AN ABSTRACT OF THE THESIS OF

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Title: THERMODYNAMICS OF THE REACTION BETWEEN

F AND M CENTERS IN KBr

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The thermal equilibrium between F centers and M centers in KBr was studied at temperatures of 75°, 85°, 95°, and 105° C, using Pick's model for the M center, i.e., F_2 = M. The binding energy obtained, 0.16 ev, is in agreement with the theoretical result based on the model of an M center imbedded in a continuous dielectric. From the temperature dependence of M center concentration, the thermodynamic quantities for the process 2 F = M were obtained. For centers/cm^3, as the reference function, $\widetilde{\Delta G}^o$ is 29.0 ± 0.4 at 348 °K and 31.6 ± 0.5 Kcal/mole at 378 °K. $\widetilde{\Delta S}^o$ was found to be -94.1 ± 1.3 at 348° K and -93.8 ± 1.4 cal/deg at 378° K. The theoretical value, considering configurational entropy alone, is -99 cal/deg. By using the mole fraction as a reference function, $\widetilde{\Delta G}^o$ is -6.27 ± 0.42 at 348° K and -6.63 ± 0.45 Kcal/mole at 378° K. $\widetilde{\Delta S}^o$ was found to be 7.2 ± 1.3 at 348° K and 7.6 ± 1.4 cal/deg at

378° K. The value of $\Delta \widetilde{H}^{O}$ is independent of reference function

chosen. Its average value is -3.76 ± 0.08 Kcal/mole which is lower

than the $\Delta \widetilde{H}^{O}$, 4.1 Kcal/mole, for KCl.

Thermodynamics of the Reaction Between
F and M Centers in KBr

by

Tsai-Chi Li

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INTRODUCTION

General Properties

Pure alkali halides are transparent from the far ultraviolet into the far infrared including the visible range. The ultraviolet absorption corresponds to electronic transitions, while the infrared absorption is related to the vibration of ions. There is thus a very broad spectral region in which changes in optical absorption arising from defects can easily be detected and studied.

Color centers in alkali halides may be formed by: (a) excitons (27), (b) x-rays and γ-rays (9, 13), (c) electronic bombardment (6), (d) additive coloration (22). All of these methods produce a main absorption band due to color centers, which always appears at the same position in the spectrum for a given crystal. Among the other bands produced, this major band has been labeled the F band, after the German word Farben, meaning color.

F Centers

de Boer (1) proposed a model for the color center responsible for the F band, which consists of an electron trapped at an anion

vacancy. Since the anion vacancy has a positive charge associated with it, the F center is electrically neutral. The de Boer model is currently the accepted model.

The shape of the F band was first considered to be Lorentzian. Assuming that the centers giving rise to the absorption do not interact with one another, the area under the absorption curve is directly proportional to the concentrations of the absorbing centers. According to classical dispersion theory, these absorption centers can be treated as damped oscillators.

Based on this consideration, Smakula (26) derived an equation dealing with the concentrations of centers, as follows:

$$N_F f_F = \frac{9\ mc^2}{2\ e^2} \cdot \frac{n}{(n^2 + 2)^2}\ \alpha_{max} \cdot H,$$

where

N_F = concentration of absorbing centers

f_F = oscillator strength of absorbing center

n = index of refraction of the pure crystal at the band maximum

H = width of band at half its peak height

α_{max} = absorption coefficient, that is, $(2.303/t)\ \log$ I_o/I, where

I = transmitted light intensity

$$I_o \qquad = \text{incident light intensity}$$

$$t \qquad = \text{crystal thickness}$$

and m, e, and c have their usual meanings. Numerically, Smakula's equation is

$$N_F f_F = 1.29 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{max} \cdot H;$$

when H is in ev unit, and t is given in centimeters, N has the units of centers/cubic centimeters.

A more recent treatment by Dexter (4) took into account: (a) that the width of the absorption band arises from interaction of the center with the lattice vibration rather than from classical dispersion, and (b) that the observed F band is more nearly Gaussian in shape rather than Lorentzian. Then the Smakula equation becomes:

$$N_F f_F = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{max} \cdot H$$

The oscillator strength of KBr has a reported value 0.48 (5). For H, the half-height band width, there are three reported values, 0.35 (16), 0.38 (23) and 0.42 (14) ev. Here, f = 0.48 and H = 0.42 ev will be used.

Secondary Centers

The family of centers giving rise to optical absorption bands on

the long wavelength side of F band have received less attention than

the F center. These so-called secondary centers are the M, R,

and N centers. They bear a strong genetic relationship to the F

center, and like the F center, they are defects containing trapped

electrons. As of this writing, more is known about the M center than

about others; therefore, we will discuss the M center more thoroughly

in the next sections.

Due to the limited information available on R and N centers,

Pick (21) speculated on the possibilities that (a) R center might consist

of three F centers, i.e., three halogen-ion vacancies with three

electrons in a two dimensional array and possess C_{3v} symmetry,

(b) N center might consist of four F centers, i..e., four halogen-ion

vacancies with four electrons in a two dimensional array and

possess C_s symmetry. These proposed models are sketched in

Figure 1.

Pick's model of the R center, a cluster of three F centers,

has received considerable experimental support, including work on

polarized luminescence (3), and polarized bleaching (17). The

observation of the zero-phonon line of the R band during axial

compression confirmed this model (25). Seidel (24), by using the

optical absorption and paramagnetic resonance of KCl crystals con-

taining preferentially oriented R centers, concluded the R center

should be the association of three F centers forming an equilateral

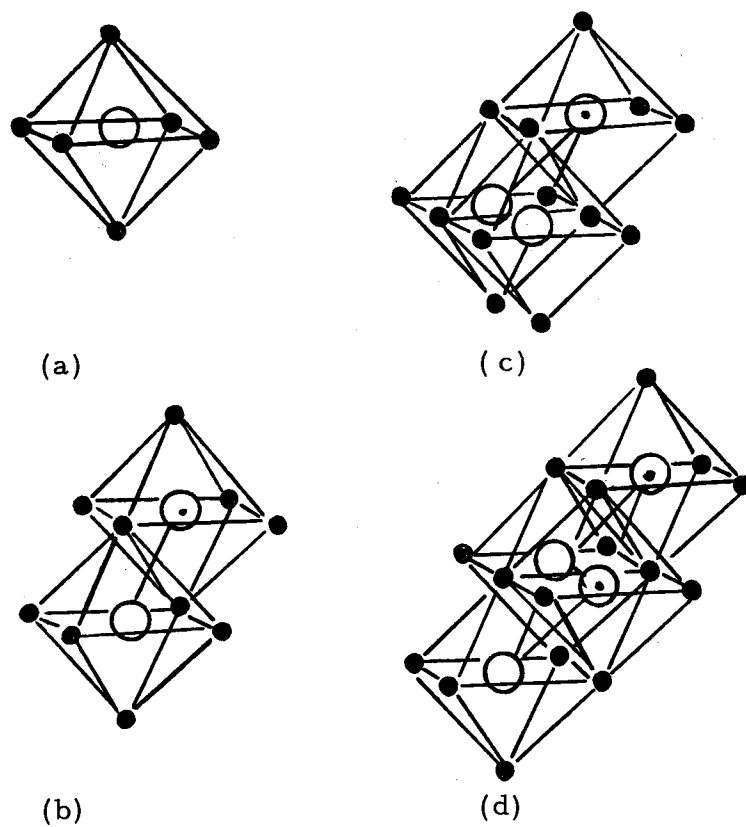Figure 1. (a) Model of the F center with symmetry, O_h;
(b) model of the M center with symmetry D_{2h};
(c) model of the R center with symmetry C_{3v};
(d) model of the N center with symmetry C_s;
[After H. Pick, Z. physik 159, 69 (1960).]

triangle in the < 111> plane of the cyrstal, as proposed by Pick. The effect of varying electric field on the contour of the zero-phonon absorption line at 5234 $\overset{o}{A}$ associated with N centers in Li F was studied at 77°K by Kaplyanskii (11). Because the Stark effect of this line has a quadratic nature, the N center should have an inversion center. Allowing for the known monoclinic symmetry of the center, its inversion point group is unambiguously determined to be C_{2h}, which is also satisfied by Pick's model.

These secondary centers can be produced both by optical bleaching of the F band and by thermal bleaching of F band. They tend to dissociate into simple F centers at high temperatures (29).
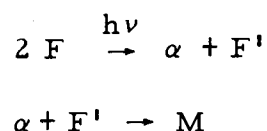
M Center

The fact that an M center contains two F centers, i.e., two neighboring halogen ion vacancies with two trapped electrons, is well established, and it has been discussed very thoroughly by Zahrt (29).

A direct test of this relation between F and M centers in thermal equilibrium is provided in the additively colored crystal itself. At the room temperature and above, it has been shown that equilibrium between F and M centers can be achieved so that the determination of the concentrations can provide an effective way of confirming the two-F model. This work in KCl has been carried out by Zahrt (29) who

showed that N_M was proportional to N_F^2 where N_M is the concentration of M center and N_F is the concentration of F center, using the centers/cm^3, as unit. For KBr, since the F center concentration used must be very high, it is very difficult to measure the F center concentration quantitatively by optical means. In this experiment, we accept the two-F model for M center and, starting from this point, investigate the thermodynamics of the reaction 2F = M.

It must be emphasized that F centers may be aggregated either photochemically, or in the dark by direct migration. Two mechanisms have been proposed for the photochemical process. van Doorn (28) considered the mechanism to be represented by

$$2 F \xrightarrow{h\nu} \alpha + F'$$

$$\alpha + F' \rightarrow M$$

here α represents the negative-ion vacancy and F' is a center, well established experimentally, consisting of an electron trapped at an F center. The second step was supposed to be rate-determining. Delbecq (2) proposed that the mechanism involved the steps
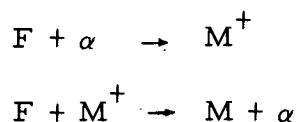
$$F \xrightarrow{h\nu} \alpha + e$$

$$\alpha + F \rightarrow M^+$$

$$e + M^+ \rightarrow M$$
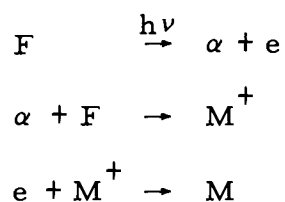
with the second step is rate-determining.

Paul and Scott (19) have recently analyzed the kinetics of the

non-photochemical reactions, which appears to occur via the steps

$$F + \alpha \rightarrow M^+$$

$$F + M^+ \rightarrow M + \alpha$$

with the first being rate-determining.

The Smakula equation is also applied to the M center concentration, that is

$$N_M f_M = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{max} \cdot H$$

where $\quad N_M$ = concentration of M centers

$\quad\quad\quad\quad f_M$ = oscillator strength

n, α and H have the same meaning as described earlier. In this experiment, $f_M = 0.27$, $H = 0.13$ ev will be used (23).

Because it is very difficult to get the equilibrium concentration of F center at different temperatures due to the limitation of the instrument, so we may get the equilibrium concentration of F centers by using the following formula:

$$N_F^\infty = N_F^\circ - 2\,[N_M^\infty - N_M^\bullet]$$

where $\quad N_F^\infty$ = concentration of F center at equilibrium state at certain temperature

$\quad\quad\quad N_F^\circ$ = initial concentration of F center

$\quad\quad\quad N_M^\infty$ = equilibrium concentration of M center at certain temperature

$N_M{}^\circ$ = initial M center concentration, that is, the

residue after the quenching process.

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EXPERIMENTAL PROCEDURES

Sample Preparation

All the crystals used in this work were obtained from the
Harshaw Chemical Company. These were additively colored by
sealing the crystal and potassium metal in a stainless steel bomb.
The crystal was wrapped with thin copper foil and put into the upper
part of the bomb supported by a sample holder. The potassium
metal, after being cleaned with petroleum ether, was put into the
bottom. A copper gasket was used to insure a good seal. Two
furnaces were used so that the temperature of the crystal can be
kept at a temperature higher than that of the reservoir of the alkali
metal.

After heating a long time in the two furnaces (12 - 18 hr), the
stainless steel bomb was rapidly placed in a pan half filled with
cold water so that the potassium vapor could be condensed into the
bottom of the tube and a colored crystal free of potassium residue
could be obtained.

The concentration of F centers was varied between samples
by varying either the temperature of metallic potassium in lower
furnace or by varying the temperature of the crystal in the upper
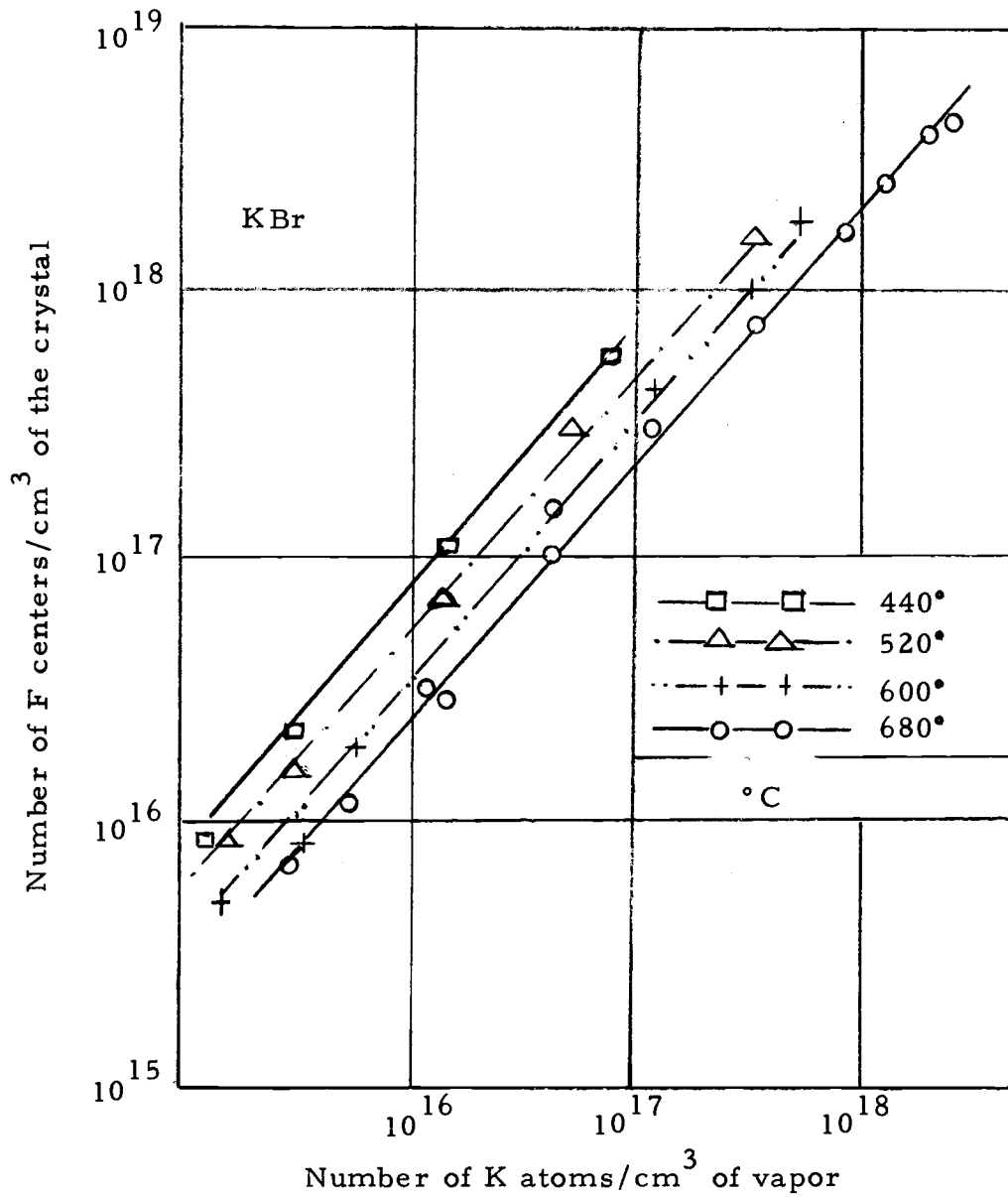furnace. As indicated in Figure 2, due to Rögener (22), the

Figure 2. Solubility of excess K in KBr. [After Rögener, Ann. Phy. 29:386, 1937]

concentration of F centers in equilibrium with the alkali metal vapor is a function both of the crystal temperature and the concentration of the vapor. The latter is set by the lower furnace temperature.

Apparatus

The cell and sample holder were specially designed in this laboratory and were described in detail by Paul (18). The cell itself was made to be interchangeable with the normal cell holder of a Beckman Model DU spectrophotometer. The cell and sample holder are schematically diagrammed in Figure 3. The cell was constructed from a block of steel. Light from the spectrophotometer passes through the window, and then the sample, and out from the other window on the opposite side of the cell to the detector. The light entrance and exit hole could be closed off by the shutter when the cell was to be moved while keeping the sample in the dark.

The sample holder was made of brass. The sample was mounted with Duco cement. There was a movable bar in the cell allowing the sample to be placed in one of three positions. Usually one position was used for the blank. When one position was lined up with the windows the others were light-blocked. The cell could be taken into the dark room for loading the sample.

The cell was heated by four 50-watt tube heaters in series. The temperature of the whole cell was controlled by a YSI Model 72
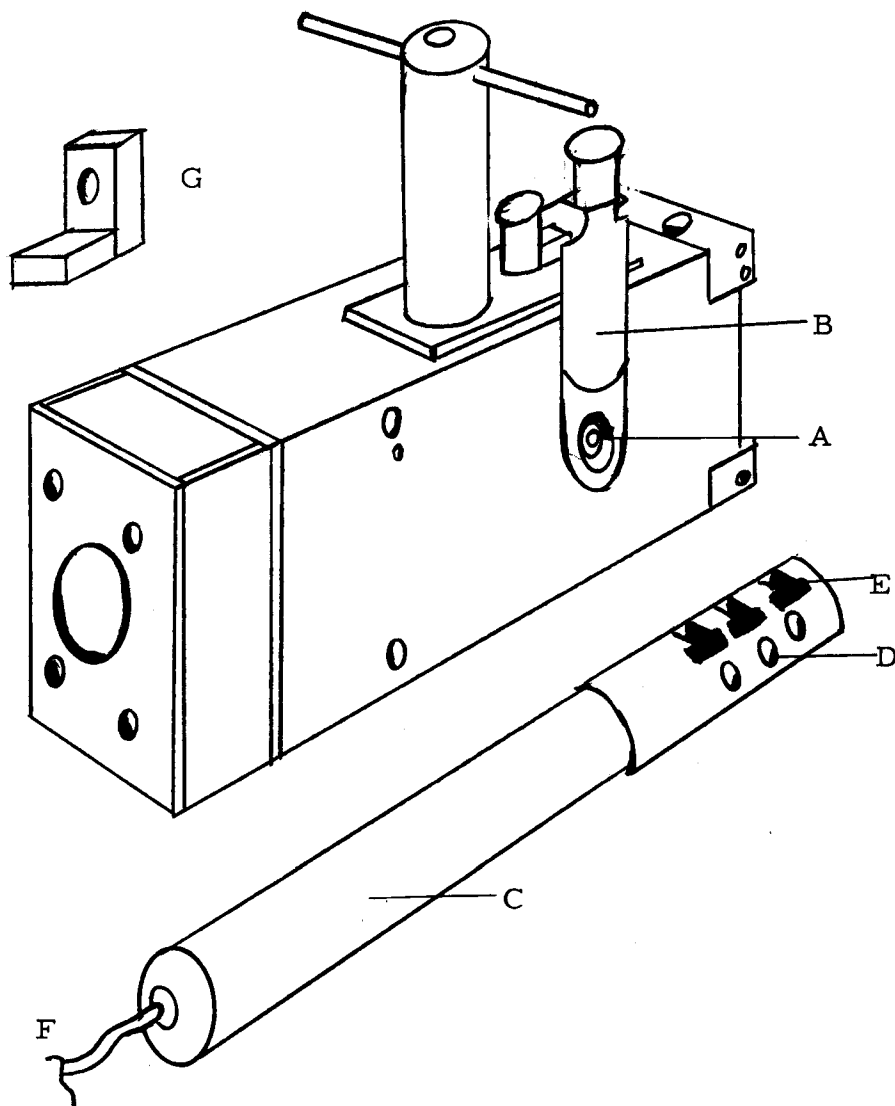
Figure 3.   Schematic diagram of the cell and sample
holder and the bar.

A. window; B.   shutter; C.   removable bar;
D. holes; E. sample holder sites; F. wires
to thermal controller; G.   sample holder.

Proportional Temperature Controller. The band width chosen was

0.1° C.

Procedures

The crystal was removed from the steel bomb in which it was

colored, and under the red light (a 25-watt Tungsten bulb with a

Kodak series 1 filter), a sample was cleaved from the colored ingot.

The sample was wrapped in several layers of aluminum foil and

introduced into the furnace at about 550° C for 1 minute to remove any

F aggregates (R, M and N) or colloidal centers. The quenching

from this temperature was made by placing the wrapped sample,

immediately after withdrawing from the furnace, sandwiched between

two copper plates just taken from a liquid nitrogen reservoir. There

was always some residual M band but never any observable R or N

bands. After quenching, the foil was removed in the dark. There

was no light exposures from this time on except during the actual

spectrophotometric measurements.

For the M center measurement, a spectrum was taken at

various time intervals depending on sample and treatment tempera-

tures. When the spectrum was the same for two measurements,

taken at different times, equilibrium was assumed to have been

established. The temperature was then changed and the process

was repeated. All the optical absorption measurements for the

equilibrium study were made by means of the Beckman Model DU spectrophotometer. The reference for the absorption comparison was air.

In order to detect the variation of M center concentration with temperature effectively, a very high concentration of F centers had to be used. This concentration for F centers was usually too high to be measured by the Beckman Model DU spectrophotometer. In this experiment, a Perkin-Elmer Model 450 double beam spectro-photometer was used to measure the F center concentration at room temperature after the sample was quenched from 550°C.

EXPERIMENTAL RESULTS

Thermal Growth and Decay Curves

Thermal equilibria were studied in the order 75, 85, 95, 105, 95, 85, and 75°C. Figures 4 and 5 show the variation of the absorption coefficient at the peak of M band, i.e., α_M with time. We find α_M at a given temperature is the same whether the equilibrium is approached from the condition of over- or under-saturation with respect to M centers, as shown in the 85°C curve in Figure 5.

Thermodynamics

Number of Centers per Cubic Centimeter as a Reference Function

We define f_i, the fugacity of the ith component by

$$d\overline{G}_i = RTd \ln f_i, \tag{1}$$

where $\overline{G}_i$ is the partial molar Gibbs free energy of the component i, R is the gas constant, and T is the absolute temperature in °K. We also define $f_i/f_i^o = a_i$, where the f_i^o is the fugacity of the component i at its standard state and we call a_i, the activity of i. Integrating equation (1), we get

$$\overline{G}_i - \overline{G}_i^o = RT \ln \frac{f_i}{f_i^o} = RT \ln a_i \tag{2}$$
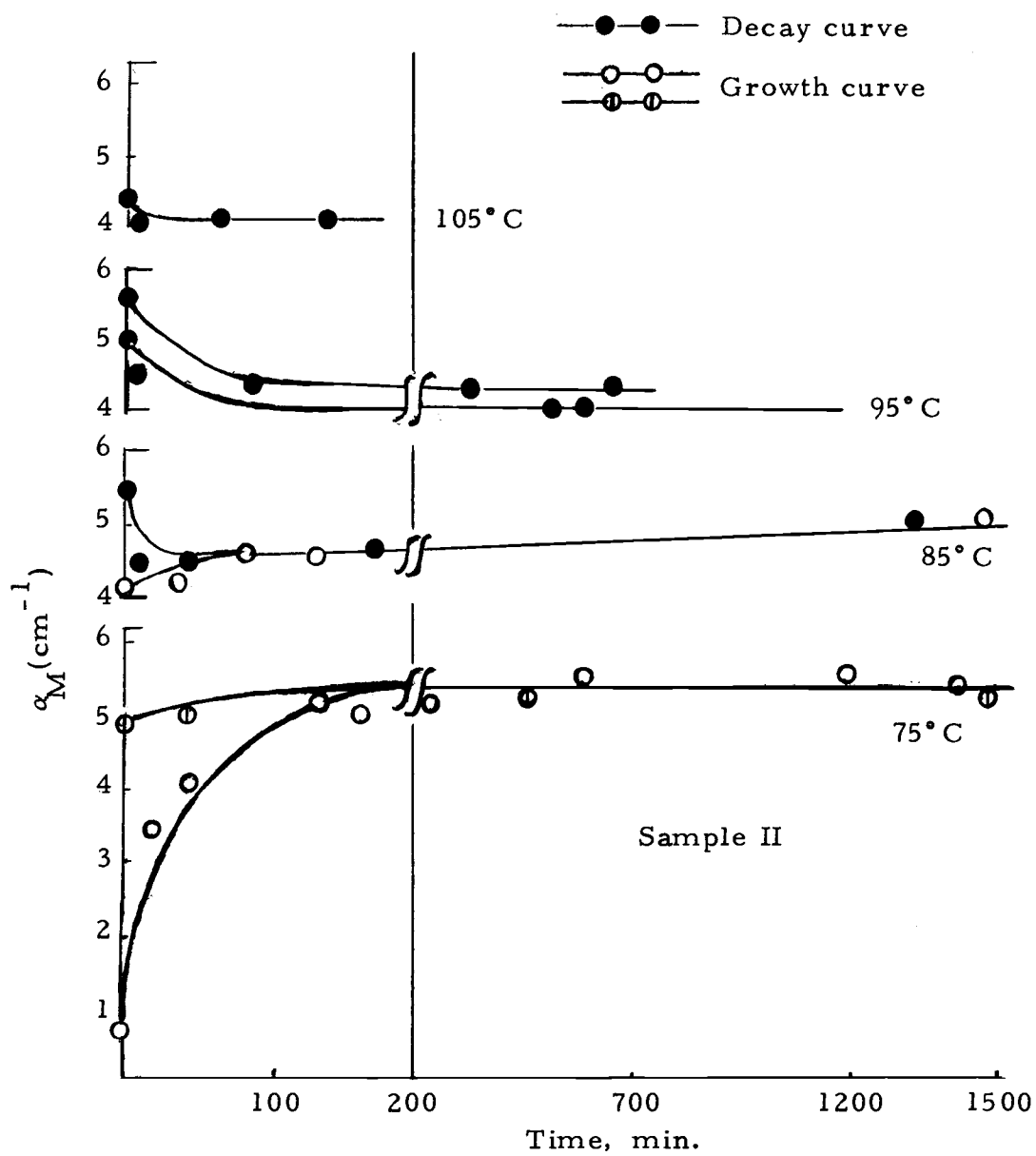
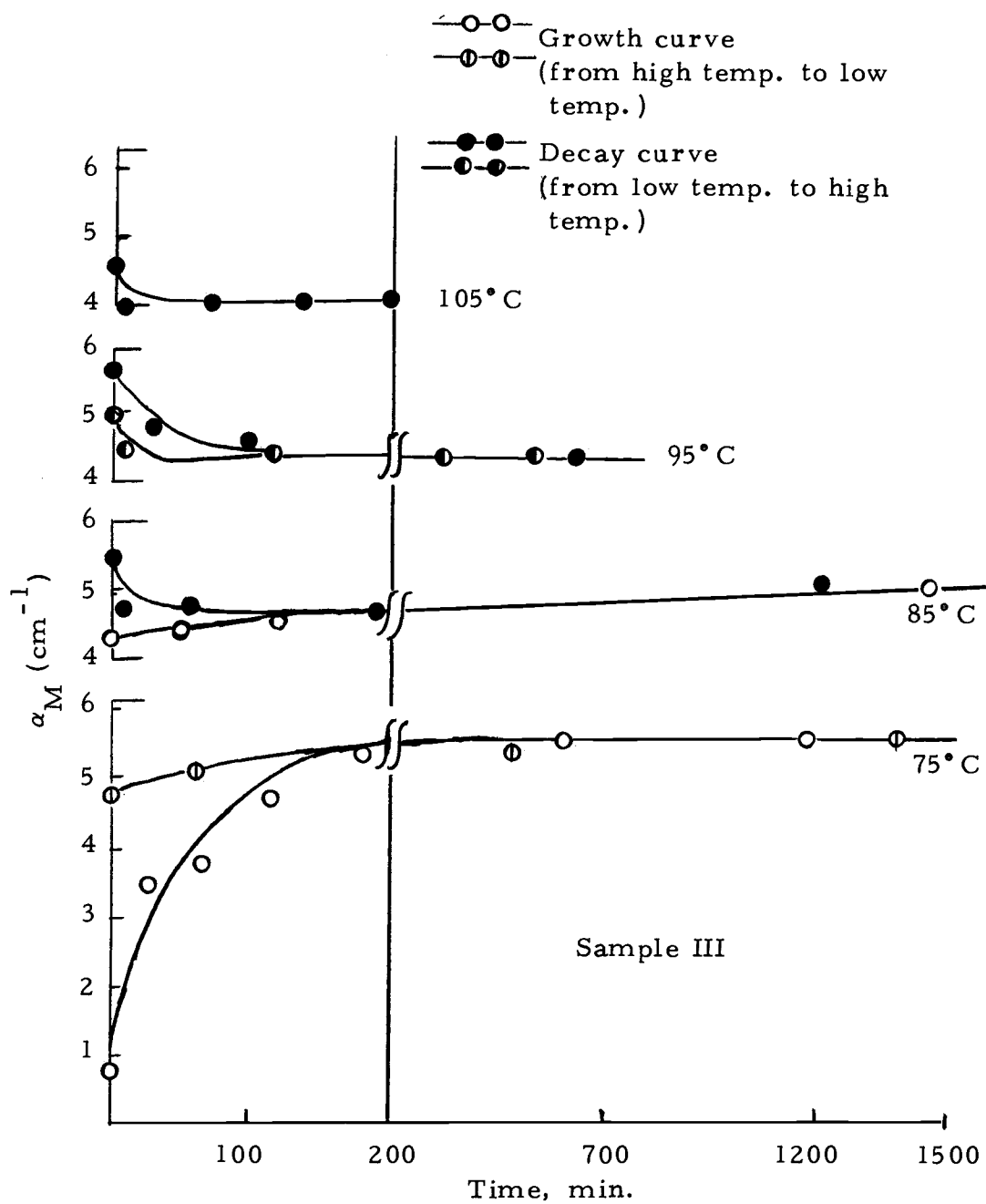Figure 4. Growth and decay curves of the M band at
75°, 85°, 95° and 105°C.

Figure 5. Growth and decay curves of the M band at
75°, 85°, 95° and 105°C.

For color centers in the crystal, we may use N_i, the number of i

centers per cubic centimeter as a reference function, and the refer-

ence state may be chosen as the state in which Henry's Law is obeyed,

i.e., $N_i \rightarrow 0$. The standard state is taken to be $N_i = 1$. Since Henry's

Law is expected to hold up to a concentration many orders of magni-

tude greater than $N_i = 1$, the standard state has the properties of

the reference state. From Henry's Law, with this choice of standard

state, we may add another definition of a_i, i.e.,

$$\lim_{N_i \rightarrow 0} \frac{a_i}{N_i} = 1$$

Considering the reaction 2 F = M,

we may write

$$\bar{G}_M - 2 \bar{G}_F = \bar{G}^o_M - \bar{G}^o_F + RT \ln a_M - 2 RT \ln a_F$$

or

$$\widetilde{\Delta G} = \widetilde{\Delta G^o} + RT \ln \frac{a_M}{a_F^2}$$

Knowing that at the equilibrium state,

$$\widetilde{\Delta G} = 0$$

so that

$$\widetilde{\Delta G^o} = - RT \ln K_1, \text{ where } K_1 = \frac{a_M}{a_F^2} \quad (3)$$

Remembering the Gibb-Helmholtz equation,

$$\frac{\partial (\widetilde{\Delta G}^o)}{\partial T} = \frac{\widetilde{\Delta G}^o - \widetilde{\Delta H}^o}{T} = -\widetilde{\Delta S}^o , \qquad (4)$$

and substituting (3) into (4), we get

$$\frac{\partial \ln K_1}{\partial (1/T)} = -\widetilde{\Delta H}^o/R .$$

Here we may make two simplifications: (a) the difference between $\widetilde{\Delta H}^o$ and $\widetilde{\Delta H}$ is negligible, and (b) since the concentration range of F center and M center is dilute enough, we may assume that $a_i = N_i$. We may calculate K, $\widetilde{\Delta G}^o$, and $\widetilde{\Delta S}^o$ for the reaction 2 F = M by utilizing equation (3), (4), (5) and the equilibrium concentrations of F and M centers calculated from the data of Figures 5 and 6. Numerical values are listed in Tables 1 and 2.

A graph in Figure 6 showing the variation of log K with respect to the reciprocal of temperature, gives approximately straight lines, with the slope of $-\widetilde{\Delta H}^o/2.303 \cdot R$.

Mole Fraction as a Reference Function

Although the above frame work is convenient to use for color center work, it does have the disadvantage that one is not able readily to compare the state function changes to those of common chemical reactions. Following an argument similar to that in the previous section, but using the mole fraction as unit of concentrations,

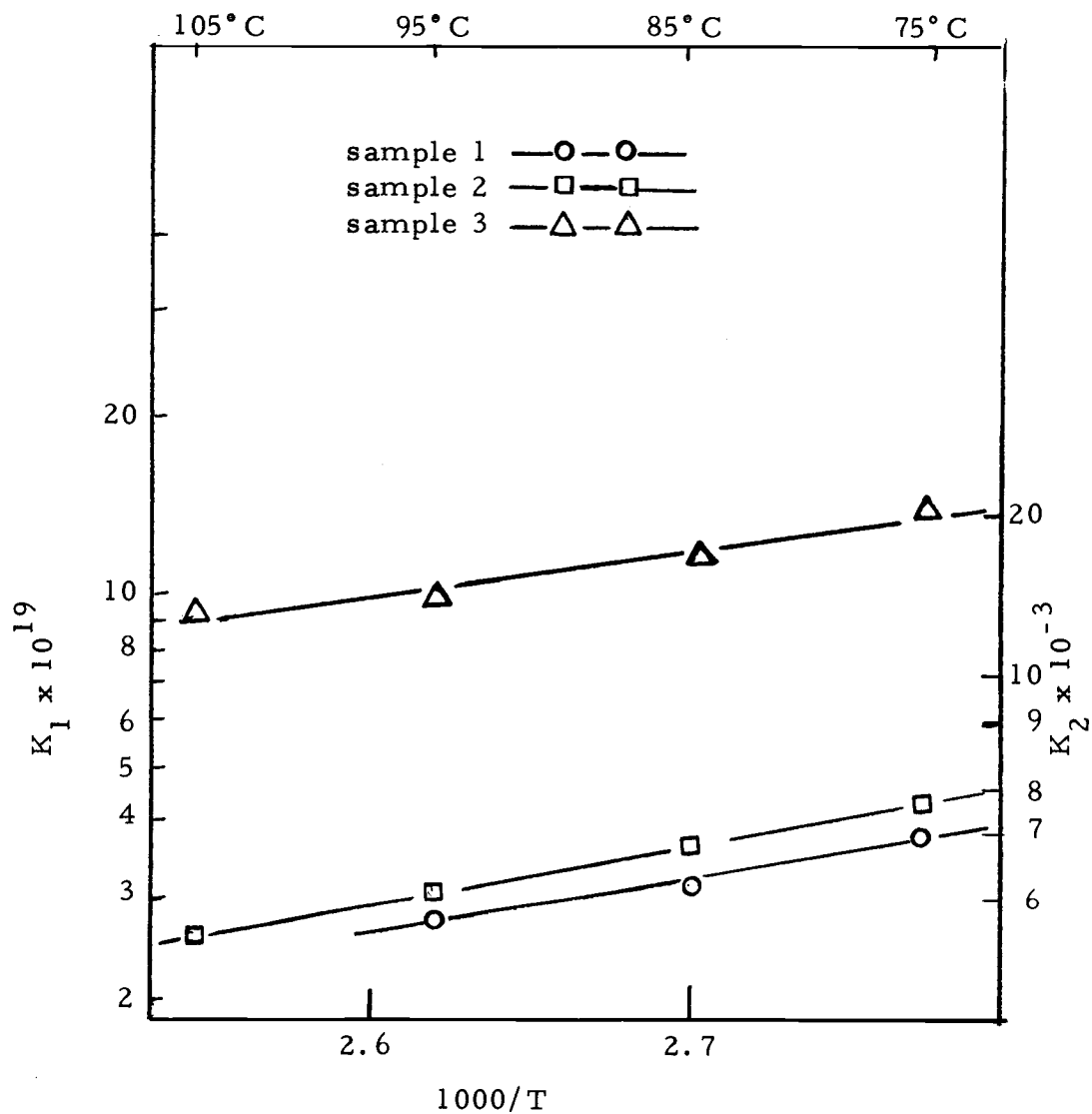Figure 6. Variation of equilibrium constant with 1/T.

K is found to be

$$K_2 = \frac{X_M}{X_F^2}$$

X_M is the mole fraction of M centers, X_F is the mole fraction of F

centers. Equation (3), (4), (5) are still valid. In this case the

standard state is a hypothetical one, that is, a state of unit mole

fraction but in which Henry's Law is obeyed. Calculated data are

tabulated in Table 3.

Table 1. Values of K and $\widetilde{\Delta H}^o$ from Figure 6.

Sample	$\widetilde{\Delta H}^o$ (Kcal)	Temp. (^oK)	K_1 x 10^{19} (CC./Centers)
1	-3.69	348	3.80
		358	3.19
		368	2.79
2	-3.88	348	4.24
		358	3.70
		368	3.10
		378	2.66
3	-3.70	348	14.8
		358	11.9
		368	10.0
		378	9.1

Average and Standard Deviation $\widetilde{\Delta H}^o$ = -3.76 ± 0.08[1]

[1] The error in $\widetilde{\Delta H}^o$ in this table and also errors in $\widetilde{\Delta G}^o$, $\widetilde{\Delta S}^o$, $\widetilde{\Delta H}^o$ in tables 2 and 3 are all based on statistical analysis only.

Table 2. $\widetilde{\Delta G}^o$ and $\widetilde{\Delta S}^o$ for the reaction $2\,F = M$ with center/cm^3 as reference function.

Sample	Temp. (^oK)	$\widetilde{\Delta G}^o$ (Kcal)	$\widetilde{\Delta S}^o$ (cal/deq)
1	348	29.3	-94.9
	358	30.3	-94.9
	368	31.2	-94.9
2	348	29.3	-95.2
	358	30.2	-95.2
	368	31.2	-95.2
	378	32.1	-95.3
3	348	28.4	-92.2
	358	29.4	-92.3
	368	30.3	-92.4
	398	31.2	-92.3
Average and Deviation	348	29.0 ± 0.4	-94.1 ± 1.3
	358	30.0 ± 0.4	-94.2 + 1.3
	368	30.9 ± 0.4	- 94.2 ± 1.3
	378	31.6 ± 0.5	-93.8 ± 1.4

Table 3. Values of $\widetilde{\Delta H}^o$, K, $\widetilde{\Delta G}^o$, and $\widetilde{\Delta S}^o$ for 2 F = M with mole fraction as a reference function.

Sample	$\widetilde{\Delta H}^o$ (Kcal)	Temp. (^oK)	$K_2 \times 10^{-3}$	$\widetilde{\Delta G}^o$ (Kcal)	$\widetilde{\Delta S}^o$ (cal/deq)
1	-3.69	348	5.32	-5.93	6.4
		358	4.34	-5.96	6.3
		368	3.92	-6.00	6.4
2	-3.88	348	5.94	-6.01	6.1
		358	5.18	-6.08	6.2
		368	4.34	-6.12	6.1
		378	3.72	-6.18	6.1
3	-3.70	348	20.80	-6.87	9.1
		358	16.66	-6.90	9.0
		368	14.00	-6.97	8.9
		378	12.74	-7.08	9.0
Average and Deviation	-3.76 ± 0.08	368		-6.27 ± 0.42	7.2 ± 1.3
		358		-6.31 ± 0.42	7.2 ± 1.3
		368		-6.36 ± 0.43	7.2 ± 1.3
		378		-6.63 ± 0.45	7.6 ± 1.4

THEORETICAL INVESTIGATION OF
BINDING ENERGY OF M CENTER IN KBr

At the beginning, we accept the F_2 model for the M center. We know that the accepted model for the F center is an electron trapped in a halogen-ion vacancy; in another words, we may consider the F center as roughly equivalent to a hydrogen atom (an electron moving in the field of a positive charge). The dielectric constant differs of course from that in vacuo. Under this circumstance, the M center can be considered as the analogue of the H_2 molecule and therefore we expect the F_2 model of the M center to have the same kind of electronic states as the H_2 molecule. The H_2 molecule may be thought of as being formed by bringing together two hydrogen atoms (separated-atom designation) or by splitting a helium atom (united-atom designation). In the process of bringing together two H atoms until finally a He atom is formed, there is a continuous variation of the electronic states of the H atom into the He atom (8). We may use Figure 7 to show how the molecular orbitals correlate with the separated and united atom states.

The three lowest-energy molecular orbitals for H_2, in order of ascending energy, are designated $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^1\Sigma_u^+$. Their energies, according to Kolos (10), as a function of internuclear
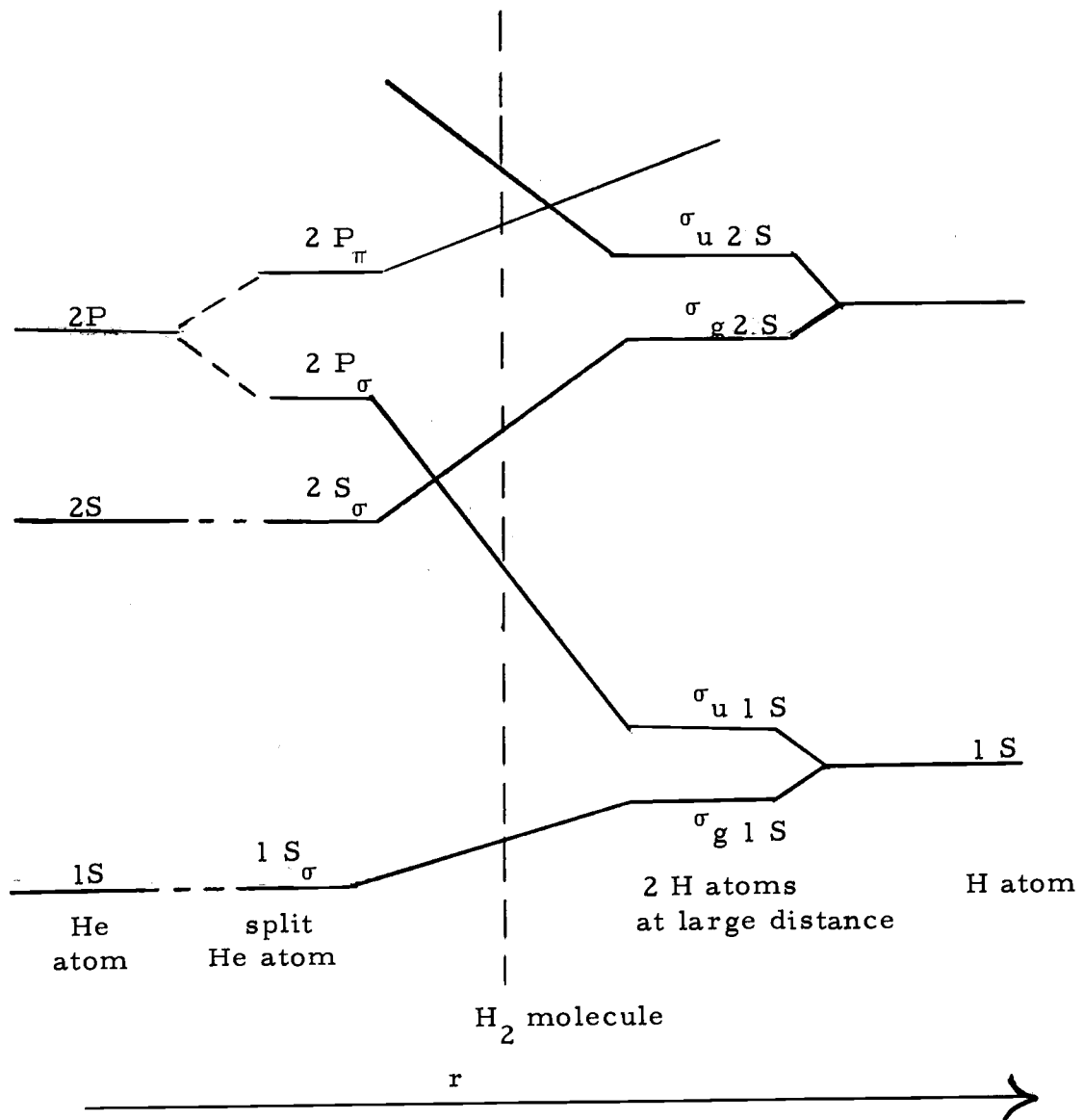
Figure 7. Correlation diagram between He and H atoms.

separation, are shown in Figure 8. The binding energy of the H_2 molecule is D_b.

Concerning with the M center problem, van Doorn (28) used a continuum model to solve it. He considered the Schrödinger equation for a hydrogen molecule with electrons of effective mass, m*, immersed in a dielectric medium with dielectric constant ϵ. This result is shown in Figure 8, in which the energy coordinate is in units of $(\epsilon^2/m*)E$ and the internuclear separation is in units of $(m*/\epsilon)r$, with E and r in customary atomic units of energy and distance.

In KBr, assuming each vacancy of the M center to be at a normal anion site, the analogue of the internuclear distance is

$$d \sqrt{2} = 3.29 \ \sqrt{2} \ = 4.62 \ \overset{o}{A},$$

where d is the cation-anion separation. We take m* for the electron to be 1, ϵ is taken to be the high frequency dielectric constant. For KBr, it is 2.43.[1] From the diagram, Figure 8:

$$m*/\epsilon \ \cdot \ r \ = \ \frac{r}{\epsilon} \ = \ \frac{4.62}{2.34} \ = 1.9$$

At this internuclear separation,

$$\epsilon^2/m* \ \cdot \ E \ = \ -0.95, \text{ and consequently,}$$

$$E = 0.16 \ (ev)$$

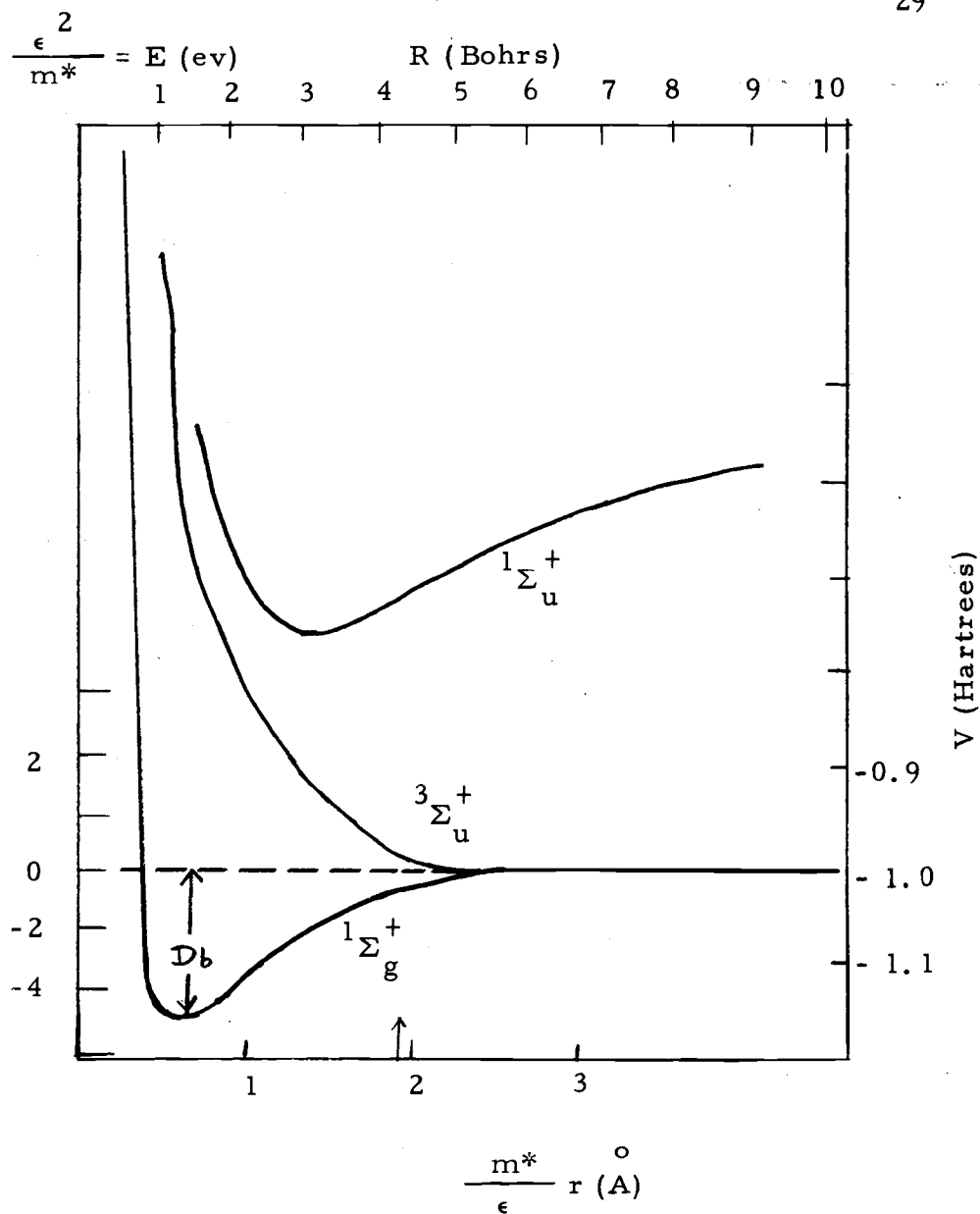[1] By using $n_\infty^2 = \epsilon$.

Figure 8. Energy of some electronic states of H_2 molecule, immersed in a dielectric medium, as a function of the internuclear distance r; also, this diagram is shown by using Bohr radius and Hartree units.

Under this kind of theoretical approach, the binding energy for KBr

is 0.16 ev. Of course, the value obtained cannot be considered as

being very reliable because of the limited applicability of the con-

tinuum model of the M center in KBr.

DISCUSSION

Dealing with KBr, the most difficult part lies in the high con-
centration of F center. To detect the change of equilibrium of M-
center concentration with temperature effectively by using the
Beckman DU spectrophotometer, a very high concentration of F
center has to be used. Usually the high absorbance of the F band is
beyond the limit of measurement of the Beckman spectrophotometer.
Although we may use another instrument (Perkin-Elmer double
.beam spectrophotometer) to measure the concentration of F band, in
this case light-attenuating screens have to be used in the reference
beam, which reduces the accuracy. The variation of equilibrium
F-center concentration with the temperature is too small to detect.

Due to the inaccurate measurement of F-center concentration,
the Gibbs free energy, the equilibrium constant and the entropy are
not highly reliable, but the binding energy, 0.16 ev, whose accuracy
is less dependent on the accuracy of the F-center concentration is in
agreement with the theoretical result, 0.16 ev, found by using the
continuum model of M center.

Matsuyama (15) also did similar work on KBr and the binding
energy was estimated as 0.08 ± 0.02 ev. In his experiment, the
points on the diagram of log K vs. 1/T are so scattered that they
think it originated from the structure-sensitivity of the growth of M

centers in KBr. (They used the crystals grown from their laboratory
as well as those from Harshaw Chemical Co.) They used the least-
square method to get a straight line, in another words, they omit
the structure-sensitivity. Also, it seems that they did not use the
technique of approaching the equilibrium states from under and over-
saturation of M centers. In this case, the final values may not be
actually the equilibrium values.

There are two values for the oscillator strength for the M
center in KBr, that is, 0.27 by Faraday and Compton (5) and 0.11
by Jain and Jain (7). By using these two values, the binding energy
can vary from 0.20 to 0.16 ev. Matsuyama (15) used the value 1.0
for the oscillator strength for KBr which may lead to some disagree-
ment in binding energy measurements. In this experiment, 0.27 for
oscillator strength was used. This value leads to much better
agreement both with the theoretical binding energy and with the
theoretical entropy change.

Let us review the meaning of the numerical values obtained
for the standard entropy change especially when the number of
centers/centimeter was used as the reference state. Consider the
reaction

$$2F = M$$
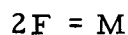
The standard state is one center/cubic centimeter. Let us calculate
the entropy change when two F centers in N sites of crystal lattice
are converted to an M center located on any one of N sites. The

number of ways to put an M center on N sites of the KBr lattice is

12 N/2 = 6 N and number of ways to put two F centers in this unit

crystal is N (N - 1) = N^2, so the $\widetilde{\Delta S}^o$ will be equal to k ln $6N/N^2$ =

k ln $\dfrac{6}{N}$ per M center with N sites/cm^3.

At the beginning we set the standard state being one center per

cubic centimeter, but actually we have two F centers in this volume

Therefore, we have to make a correction, that is

$$\widetilde{\Delta S}^o = k \ln \frac{6}{N} - k \ln 2$$

per M center or

$$\widetilde{\Delta S}^o = R \ln \frac{6}{N} - R \ln 2 = -99.32 \text{ cal/deg.}$$

per mole of M centers. This agrees well with the observed values

(Table 2), showing that the configurational entropy constitutes prac-

tically the entire contribution to $\widetilde{\Delta S}^o$.

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