vapor, vapor pressures of graphite and liquid silicon, and the standard free-energy increment for the change

$$C(graphite) + Si(liquid) = SiC(solid) .$$

A study is made of the equilibrium: vapor and solution of carbon in liquid silicon.

ACKNOWLEDGMENTS

TABLE OF CONTENTS

THE GASEOUS EQUILIBRIA IN THE CARBON-SILICON BINARY SYSTEM

1. INTRODUCTION

This report is prepared with a primary purpose: To arouse the interest of colleagues working in molecular and mass spectroscopy, thermochemistry, and general physical chemistry in the carbon-silicon binary system. With the new semiconductor silicon carbide rapidly emerging, the practical importance of the carbon-silicon system has greatly increased. In order to perform numerical calculations, we still need unquestionable values for the vapor pressure of liquid silicon and the heat of formation of silicon carbide, together with, possibly, a large set of molecular constants for the species present in the binary vapor phase. It is hoped that with more workers interested in the problem, these data will gradually become available.

Since the calculations involve sums of terms with two running indices, some of the derivations (especially towards the end of the work) contain large, though not complicated, equations. With one exception, nevertheless, the final results are brief forms. It may appear that some elementary steps and repetitions in the derivations could have been omitted. However, in view of the preliminary nature of the report, one should not be too concerned about this, inasmuch as it is our purpose to familiarize the reader with the mathematical device used.

2. TENTATIVE SKETCH OF THE PHASE DIAGRAM

At the outset it is clear that pressure must be considered along with composition and temperature. Thus the complete phase diagram should be visualized as a prismatic body with composition, temperature, and pressure coordinate axes as its edges. We have studied an isothermal composition-pressure section of this body. Figure 1 shows the initial sketch of such a section, supposedly as projected. The sketch is based on the following considerations:
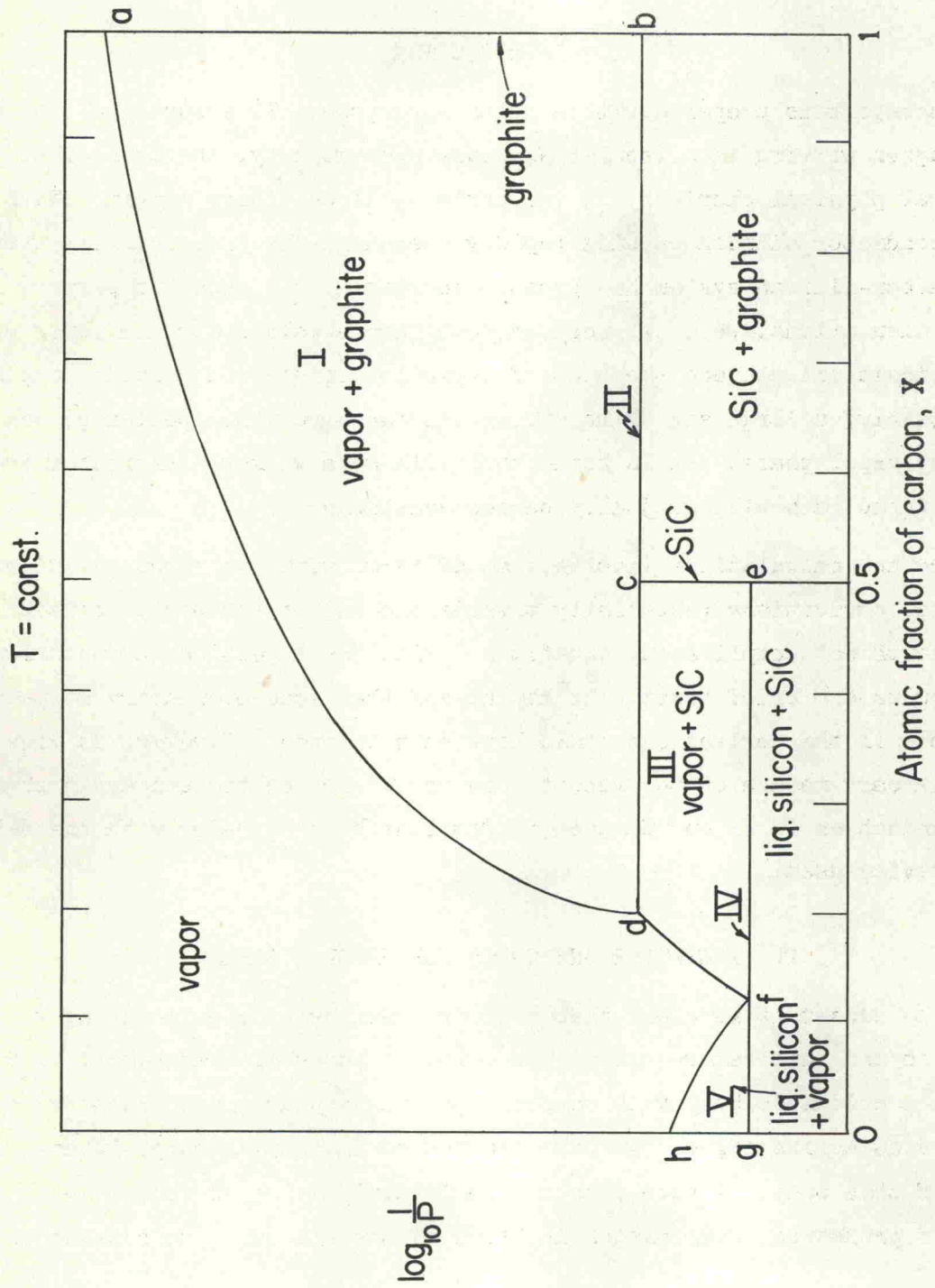
Fig. 1. A tentative isothermal cross section of the carbon-silicon phase diagram.

(1) The positions of points a and h are given by the vapor pressures of pure carbon and silicon, respectively.

(2) At very low pressure, i.e., corresponding to the top region of Fig. 1, there will be only binary vapor phase.

(3) As the pressure is increased, the first condensed phase which appears is graphite. Then the other two condensed phases, silicon carbide and liquid silicon appear.

(4) According to the studies of Ruff and Konschak,[1] there exist no other silicon carbides than SiC.

(5) It is assumed that silicon does not substitute for carbon in graphite. Silicon carbide is considered to be stoichiometric only.[2] At temperatures around the melting point of silicon, the solubility of carbon in liquid silicon is negligible. Thus we can draw three vertical lines: ab and extension; ce and extension; also hg and extension for the three condensed phases: graphite, silicon carbide, and liquid silicon. At higher temperatures, the solubility of carbon in liquid silicon becomes appreciable. The extension of the problem is treated in the final part of this work.

(6) In application for present purposes, Gibbs' phase rule is formulated as follows: the maximal number of coexistent phases equals the number of components plus two. There are two components: silicon and carbon. Hence the maximal number of phases is four. This corresponds to a quadruple point - a singular pair of temperature and pressure. On the line bcd, three coexistent phases have been indicated: graphite b, silicon carbide c, and vapor d. This combination of phases being short of the maximal number of phases by one phase, therefore, has one degree of freedom. Analytically, pressure at the bcd level is a function of temperature. Above the line bcd, we have a combination of only two phases: graphite ab and vapor ad. Here there are two degrees of freedom. Analytically, at a given temperature this combination of phases can exist at a range of pressures from a to b. Analogously, the line efg has been established.

1. O. Ruff and M. Konschak, Z. Elektrochem. 32, 515 (1926).
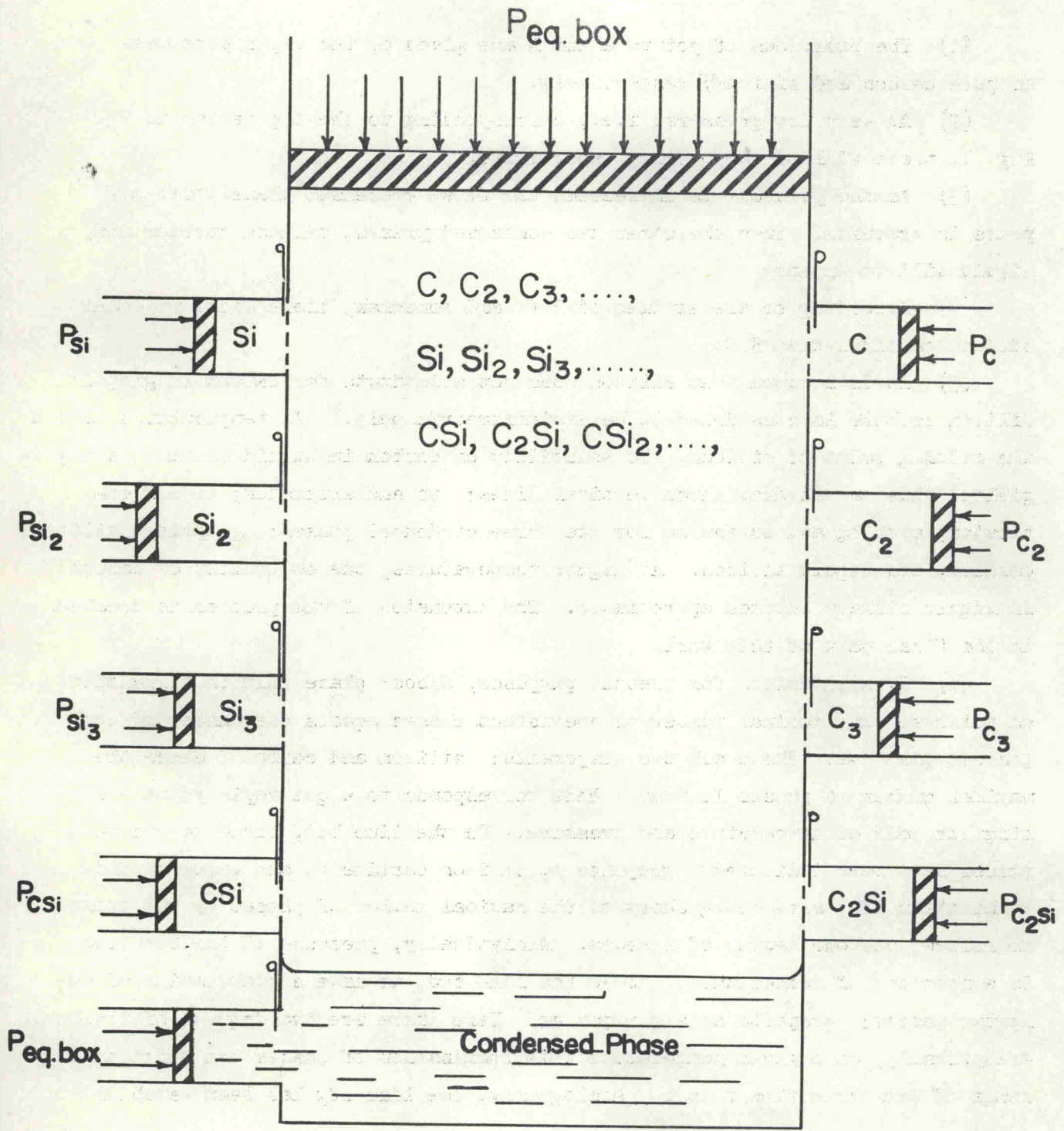2. J. A. Lely, Ber. deut. keram. Ges., 32, 229 (1955).

Fig. 2. Van't Hoff's equilibrium box.

An extensive use of the thermodynamical concept of van't Hoff's equilibrium box[3,4] has been made here (Fig. 2). It is an ideal vessel supplied with a set of hypothetical membranes, each of which is permeable to only one of the molecular species present in the binary vapor in the box. P_C , P_{Si} , P_{Si_2} , ... are the partial pressures of the respective molecular species, and $P_{eq\ box}$ is the total pressure of the mixture. By reversible operation of the pistons, certain species can be withdrawn or introduced into the box. From these mental experiments, the free-energy increments for changes involving molecular species within the box can be calculated.

In Fig. 1, the areas I, III, and V, and the lines II and IV can be thought to correspond to van't Hoff's equilibrium boxes. As already mentioned, pressure of the boxes I, III, and V is variable within a certain range. In the boxes II and IV, it is constant. After some preliminary arrangements that will be made in the next chapter, we will again return to the equilibrium boxes, deriving from them information regarding curves ad, df, and fh.

3. PRELIMINARIES

Let us denote a general molecule present in the binary vapor phase by $C_i Si_j$. Further, consider a volume V cm^3 of vapor phase, and let the number of $C_i Si_j$ molecules present in this volume be N_{ij}. At this point it should be mentioned that the quantity V will cancel out in the derivation, and therefore we do not have to be concerned about its magnitude. Our treatment is confined only to the low-density vapor cases when the forces of cohesion between the molecules can be neglected. Then, according to statistical

3. J. H. van't Hoff, Z. physik. Chem., 1, 481 (1887).
4. S. Glasstone, Textbook of Physical Chemistry (New York: D. Van Nostrand Co., 1948), cf. p. 818.

mechanics,[5,6,7]

$$\frac{N_{ij}}{N_{1,0}^i \, N_{0,1}^j} = \frac{Q_{ij} \, e^{\frac{w_{ij}}{kT}}}{Q_{1,0}^i \, Q_{0,1}^j} \quad , \qquad (1)$$

where

Q_{ij}, $Q_{1,0}$, and $Q_{0,1}$ are the partition functions of the $C_i Si_j$ molecule, monatomic carbon, and monatomic silicon, respectively;

w_{ij} is the work of formation, in ergs, of the molecule $C_i Si_j$.

It is the work which the world's work bank gains when i atoms of carbon, separated at infinitely large distances, at rest and at ground state of excitation, come together with j atoms of silicon, initially at the same conditions, and form a $C_i Si_j$ molecule, also at rest and at ground state. This work is usually called the dissociation energy $D_{0\ ij}^{0}$, and is given in electron volts. The relationship between w_{ij} and $D_{0\ ij}^{0}$ is:

$$w_{ij} = 1.60186 \cdot 10^{-12} \, D_{0\ ij}^{0},$$

$$k = \text{Boltzmann's constant} = 1.38026 \cdot 10^{-16},$$

$$T = \text{temperature in } {}^{\circ}K.$$

5. G. S. Rushbrooke, Introduction to Statistical Mechanics (Oxford: Clarendon Press, 1949), cf. p. 182, Eq. (37').

6. R. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge: University Press, 1949), cf. p. 165, Eqs. (506,7), (507,1).

7. R. H. Fowler, Statistical Mechanics (Cambridge: University Press, 1955), cf. p. 164, Eq. (479).

Equation (1) can be rewritten:

$$N_{ij} = \left(\frac{N_{1,0}}{Q_{1,0}}\right)^i \left(\frac{N_{0,1}}{Q_{0,1}}\right)^j Q_{ij} \, e^{\frac{w_{ij}}{kT}} . \tag{2}$$

We shall denote

$$\frac{N_{1,0}}{Q_{1,0}} \equiv \alpha \tag{3}$$

and

$$\frac{N_{0,1}}{Q_{0,1}} \equiv \lambda . \tag{4}$$

Then (2) becomes

$$N_{ij} = \alpha^i \lambda^j Q_{ij} \, e^{\frac{w_{ij}}{kT}} . \tag{5}$$

Also, either from the definitive equations (3) and (4), or from (5), considering that both $w_{1,0}$ and $w_{0,1}$ are zero, we obtain:

$$N_{1,0} = \alpha \, Q_{1,0} , \tag{6}$$

and

$$N_{0,1} = \lambda \, Q_{0,1} . \tag{7}$$

The partition function Q_{ij} can be rigorously decomposed into two factors: the translational partition function $Q_{trans\ ij}$ and the internal partition function $Q_{int\ ij}$.

$$Q_{ij} = Q_{trans\ ij} \, Q_{int\ ij} . \tag{8}$$

The translational partition function is

$$Q_{\text{trans } ij} = \left(\frac{2\pi M_{ij} kT}{h^2 N_{Av}} \right)^{\frac{3}{2}} \cdot V , \tag{9}$$

where

M_{ij} = the molecular weight of the $C_i Si_j$,

h = Planck's constant = $6.6238 \cdot 10^{-27}$,

N_{Av} = Avogadro's number = $6.0254 \cdot 10^{23}$.

The internal partition function $Q_{\text{int } ij}$ has to be calculated from the energy levels of the $C_i Si_j$ molecule, due to internuclear vibration, rotation, and electronic excitation of the molecule.

When $Q_{\text{trans } ij}$ in (8) is replaced by the right-hand side of (9), and the new expression for Q_{ij} thus obtained is substituted into (5), we get

$$N_{ij} = \left(\frac{2\pi k}{h^2 N_{Av}} \right)^{\frac{3}{2}} T^{\frac{3}{2}} V \, \alpha^i \lambda^j \, M_{ij}^{\frac{3}{2}} \, Q_{\text{int } ij} \, e^{\frac{w_{ij}}{kT}} . \tag{10}$$

The product of the last three factors on the right-hand side of (10) is a characteristic of the $C_i Si_j$ molecule alone. Let us denote it by k_{ij}:

$$k_{ij} \equiv M_{ij}^{\frac{3}{2}} \, Q_{\text{int } ij} \, e^{\frac{w_{ij}}{kT}} . \tag{11}$$

Then, upon calculating the numerical value of the aggregate of universal constants, (10) becomes

$$N_{ij} = 1.8789 \cdot 10^{20} \, T^{\frac{3}{2}} V \, \alpha^i \lambda^j \, k_{ij} . \tag{12}$$

Each C_iSi_j molecule contains i atoms of carbon. Therefore, the total number of carbon atoms, free and combined, in the volume V, is

$$\sum_{ij} i\, N_{ij}\, ,$$ (13)

and the total number of silicon atoms is

$$\sum_{ij} j\, N_{ij}\, .$$ (14)

The ratio of carbon to silicon atoms in the vapor then is

$$x = \frac{\sum_{ij} i\, N_{ij}}{\sum_{ij} j\, N_{ij}} = \frac{\sum_{ij} i\, \alpha^i \lambda^j k_{ij}}{\sum_{ij} j\, \alpha^i \lambda^j k_{ij}}\, .$$ (15)

To indicate composition in Fig 1, we used the atomic fraction of carbon X, which is the conventional usage. However, for our present purposes, x as defined by (15), and which also corresponds to x in SiC_x, will be a more convenient variable. For pure carbon, $x = \infty$, and the line ab in Fig. 1 is removed to infinity. However, it will be shown that the curve ad when plotted as $\log_{10} \frac{1}{P}$ versus x reaches infinity at zero slope, which is a simplifying feature. Also, the new variable x is convenient in the treatment of the solution of carbon in liquid silicon.

The total number of all kinds of particles in the volume V is

$$\sum_{ij} N_{ij} = 1.8789 \cdot 10^{20}\, T^{\frac{3}{2}}\, V \sum_{ij} \alpha^i \lambda^j k_{ij}.$$ (16)

At any instant, the pressure, volume, and temperature of the vapor will be connected by the gas law:

$$PV = \frac{\sum_{ij} N_{ij}}{N_{Av}} \cdot RT\, ,$$ (17)

where R = 82.079, when P is measured in atmospheres.

In (17), when $\sum_{ij} N_{ij}$ is substituted by the right-hand side of (16), V on both sides of the equation cancels out, and upon multiplying and dividing of the constants, we get

$$P = 2.5595 \cdot 10^{-2} \, T^{\frac{5}{2}} \sum_{ij} \alpha^i \lambda^j k_{ij} . \qquad (18)$$

The product $2.5595 \cdot 10^{-2} \, T^{\frac{5}{2}}$, which is a temperature-dependent constant, we shall denote by a.

Then

$$P = a \sum_{ij} \alpha^i \lambda^j k_{ij} , \qquad (19)$$

and the partial pressure of the species $C_i Si_j$ is

$$P_{ij} = a \, \alpha^i \lambda^j k_{ij} . \qquad (20)$$

In the case of pure carbon vapor (16) becomes

$$P_{carbon} = a \sum_i \alpha_o^i k_{i0} , \qquad (21)$$

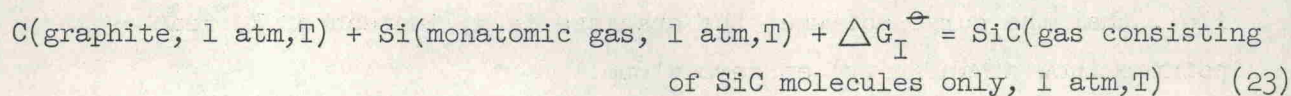the subscript "o" indicating absence of silicon; and for pure silicon vapor

$$P_{silicon} = a \sum_j \lambda_o^j k_{0j} , \qquad (22)$$

the subscript "o" indicating absence of carbon.

The quantities α_o and λ_o formally are temperature-dependent constants; we shall need them later. They can be calculated from the experimentally measured vapor pressures of carbon and silicon by means of (21) and (22), respectively, provided that a sufficient number of k_{i0} and k_{0j} values is available.

4. THE CONDITIONS DERIVED FROM THE FIVE EQUILIBRIUM BOXES

The First Equilibrium Box. Curve ad. - In the first equilibrium box, the condensed phase is graphite, and the pressure of this box can be any fixed value in the range ab. By means of this box, we can find the Gibbs' free-energy increment $\triangle G_I^{\ominus}$ for the change

$$C(\text{graphite, 1 atm,T}) + Si(\text{monatomic gas, 1 atm,T}) + \triangle G_I^{\ominus} = SiC(\text{gas consisting}$$
$$\text{of SiC molecules only, 1 atm,T}) \quad (23)$$

as

$$\triangle G_I^{\ominus} = RT \ln \frac{P_{0,1 \text{ eq b I}}}{P_{1,1 \text{ eq b I}}} . \quad (24)$$

In order to calculate $\triangle G_I^{\ominus}$ in calories, R = 1.98773 must be used.

According to thermodynamics, the value $\triangle G_I^{\ominus}$ is independent of the pressure, which has been chosen in the range ab, of the box. Therefore, if in (24) $P_{0,1 \text{ eq b I}}$ and $P_{1,1 \text{ eq b I}}$ are substituted by $a\lambda_{\text{eq b I}} k_{0,1}$ and $a\alpha_{\text{eq b I}} \cdot \lambda_{\text{eq b I}} k_{1,1}$, respectively, we get

$$\alpha_{\text{eq b I}} = \frac{k_{0,1}}{k_{1,1}} e^{-\frac{\triangle G_I^{\ominus}}{RT}}, \quad (25)$$

which is a constant for given temperature. The condition (25) subsists along the whole extent of the curve ad; consequently, also at the terminal point a. Therefore

$$\alpha_{\text{eq b I}} = \text{const} = \alpha_o , \quad (26)$$

which expresses in our way the fact that the pressure of carbon vapor in this box, on account of graphite being present as a condensed phase, is constant.

By means of (26), (19), and (15), the curve ad can be calculated. We need only find the λ value for the terminal point d; this will be possible from the second equilibrium box.

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Before leaving the first equilibrium box, we shall furnish the proof
that

$$\lim_{x \to \infty} \left. \frac{d \log_{10} \frac{1}{P}}{dx} \right|_{\alpha = \alpha_0} = \left. \frac{d \log_{10} \frac{1}{P}}{dx} \right|_{\substack{\alpha = \alpha_0 \\ \lambda = 0}} = 0; \tag{27}$$

i.e., that the curve ad, when the abscissa is x, instead of X, reaches the
point a (now at infinity) at zero slope.

We shall proceed as follows:

$$\left. \frac{d \log_{10} \frac{1}{P}}{dx} \right|_{\alpha = \alpha_0} = \left. \frac{\dfrac{d \log_{10} \frac{1}{P}}{d\lambda}}{\dfrac{dx}{d\lambda}} \right|_{\alpha = \alpha_0} \tag{28}$$

$$\left. \frac{d \log_{10} \frac{1}{P}}{d\lambda} \right|_{\alpha = \alpha_0} = \left. - 0.4343 \frac{1}{P} \frac{dP}{d\lambda} \right|_{\alpha = \alpha_0}. \tag{29}$$

From (19)

$$\left. \frac{dP}{d\lambda} \right|_{\alpha = \alpha_0} = a \sum_{ij} j \, \alpha_0^i \, \lambda^{j-1} \, k_{ij}. \tag{30}$$

At $\lambda = 0$ in (30), all terms which contain λ vanish, and we get

$$\left. \frac{dP}{d\lambda} \right|_{\substack{\alpha = \alpha_0 \\ \lambda = 0}} = a \, (k_{0,1} + \alpha_0 \, k_{1,1}). \tag{31}$$

Then (29) becomes

$$\left. \frac{d \log_{10} \frac{1}{P}}{d\lambda} \right|_{\substack{\alpha=\alpha_o \\ \lambda=0}} = - 0.4343 \; a \; (k_{0,1} + \alpha_o k_{1,1}) \frac{1}{P}_{carbon} . \tag{32}$$

From (15)

$$\left. \frac{dx}{d\lambda} \right|_{\alpha=\alpha_o} = \frac{(\sum_{ij} ij \; \alpha_o^i \lambda^{j-1} k_{ij})(\sum_{ij} j \; \alpha_o^i \lambda^j k_{ij}) - (\sum_{ij} j^2 \alpha_o^i \lambda^{j-1} k_{ij})(\sum_{ij} i \; \alpha_o^i \lambda^j k_{ij})}{\left(\sum_{ij} j \; \alpha_o^i \lambda^j k_{ij}\right)^2}, \tag{33}$$

which at $\lambda = 0$ becomes

$$\left. \frac{dx}{d\lambda} \right|_{\substack{\alpha=\alpha_o \\ \lambda=0}} = \frac{(k_{0,1} + \alpha_o k_{1,1}) \cdot 0 - (k_{0,1} + \alpha_o k_{1,1}) \sum_{i} i \; \alpha_o^i k_{i0}}{0} = -\infty. \tag{34}$$

Therefore from (28), (29), (31), and (34), indeed,

$$\left. \frac{d \log_{10} \frac{1}{P}}{dx} \right|_{\substack{\alpha=\alpha_o \\ \lambda=0}} = 0 . \tag{35}$$

We can arrive at the same result by a simpler method: As $\lambda \longrightarrow 0$ in the P and x functions, all terms which contain λ with exponents > 1 vanish as small of higher order. Thus (19) becomes

$$P = a \sum_i \alpha^i (k_{i0} + \lambda k_{i1}) , \qquad (36)$$

and (15) by a still more drastic simplification becomes

$$x = \frac{\sum_i i \, \alpha^i k_{i0}}{\lambda \sum_i \alpha^i k_{i1}} , \qquad (37)$$

which at $\alpha = \alpha_o$ gives

$$\left. \frac{dP}{d\lambda} \right|_{\alpha = \alpha_o} = a \sum_i \alpha_o^i k_{i1} \qquad (38)$$

and

$$\left. \frac{dx}{d\lambda} \right|_{\alpha = \alpha_o} = - \frac{\sum_i i \, \alpha_o^i k_{i0}}{\sum_i \alpha_o^i k_{i1}} \frac{1}{\lambda^2} . \qquad (39)$$

Therefore,

$$\left. \frac{dP}{dx} \right|_{\alpha = \alpha_o} = - \frac{a (\sum_i \alpha_o^i k_{i1})^2}{\sum_i i \, \alpha_o^i k_{i0}} \lambda^2 , \qquad (40)$$

which at $\lambda = 0$ becomes zero. This result when substituted in (29), in which λ previously has been formally replaced by x, gives (35).

The Second Equilibrium Box. Point d. - The condensed phases in this box are graphite and silicon carbide. The pressure is a single value, P_d. By means of this box, we can find the free-energy increment $\Delta G_{II}^{\ominus}$ for the change

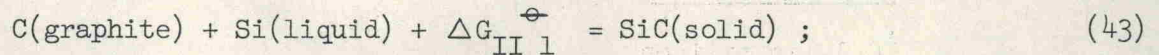$$C(\text{graphite}) + Si(\text{monatomic gas}) + \Delta G_{II}^{\ominus} = SiC(\text{solid}). \qquad (41)$$
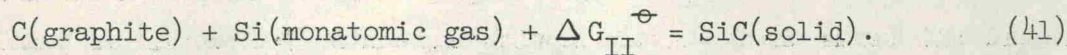
We have omitted the "1 atm, T" in the parentheses at the chemical symbols, since it is understood that in the future the superscript $\ominus$ at the free-energy increment (the standard free-energy increment) will be a sufficient indication of this.
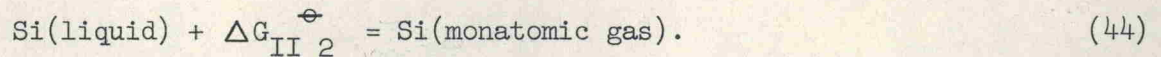
It can be shown that

$$\Delta G_{II}^{\ominus} = RT \ln P_{0,1 \, eq \, b \, II} . \qquad (42)$$

On the other hand, $\Delta G_{II}^{\ominus}$ can also be found from the two changes: first,

$$C(\text{graphite}) + Si(\text{liquid}) + \Delta G_{II \, 1}^{\ominus} = SiC(\text{solid}) ; \qquad (43)$$

and second,

$$Si(\text{liquid}) + \Delta G_{II \, 2}^{\ominus} = Si(\text{monatomic gas}). \qquad (44)$$

$\Delta G_{II \, 1}^{\ominus}$ is the standard free-energy increment for a change with all phases in condensed state. This increment can be calculated by conventional methods from the heat of formation of silicon carbide, the heat of fusion of silicon, and the heat capacities of graphite, silicon (solid and liquid), and silicon carbide. Since this quantity is important throughout the whole work, we shall change the notation

$$\Delta G_{II \, 1}^{\ominus} \equiv \Delta G_{cond}^{\ominus} . \qquad (45)$$

The standard free-energy increment for the second change (44), can be shown as

$$\Delta G_{II \, 2}^{\ominus} = - RT \ln P_{0,1 \, liq \, silicon} , \qquad (46)$$

where $P_{0,1 \, liq \, silicon}$ is the partial pressure of monatomic silicon above pure liquid silicon at the temperature under consideration.

Eq. (44) can be transposed to

$$Si(\text{liquid}) = Si(\text{monatomic gas}) - \Delta G_{II \, 2}^{\ominus} . \qquad (47)$$

When (47) is substituted for Si(liquid) in (43), we shall get (41), and consequently $\Delta G_{II}^{\ominus}$ must be

$$\Delta G_{II}^{\ominus} = \Delta G_{cond}^{\ominus} - \Delta G_{II \, 2}^{\ominus} . \qquad (48)$$

When in (48), $\Delta G_{II}^{\ominus}$ is substituted by (42) and $\Delta G_{II\,2}^{\ominus}$ by (46), we get

$$RT \ln P_{O,1 \text{ eq b II}} = \Delta G_{\text{cond}}^{\ominus} + RT \ln P_{O,1 \text{ liq silicon}} \qquad (49)$$

or,

$$\frac{P_{O,1 \text{ eq b II}}}{P_{O,1 \text{ liq silicon}}} = e^{\frac{\Delta G_{\text{cond}}^{\ominus}}{RT}}, \qquad (50)$$

or,

$$\lambda_{\text{eq b II}} = \lambda_o \, e^{\frac{\Delta G_{\text{cond}}^{\ominus}}{RT}}. \qquad (51)$$

Therefore, the coordinates of the point d are

$$\lambda_d = \lambda_o \, e^{\frac{\Delta G_{\text{cond}}^{\ominus}}{RT}}, \qquad (52)$$

and

$$\alpha_d = \alpha_o. \qquad (53)$$

The Third Equilibrium Box. Curve df. - By analogous reasoning, we can find that the equation of the curve df is

$$\alpha\lambda = \alpha_o \lambda_o \, e^{\frac{\Delta G_{\text{cond}}^{\ominus}}{RT}}. \qquad (54)$$

The Fourth Equilibrium Box. Point f. - Here

$$\alpha_f = \alpha_o \, e^{\frac{\Delta G_{\text{cond}}^{\ominus}}{RT}} \qquad (55)$$

and

$$\lambda_f = \lambda_o, \qquad (56)$$

the product $\alpha_f \lambda_f$ satisfying the condition (54).

The Fifth Equilibrium Box. Curve fh. - The equation for the curve fh is

$$\lambda = \lambda_o \ . \tag{57}$$

Let us calculate

$$\frac{d \log_{10} \frac{1}{P}}{dx} \Bigg|_{\substack{\lambda = \lambda_o \\ \alpha = 0}}, \tag{58}$$

i.e., the slope of curve fh at point h. Again, for the sake of exercise, we shall use both the general and the simplified methods.

The general method: As in (28) and (29) ,

$$\frac{d \log_{10} \frac{1}{P}}{dx} \Bigg|_{\lambda = \lambda_o} = \frac{- 0.4343 \cdot \frac{1}{P} \frac{dP}{d\alpha} \Big|_{\lambda = \lambda_o}}{\frac{dx}{d\alpha} \Big|_{\lambda = \lambda_o}} \ . \tag{59}$$

From (19)

$$\frac{dP}{d\alpha} \Bigg|_{\lambda = \lambda_o} = a \sum_{ij} c_i \, \alpha^{i-1} \lambda_o^j k_{ij} \tag{60}$$

and

$$\frac{dP}{d\alpha} \Bigg|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = a \sum_{j} \lambda_o^j k_{1j} \ . \tag{61}$$

From (15)

$$\frac{dx}{d\alpha} \Bigg|_{\lambda = \lambda_o} = \frac{\left(\sum_{ij} i^2 \alpha^{i-1} \lambda_o k_{ij} \right) \left(\sum_{ij} j\alpha^i \lambda_o^j k_{ij} \right) - \left(\sum_{ij} ij\alpha^{i-1} \lambda_o^j k_{ij} \right) \left(\sum_{ij} i\alpha^i \lambda_o^j k_{ij} \right)}{\left(\sum_{ij} j \, \alpha^i \lambda_o^j k_{ij} \right)^2} \tag{62}$$

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and

$$\frac{dx}{d\alpha}\Bigg|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = \frac{\left(\sum_j \lambda_o^j k_{1j}\right)\left(\sum_j j \lambda_o^j k_{0j}\right) - \left(\sum_j j \lambda_o^j k_{1j}\right) \cdot 0}{\left(\sum_j j \lambda_o^j k_{0j}\right)^2}$$

$$= \frac{\sum_j \lambda_o^j k_{1j}}{\sum_j j \lambda_o^j k_{0j}} \ . \tag{63}$$

Then, from (59)

$$\frac{d \log_{10} \frac{1}{P}}{dx}\Bigg|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = \frac{-0.4343 \frac{1}{P_{\text{liq silicon}}} a \sum_j \lambda_o^j k_{1j}}{\dfrac{\sum_j \lambda_o^j k_{1j}}{\sum_j j \lambda_o^j k_{0j}}}$$

$$= -0.4343 \frac{a \sum_j j \lambda_o^j k_{0j}}{P_{\text{liq silicon}}}$$

$$= -0.4343 \frac{\sum_j j \lambda_o^j k_{0j}}{\sum_j \lambda_o^j k_{0j}} \ , \tag{64}$$

which is a negative quantity and, in general, < -0.4343 .

The simplified method: As $\alpha \to 0$ in the P and x functions, all terms which contain α with exponents > 1 vanish as small of higher order. Thus (19) becomes

$$P = a \sum_j \lambda_o^j (k_{01} + \alpha k_{1j}) , \qquad (65)$$

and (15), by a still more drastic approximation becomes

$$x = \frac{\alpha \sum_j \lambda_o^j k_{1j}}{\sum_j j \lambda_o^j k_{0j}} . \qquad (66)$$

Therefore,

$$\left. \frac{dP}{d\alpha} \right|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = \left. \frac{dP}{d\alpha} \right|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = a \sum_j \lambda_o^j k_{1j} , \qquad (67)$$

and

$$\left. \frac{dx}{d\alpha} \right|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = \left. \frac{dx}{d\alpha} \right|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = \frac{\sum_j \lambda_o^j k_{1j}}{\sum_j j \lambda_o k_{0j}} . \qquad (68)$$

Then

$$\left. \frac{dP}{dx} \right|_{\substack{\lambda = \lambda_o \\ \alpha = 0}} = a \sum_j j \lambda_o^j k_{0j} . \qquad (69)$$

When the right-hand side of (69) is substituted for dP/dx in (29), in which previously λ has been formally replaced by x, $\alpha = \alpha_o$ replaced by $\alpha = 0$, and 1/P by $1/P_{\text{liq silicon}}$, we again obtain (64).

What relationships can be extracted from the present mathematical device when the solubility of carbon in liquid silicon cannot be neglected?

Let us consider the change in which x is a positive fractional number, e.g., 0.2 :

$$(1-x) \text{ C(monatomic gas)} + \text{SiC}_x\text{(liquid)} + \triangle G_V{}^{\ominus}{}_1 = \text{SiC(gas consisting of SiC molecules only)} \quad (70)$$
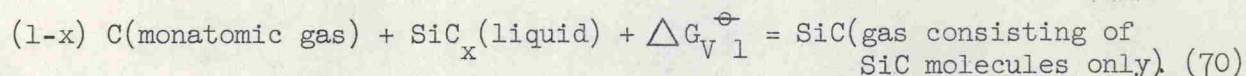
Again, the superscript ⊖ at the Gibbs' free-energy increment stands for a change when all reactants and products are at 1 atm and at the same temperature T; we therefore, as previously agreed, do not indicate these conditions in the parentheses at the symbol of the substance concerned. The formula SiC_x is used only as a shorthand symbol to denote a solution of carbon in silicon, in which on every atom of silicon there are x (a fraction) atoms of carbon. It implies no structural notions.

It can be shown that

$$\triangle G_V{}^{\ominus}{}_1 = RT \ln \frac{P_{1,0}{}^{1-x}}{P_{1,1}} \,, \quad (71)$$

where $P_{1,0}$ and $P_{1,1}$ are the partial pressures of the species C and SiC above the solution SiC_x.

Let us consider another change:

$$x \text{ C(monatomic gas)} + \text{Si(liquid)} + \triangle G_V{}^{\ominus}{}_2 = \text{SiC}_x\text{(liquid)}. \quad (72)$$
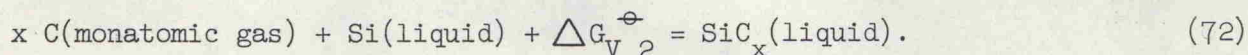
It can be shown that

$$\triangle G_V{}^{\ominus}{}_2 = RT \int_0^X \ln P_{1,0} \, dx \,. \quad (73)$$

By adding (70) and (72), we find that the standard free-energy increment for the change

$$\text{C(monatomic gas)} + \text{Si(liquid)} + \triangle G_V{}^{\ominus}{}_3 = \text{SiC(gas consisting of SiC molecules only)} \quad (74)$$
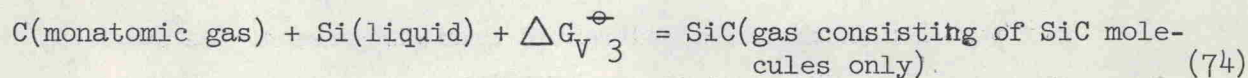
must be

$$\triangle G_V{}^{\ominus}{}_3 = \triangle G_V{}^{\ominus}{}_1 + \triangle G_V{}^{\ominus}{}_2 \,. \quad (75)$$

Upon substituting in (75) for $\Delta G_{V\,1}^{\ominus}$ the right-hand side of (71), and for $\Delta G_{V\,2}^{\ominus}$ the right-hand side of (73), we obtain

$$\Delta G_{V\,3}^{\ominus} = RT \ln \frac{P_{1,0}^{\,1-x}}{P_{1,1}} + RT \int_0^x \ln P_{1,0} \, dx \, . \tag{76}$$

Now, as can be seen from (74), the $\Delta G_{V\,3}^{\ominus}$ is independent of x. When $P_{1,0}$ is replaced by $a\alpha\, k_{1,0}$ and $P_{1,1}$ by $a\alpha\, \lambda\, k_{1,1}$, (76) can be simplified:

$$x \ln \alpha - \int_0^x \ln \alpha \, dx + \ln \lambda = \frac{\Delta G_{V\,3}^{\ominus}}{RT} \ln \frac{k_{1,1}}{k_{1,0}} \, . \tag{77}$$

The limit for (77) as $x \to 0$ is:

$$\lim_{x \to 0} (x \ln \alpha) + \ln \lambda_o = \frac{\Delta G_{V\,3}^{\ominus}}{RT} \ln \frac{k_{1,1}}{k_{1,0}} \, . \tag{78}$$

Therefore (77) can be rewritten as

$$x \ln \alpha - \int_0^x \ln \alpha \, dx + \ln \lambda = \lim_{x \to 0} (x \ln \alpha) + \ln \lambda_o \tag{79}$$

or,

$$x \ln \alpha - \lim_{x \to 0} (x \ln \alpha) - \int_0^x \ln \alpha \, dx = -\ln \lambda + \ln \lambda_o \tag{80}$$

or,

$$\int_0^x x \, d\ln \alpha = - \int_0^x d\ln \lambda \, . \tag{81}$$

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When the integral signs of (81) are dropped, we obtain

$$\frac{d \ln \lambda}{d \ln \alpha} = - x_{soln} , \tag{82}$$

which can be recognized as the Gibbs-Duhem equation.[8] We have attached the subscript "soln" at x in order to emphasize that x is the atomic ratio of carbon to silicon in the solution, whereas α and λ are the effective concentrations of monatomic carbon and silicon in the gas phase equilibrating with the solution.

We shall rewrite (82) as

$$\frac{d\lambda}{d\alpha} = - \frac{\lambda}{\alpha} x_{soln} . \tag{83}$$

By means of (83), we can approach the problem of the slope $d \log_{10}(1/P)/dx$.

By differentiation,

$$\frac{d \log_{10} \frac{1}{P}}{dx} = - 0.4343 \frac{1}{P} \frac{dP}{dx} . \tag{84}$$

As the case is general, all we can write for dP/dx is

$$\frac{dP}{dx} = \frac{\left(\frac{\partial P}{\partial \alpha}\right)_\lambda + \left(\frac{\partial P}{\partial \lambda}\right)_\alpha \frac{d\lambda}{d\alpha}}{\left(\frac{\partial x}{\partial \alpha}\right)_\lambda + \left(\frac{\partial x}{\partial \lambda}\right)_\alpha \frac{d\lambda}{d\alpha}} . \tag{85}$$

From (19)

$$\left(\frac{\partial P}{\partial \alpha}\right)_\lambda = a \sum_{ij} i \, \alpha^{i-1} \lambda^j k_{ij} \tag{86}$$

and

$$\left(\frac{\partial P}{\partial \lambda}\right)_\alpha = a \sum_{ij} j \, \alpha^i \lambda^{j-1} k_{ij} . \tag{87}$$

---

8. G. N. Lewis and M. Randall, Thermodynamics and the Free Energy of Chemical Substances (New York: McGraw-Hill Book Co., 1923), cf. pp. 207-210.

When $d\lambda/d\alpha$ in the numerator of (85) is substituted by the right-hand side of (83), we obtain

$$\frac{a}{\alpha}\left(\sum_{ij} i\,\alpha^i\,\lambda^j\,k_{ij} - x_{soln}\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}\right).\tag{88}$$

When in (88) we carry $\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}$ before the parentheses, we get

$$\frac{a}{c\alpha}(x_{vap} - x_{soln})\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}.\tag{89}$$

For the first term in the denominator of (85), we get from (15)

$$\left(\frac{\partial x}{\partial \alpha}\right)_\lambda = \frac{\left(\sum_{ij} i^2\alpha^{i-1}\lambda^j\,k_{ij}\right)\sum_{ij} j\,\alpha^i\lambda^j\,k_{ij} - \left(\sum_{ij} ij\,\alpha^{i-1}\lambda^j k_{ij}\right)\sum_{ij} i\,\alpha^i\,\lambda^j k_{ij}}{\left(\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}\right)^2},\tag{90}$$

which, when divided in the numerator and denominator by $\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}$ simplifies to

$$\left(\frac{\partial x}{\partial \alpha}\right)_\lambda = \frac{\sum_{ij} i^2\,\alpha^{i-1}\,\lambda^j\,k_{ij} - x_{vap}\sum_{ij} ij\,\alpha^{i-1}\lambda^j\,k_{ij}}{\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}}.\tag{91}$$

For the $(\partial x/\partial \lambda)_\alpha$ in the second term of the denominator of (85), we get

$$\left(\frac{\partial x}{\partial \lambda}\right)_\alpha = \frac{\left(\sum_{ij} ij\,\alpha^i\,\lambda^{j-1}\,k_{ij}\right)\sum_{ij} j\,\alpha^i\,\lambda^j k_{ij} - \left(\sum_{ij} j^2\,\alpha^i\lambda^{j-1}k_{ij}\right)\sum_{ij} i\,\alpha^i\lambda^j\,k_{ij}}{\left(\sum_{ij} j\,\alpha^i\,\lambda^j\,k_{ij}\right)^2},\tag{92}$$

which when divided in the numerator and denominator by $\sum_{ij} j \, \alpha^i \lambda^j k_{ij}$

gives

$$\left(\frac{\partial x}{\partial \lambda}\right)_\alpha = \frac{\sum_{ij} ij \, \alpha^i \lambda^{j-1} k_{ij} - x_{vap} \sum_{ij} j^2 \alpha^i \lambda^{j-1} k_{ij}}{\sum_{ij} j \, \alpha^i \lambda^j k_{ij}} \; . \tag{93}$$

When in the denominator of (85) the factor $d\lambda/d\alpha$ is substituted by the right-hand side of (83), we get

$$\frac{1}{\alpha} \left[\alpha \left(\frac{\partial x}{\partial \alpha}\right)_\lambda - \left(\frac{\partial x}{\partial \lambda}\right)_\alpha \lambda \; x_{soln} \right] . \tag{94}$$

From (91),

$$\alpha \left(\frac{\partial x}{\partial \alpha}\right)_\lambda = \frac{\sum_{ij} i^2 \alpha^i \lambda^j k_{ij} - x_{vap} \sum_{ij} ij \, \alpha^i \lambda^j k_{ij}}{\sum_{ij} j \, \alpha^i \lambda^j k_{ij}} , \tag{95}$$

and from (93)

$$\lambda \left(\frac{\partial x}{\partial \lambda}\right)_\alpha = \frac{\sum_{ij} ij \, \alpha^i \lambda^j k_{ij} - x_{vap} \sum_{ij} j^2 \alpha^i \lambda^j k_{ij}}{\sum_{ij} j \, \alpha^i \lambda^j k_{ij}} \; . \tag{96}$$

Then (94) becomes

$$\frac{1}{\alpha} \frac{\sum_{ij} i^2 \alpha^i \lambda^j k_{ij} - x_{vap} \sum_{ij} ij \, \alpha^i \lambda^j k_{ij} - x_{soln} \sum_{ij} ij \, \alpha^i \lambda^j k_{ij} + x_{soln} x_{vap} \sum_{ij} j^2 \alpha^i \lambda^j k_{ij}}{\sum_{ij} j \, \alpha^i \lambda^j k_{ij}} \; . \tag{97}$$

The numerator of (97) can be factored to

$$\sum_{ij} \alpha^i \lambda^j k_{ij} (i - j \, x_{vap})(i - j \, x_{soln}) \; . \tag{98}$$

Thus we finally obtain for (94)

$$\frac{\sum_{ij} \alpha^i \lambda^j k_{ij} (i-j\, x_{vap})(i-j\, x_{soln})}{\alpha \sum_{ij} j\, \alpha^i \lambda^j k_{ij}} \quad . \tag{99}$$

From (89) and (99) we get

$$\frac{dP}{dx} = \frac{\dfrac{a}{\alpha} (x_{vap} - x_{soln}) \sum_{ij} j\, \alpha^i \lambda^j k_{ij}}{\dfrac{\sum_{ij} \alpha^i \lambda^j k_{ij} (i-j\, x_{vap})(i-j\, x_{soln})}{\alpha \sum_{ij} j\, \alpha^i \lambda^j k_{ij}}} \quad , \tag{100}$$

which simplifies to

$$\frac{dP}{dx} = a\, (x_{vap} - x_{soln}) \frac{\left(\sum_{ij} j\, \alpha^i \lambda^j k_{ij}\right)^2}{\sum_{ij} \alpha^i \lambda^j k_{ij}(i-j\, x_{vap})(i-j\, x_{soln})} \quad . \tag{101}$$

When in (84) the factor dP/dx is substituted by the right-hand side of (101), and P is substituted by the right-hand side of (19), we finally obtain:

$$\frac{d \log_{10} \frac{1}{P}}{dx} = -\, 0.4343\, (x_{vap} - x_{soln}) \frac{\left(\sum_{ij} j\, \alpha^i \lambda^j k_{ij}\right)^2}{\left(\sum_{ij} \alpha^i \lambda^j k_{ij}\right) \left[\sum_{ij} \alpha^i \lambda^j k_{ij}(i-j\, x_{vap})(i-j\, x_{soln})\right]} \quad . \tag{102}$$

When $x_{vap} = x_{soln}$ the slope becomes zero, in agreement with the Gibbs-Konovalov theorem.[9]

It remains only to be proved that at $x_{soln} = 0$ and $\alpha = 0$, (102) becomes (64).

The proof follows: In (102) we remove x_{soln} and replace x_{vap} by the right-hand side of (15). Accordingly,

$$\frac{d \log_{10} \frac{1}{P}}{dx} = -0.4343 \frac{\sum_{ij} j\, \alpha^i \lambda^j k_{ij}}{\sum_{ij} \alpha^i \lambda^j k_{ij}} \cdot \frac{\sum_{ij} i\, \alpha^i \lambda^j k_{ij}}{\sum_{ij} i^2 \alpha^i \lambda^j k_{ij} - x_{vap} \sum_{ij} ij\, \alpha^i \lambda^j k_{ij}} \,. \tag{103}$$

At $\alpha = 0$ the first fractional factor in (103) becomes

$$\frac{\sum_{j} j\, \lambda_o^j k_{0j}}{\sum_{j} \lambda_o^j k_{0j}} \,, \tag{104}$$

and the second fractional factor becomes an indeterminate form. Let us resolve it. By differentiating both the numerator and the denominator with respect to α, we get

$$\frac{\sum_{ij} i^2 \alpha^{i-1} \lambda^j k_{ij}}{\sum_{ij} i^3 \alpha^{i-1} \lambda^j k_{ij} - \left(\frac{\partial x_{vap}}{\partial \alpha}\right)_\lambda \sum_{ij} ij\, \alpha^i \lambda^j k_{ij} - x_{vap} \sum_{ij} i^2 j\, \alpha^{i-1} \lambda^j k_{ij}} \,. \tag{105}$$

9. I. Prigogine and R. Defay, _Chemical Thermodynamics_ (New York: Longmans, Green and Co., 1954), cf. p. 282.

When $\alpha = 0$, the numerator and the first term in the denominator of (105) become $\sum_{j} \lambda_o^j \, k_{1j}$. The second term in the denominator becomes zero because, from (91), the first factor in this term is $(\sum_{j} \lambda_o^j \, k_{1j})/(\sum_{j} j \, \lambda_o^j \, k_{0j})$, and the second factor is zero. The third term in the denominator is also zero because the first factor in this term is zero, and the second factor is $\sum_{j} j \, \lambda_o^j \, k_{1j}$. Therefore, since (105) is unity, (103) reduces to (64).

APPENDIX 1

THE PRESENT STATUS OF THE VAPOR PRESSURE OF LIQUID SILICON

In Fig. 3, data are assembled on the vapor pressure of liquid silicon as given by Ruff and Konschak,[1] Baur and Brunner,[10] Grieger,[11] and Honig.[12] In their experiments, Ruff and Konschak, and also Grieger, used a silicon carbide crucible as a container for the liquid silicon. Therefore, their measurements actually represent the pressure for the level efg in Fig.1. Calculating the separation hg for 1700°K, the temperature at which it is safe to assume no solubility of carbon in liquid silicon, one finds a very small value. This is due to the vapor pressure of graphite being much lower than the vapor pressure of liquid silicon. Hence the silicon carbide container is permissible. At temperatures above 1700°K, this discrepancy may increase considerably. Baur and Brunner have used an aluminum oxide crucible, which may have distorted their results.

Honig developed his function from mass spectroscopic measurements and from comparison with germanium. In the range of low $10^4/T$, we have extrapolated somewhat beyond Honig's original limit ($10^4/T = 3.6$). Since his function is lightly curved, this may have affected the slope of our plot. It is believed that the error thus introduced is small.

10. E. Baur and R. Brunner, Helv. Chim. Acta 17, 958 (1934).
11. O. Ruff, Trans. Electrochem. Soc. 68, 87 (1935), cf. curve 3 in Fig. 6.
12. R. E. Honig, R C A Rev. 18, 195 (1957).

APPENDIX 1
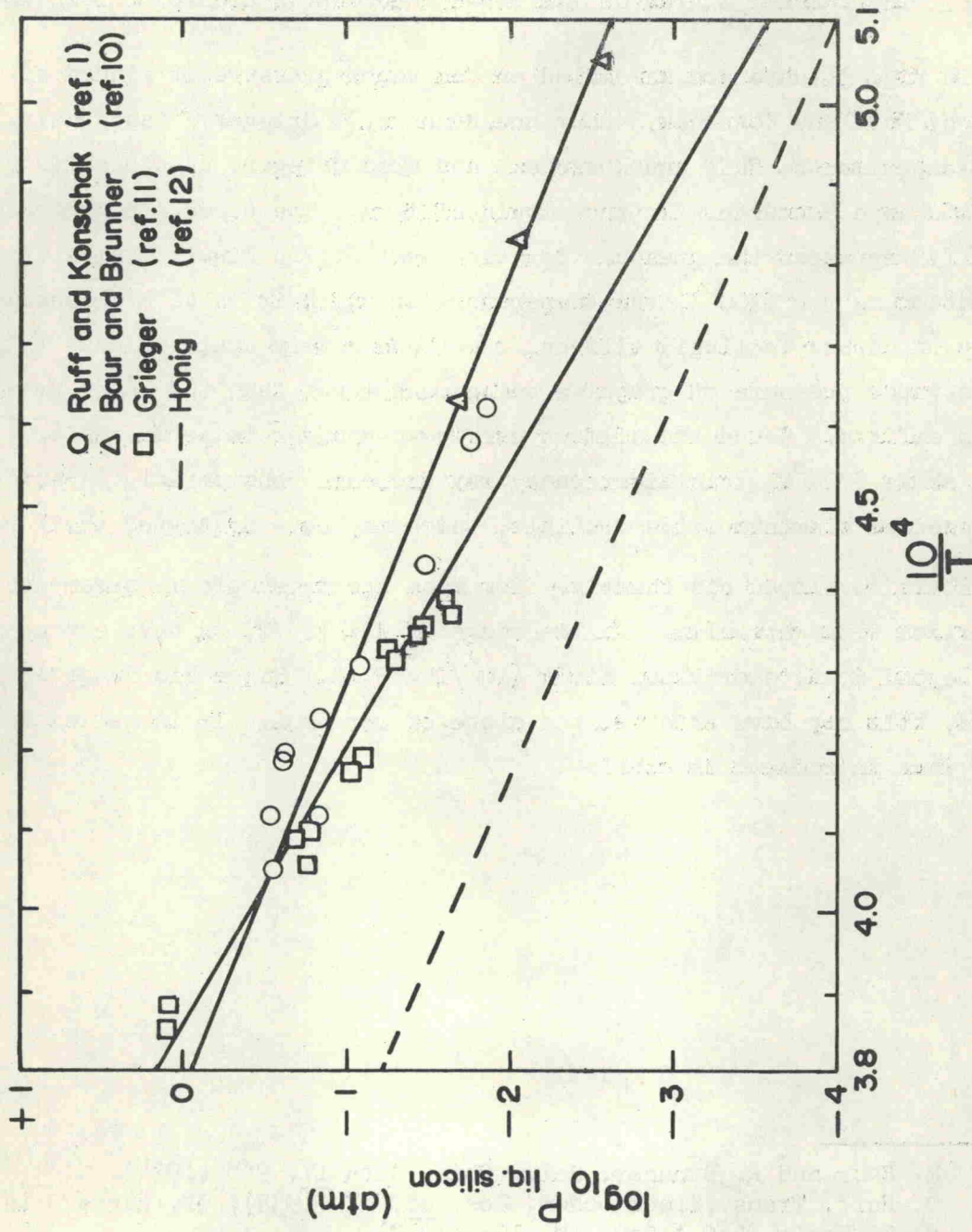
Fig. 3. The vapor pressure of liquid silicon.

APPENDIX 2

Equation (107) has been calculated by Humphrey and his co-workers. It represents the average function for both the hexagonal and cubic modifications, their difference being small. Equation (108) has been calculated in this work. The numerical values of thermochemical data used are given in Table 1.

APPENDIX 2

TABLE 1

THERMOCHEMICAL DATA USED FOR CALCULATION OF EQUATION (108)

$$C_P = a + b \cdot 10^{-3}T + c \cdot 10^5 T^{-2}$$

SUBSTANCE Form	Formula Weight	$S^{\ominus}_{298.16}$ cal/fwt deg	Reference	a	b	c	Range of Validity °K	Deviation ± percent	Reference
Graphite	12.010	1.3609	15	4.10	1.02	-2.10	298 - 2300	2.5	16
Silicon, solid	28.06	4.47	15	5.79	0.56	-1.09	298 - 1200	2	16
Silicon, liquid	not given	......	..	6.12	0	0	< 1825	0.4	17
SiC, solid, hex.(?)	40.07	3.935	15	8.93	3.00	-3.07	298 - 1700	3	16

The $\frac{cal}{fwt\ deg}$ units apply to $S^{\ominus}_{298.16}$ and to C_P.

Si(solid, 1 atm, T_f) + $\Delta H_f^{\ominus}$ = Si(liquid, 1 atm, T_f) $T_f = 1685 \pm 2°K$ (ref. 17) $\Delta H_f^{\ominus} = 12095 \pm 100$ cal (ref. 17).

C(graphite, 1 atm, 298.16°K) + Si(solid, 1 atm, 298.16°K) + $\Delta H_{f\ 298.16}^{\ominus}$ = SiC(solid, hex.(?), 1 atm, 298.16°K) $\Delta H_{298.16}^{\ominus}$

$= -26700 \pm 2100$ cal (ref. 14).

15. F. D. Rossini et al., Selected Values of Chemical Thermodynamic Properties (Circular of the National Bureau of Standards 500, Ser. I [Washington, D. C., 1952]).
16. K. K. Kelley, Contributions to the Data on Theoretical Metallurgy (U. S. Department of the Interior, Bureau of Mines, Bulletin 476 [Washington, D. C., 1949]).
17. M. Olette, Compt. rend. 244, 1033 (1957).

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molecular species present in the vapor, vapor pres-
sures of graphite and liquid silicon, and the
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C(graphite) + Si(liquid) = SiC(solid) .

A study is made of the equilibrium: vapor and so-
lution of carbon in liquid silicon.

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   phase diagram
2. Silicon-carbon -
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SUPPLEMENT

To

THE GASEOUS EQUILIBRIA IN THE CARBON-SILICON BINARY SYSTEM

By

J. SMILTENS

APPENDIX 2

Let us denote by primes all quantities measured at the level bcd (Fig. 1) and by double primes those measured at efg:

$$P'_{ij} = a\alpha'^i \lambda'^j k_{ij} = a\alpha_o^i \lambda_o^j e^{\frac{j\Delta G^{\ominus}_{cond}}{RT}} k_{ij}, \tag{S1}$$

and, at temperatures somewhat above the melting point of silicon,

$$P''_{ij} = a\alpha''^i \lambda''^j k_{ij} = a\alpha_o^i e^{\frac{i\Delta G^{\ominus}_{cond}}{RT}} \lambda_o^j k_{ij}. \tag{S2}$$

On dividing (S1) by (S2), we obtain:

$$\frac{P'_{ij}}{P''_{ij}} = e^{\frac{(j-i)\Delta G^{\ominus}_{cond}}{RT}}. \tag{S3}$$

Thus the $\Delta G^{\ominus}_{cond}$ can also be determined from the pressure ratios.