

## Errata: Temperature Independent Factor in the Relative Rates of Isotopic Three Center Reactions

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## Hafnium Silicides

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(Received April 27, 1954)

CRYSTAL structure<sup>1,2</sup> and phase diagram<sup>3</sup> investigations of the zirconium-silicon system have confirmed the existence of the compounds ZrSi and ZrSi<sub>2</sub>. In this note, the analogous hafnium compounds are described.

Hafnium metal (97+ percent pure) and silicon powders were mixed in the desired proportions and hot pressed at 1200°C into small pellets. One group of pellets was then sealed into an evacuated quartz tube which had been flushed with argon prior to evacuation, and heated for 88 hours at 1125°C. Another group was heated for several minutes in a helium atmosphere at 1500°C.

X-ray diffraction diagrams of the powdered products revealed two phases which were identified as HfSi and HfSi<sub>2</sub>, by analogy with the corresponding zirconium silicides. Both phases were present in all preparations.

TABLE I. Lattice constants of hafnium and zirconium silicides (in Å).

	HfSi	ZrSi <sup>3</sup>	HfSi <sub>2</sub>	ZrSi <sub>2</sub> <sup>2</sup>
<i>a</i>	6.86	7.005	3.67	3.72
<i>b</i>			14.56	14.61
<i>c</i>	12.60	12.772	3.64	3.67
<i>c/a</i>	1.84	1.823		

HfSi is hexagonal; HfSi<sub>2</sub> is orthorhombic. The lattice constants of these silicides are listed in Table I, together with those of the isomorphous ZrSi and ZrSi<sub>2</sub>.

<sup>1</sup> H. Seyfarth, Z. Krist. **67**, 295 (1928).<sup>2</sup> S. v. Naray Szabo, Z. Krist. **A97**, 223 (1937).<sup>3</sup> Lundin, McPherson, and Hansen, Am. Soc. Metals.

## Errata: Temperature Independent Factor in the Relative Rates of Isotopic Three Center Reactions\*

[J. Chem. Phys. **21**, 1972 (1953)]JACOB BIGEISEN AND MAX WOLFSBERG  
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(Received May 7, 1954)

D. R. N. B. Slater has kindly called our attention to an ambiguous definition of  $\nu_L$  and an error in the sign in Eqs. (9) and (10), relating  $\nu_L$  and  $m_B$ . The alternate definition of  $\nu_L$  following Eq. (7) is not rigorously tenable. Equation (9) should read

$$\nu_L \alpha \{ \alpha^2 (m_B^{-1} + m_C^{-1}) + \beta^2 (m_B^{-1} + m_A^{-1}) + 2\alpha\beta m_B^{-1} \}^{\frac{1}{2}}$$

for the collinear model. A similar change should be made in Eq. (10).

Some of the curves published as Fig. 1 are, therefore, incorrect and the accompanying figure replaces it. The discussion of Eq. (10) and Fig. 1 is somewhat modified by the change in sign of the  $p^{\frac{1}{2}}$  term. In the discussion of the decomposition of ammonium nitrate, the experimental fractionation factor of 1.023 now corresponds to  $p$  equal to 0.125, while the model, which gives 1.026 for the over-all fractionation factor, corresponds to  $p$  equal to 0.085. The agreement in this respect is, therefore, improved.

Application of the corrected equation for  $\nu_L$  to the reactions of the isotopic hydrogen atoms and molecules, now serves to emphasize the inherent difference between the motion associated with  $\nu_L$  and the conventional normal coordinates. A comparison between  $\nu_L$  and the asymmetric stretching vibration of the linear

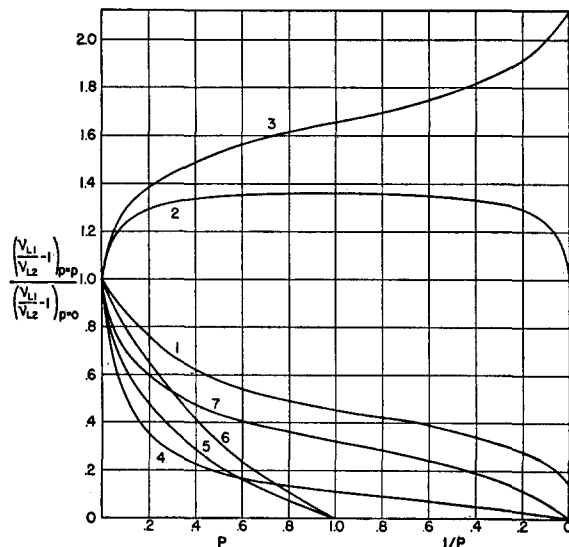


FIG. 1. Plot of the ratio  $[(\nu_{L1}/\nu_{L2}) - 1]_{p=p} / [(\nu_{L1}/\nu_{L2}) - 1]_{p=0}$  as a function of  $p$  or  $1/p$ . The curves are for the following cases: (1)  $m_B = m_C = 12$ ,  $m_A = 1$ ,  $m_B' = 14$ ; (2)  $m_A = m_B = m_C = 12$ ,  $m_B' = 14$ ; (3)  $m_B = m_C = 12 \ll m_A$ ,  $m_B' = 14$ ; (4)  $m_B = m_C = 12$ ,  $m_A = 1$ ,  $m_C' = 14$ ; (5) intramolecular isotope effect  $m_A = 13, 14$ ,  $m_A' = 12$ ,  $m_B = 12$ ,  $m_C = 12$ ,  $m_C' = 13, 14$ ; (6) intramolecular isotope effect  $m_A = 13, 14$ ,  $m_A' = 12$ ,  $m_B = \infty$ ,  $m_C = 12$ ,  $m_C' = 13, 14$ ; (7)  $m_A = m_B = m_C = 12$ ,  $m_A' = 14$ .

XYZ molecule is no longer fruitful. If one assumes that the zero point energy difference on isotopic substitution is correctly represented in both cases, then the product rule assures that calculated isotopic effects on the rate will be identical by both methods.

In passing it may be noted that Eq. (9) as corrected above leads, when  $p$  equals unity, to the asymmetric stretching vibration for the linear  $XY_2$  molecule. If  $\cos ABC$  is left explicitly in Eq. (9), the similar formula for the bent  $XY_2$  molecule is obtained.

\* Research carried out under the auspices of the U. S. Atomic Energy Commission.

A New Analysis of the Effect of Polar Solvents Upon  $\nu(\text{NH})$  of Pyrrole\*MARIE-LOUISE JOSIEN AND NELSON FUSON  
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(Received May 3, 1954)

IN our recent study<sup>1</sup> of the effect of solvent upon the NH-stretching frequency of pyrrole and other compounds, we chose to present the data in the form of points on the graph of  $(\nu_o - \nu_s)/\nu_o$  as ordinate versus  $(D-1)/(2D+1)$  as abscissa,  $\nu_o$  and  $\nu_s$  being the pyrrole NH vapor and solution frequencies respectively, and  $D$  being the dielectric constant of the solvent in which the pyrrole is dissolved. The result is a grouping of nonpolar points through which a line drawn from the origin establishes what we have termed the Kirkwood-Bauer or KB line. The aromatic and most of the nonpolar points fall to the right of this line, only the few chlorinated solvent points lying to the left of the line. Jones and Badger, who obtained similar results for methanol,<sup>2</sup> suggested that the bonding of the methanol oxygen with, for example, the chloroform hydrogen was responsible for the increase in the frequency over that which would be expected from the effect of dielectric constant alone.

More recently an analysis of the effect of solvent upon  $\nu(\text{C}=\text{O})$  of acetone, acetophenone, and cyclohexanone<sup>3</sup> has shown that most of the solvent points plotted in the same way fall on the

TABLE I.

Name	Solvent	Structure	$\frac{D-1}{2D+1} \times 10^3$	$\frac{N^2-1}{2N^2+1} \times 10^3$	$\frac{\nu_v - \nu_s}{\nu_v} \times 10^2$
n-Hexane	C <sub>6</sub> H <sub>14</sub>		183	186	0.85
Cyclohexane	C <sub>6</sub> H <sub>12</sub>		205	205	0.91
Carbon tetrachloride	CCl <sub>4</sub>		225	216	0.94
Benzene	C <sub>6</sub> H <sub>6</sub>		229	228	2.04
Mesitylene	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>		236	227	2.58
m-Xylene	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>		237	226	2.41
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>		239	226	2.32
Carbon disulfide	CS <sub>2</sub>		261	262	1.39
Chloroform	CHCl <sub>3</sub>		360	210	1.25
1,2-Dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>		428	210	1.84
Pyridine	C <sub>5</sub> H <sub>5</sub> N		443	230	8.0
Acetophenone	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>		459	237	3.6
Acetone	CH <sub>3</sub> COCH <sub>3</sub>		466	180	4.0
Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>		478	242	2.30
Pyrrole (pure liquid)	C <sub>4</sub> H <sub>4</sub> NH		406	228	3.82

left side of the KB line, even though in some of these cases it is known that association between solute and solvent molecules is taking place. Whiffen's data on the  $\nu(\text{C}-\text{Cl})$  of chloroform<sup>4</sup> in different solvents when analyzed<sup>3</sup> in the same manner, also gives most of the points to the left of the KB line.

These additional results make clear that polar solvent points appear to the left of the KB line almost as frequently as to the right. The left-hand points are thus not limited to, nor are they characteristic of, halogenated solvents. At this stage<sup>3</sup> our attention was drawn to the remark of Bauer and Magat<sup>5</sup> that the dielectric constant  $D$  in the relationship  $(\nu_v - \nu_s)/\nu_v = C(D-1)/(2D+1)$  should not be that which is measured at low frequencies but should be slightly greater than that which is calculated from index of refraction measurements,<sup>5</sup> i.e., slightly greater than the square of the index of refraction  $N$ .

When  $N^2$  is used in place of  $D$  (see Table I), although the non-polar solvent points on the  $(\nu_v - \nu_s)/\nu_v$  versus  $(N^2-1)/(2N^2+1)$  graph are essentially unchanged, the positions of the polar solvent points are markedly different from that previously given.<sup>1</sup> From Fig. 1 it can be seen that the chloroform, dichloroethane, and nitrobenzene points for  $\nu(\text{NH})$  of pyrrole have been lowered across to the right side of the KB line.<sup>6</sup>

While a more comprehensive analysis of this matter will be given elsewhere we should like to point out here that on the basis of solvent induced frequency shifts alone there is no clear-cut

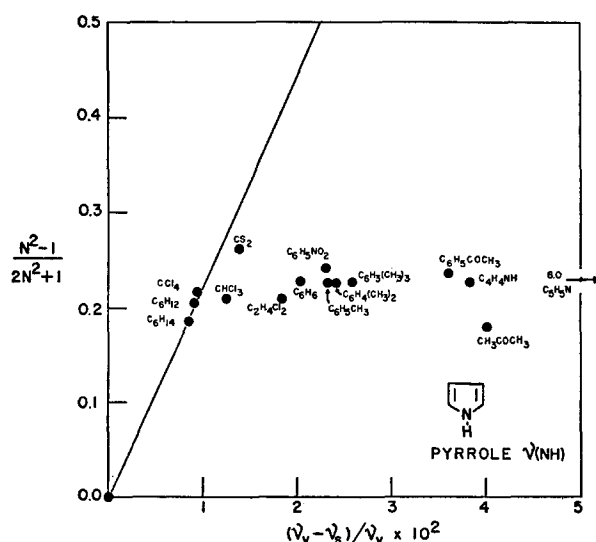


FIG. 1. A new analysis of the effect of polar solvents upon  $\nu(\text{NH})$  of pyrrole.

differentiation between polar solvents which enter into solvent-solute complexes with pyrrole and those which do not. However, the use of the mixed solvent technique in addition enables one to show<sup>1</sup> that at room temperature pyridine, acetophenone, acetone, toluene, and nitrobenzene form complexes while dichloroethane does not. From the position of the solvent points in the above figure it appears that at room temperature the division between polar or aromatic solvents forming complexes with pyrrole and polar solvents not forming such complexes occurs at a pyrrole  $\text{NH}$ -relative frequency shift of about 2 percent. At a higher temperature the complexes being less stable, the assumption is that this division would be displaced to the right, i.e., toward higher percentages.

\* This work has been supported jointly by research grant No. C-1520 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service, and by a Frederick Gardner Cottrell grant from the Research Corporation.

<sup>1</sup> M. L. Josien and N. Fuson, *J. Chem. Phys.* **22**, 1264 (1954).

<sup>2</sup> L. H. Jones and R. M. Badger, *J. Am. Chem. Soc.* **73**, 3132 (1951).

<sup>3</sup> M. L. Josien *et al.*, *Compt. rend.* **236**, (to be published) (1954).

<sup>4</sup> D. H. Whiffen, *Trans. Faraday Soc.* **49**, 878 (1953).

<sup>5</sup> E. Bauer and M. Magat, *J. phys. radium* **9**, 319 (1938).

<sup>6</sup> This contrast can be seen most easily by comparing the figure given in this letter with Fig. 1 of reference 1 (to be found in this same issue).

## The Critical Point and the Phase Rule

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(Received April 12, 1954)

IF we apply the phase rule of Gibbs on a one-component system in the critical state, we have, according to Van der Waals, three phases.<sup>1</sup> The number of degrees of freedom of this system at the critical point is therefore equal to zero ( $P=3$ ,  $C=1$ , and  $F=C-P+2=0$ ).

It is better, in our opinion, to consider the critical state as representing one phase and thus having two degrees of freedom. To elucidate this point of view it is necessary to consider accurately the ordinary definition for the number of degrees of freedom of a system. This definition runs as follows: the number of degrees of freedom of a system is the number of variable factors, such as temperature, pressure or concentration, which need to be fixed in order that the condition of a system at equilibrium may be completely defined. An equivalent definition states that the number of degrees of freedom is the number of variable factors, which can be altered, without changing the number of phases.

If now we consider the fact that the critical point is the end point of the gas-liquid equilibrium curve, we see that it is possible to alter the pressure and the temperature, thus having two degrees of freedom and to remain in the homogeneous one-phase region. When we diminish the temperature or increase the pressure this homogeneous phase is called the liquid state; when we increase the temperature or diminish the pressure the system is in the gaseous state. The number of phases has therefore not been changed, but remains one; only the name of the phase changes.

In view of the first definition we can say that the difference between the critical point and for instance the triple point of a substance is, that when we consider this substance at its critical point we have already fixed pressure and temperature, whereas when we consider the triple point, we have chosen to have three phases in equilibrium. This problem is connected with the fact that by applying the theory of Van der Waals in this way, we mix up exact thermodynamics (the phase rule of Gibbs) with a semi-empirical formula.

Some time ago the author has enunciated the hypothesis that the critical point is the result of the fact that at the critical point the kinetic energy is equal to the potential energy.<sup>2</sup> The question has been raised whether this hypothesis is, from a physical point of view, unambiguous.<sup>3</sup> It has to be emphasized, however, that the critical point has no significance unless liquid and vapor are present. If we heat a liquid under a pressure higher than its vapor-