

Compensation effect in thermally activated processes

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We explain the compensation effect by counting the ways in which the heat bath can furnish the energy necessary to surmount the barriers.

I. INTRODUCTION

In most thermally activated processes a plot of the logarithm of the reaction rate versus the inverse of the absolute temperature is a straight line. This so-called Arrhenius law may be written

$$\ln k = \ln A - \beta \epsilon_b,$$

where ϵ_b , the slope of the Arrhenius plot, is the so-called activation or barrier energy, k is the reaction rate, $\beta = 1/k_B T$, k_B is Boltzmann's constant, T is the absolute temperature, and A is a preexponential factor [so called because the law can be written $k = A \exp(-\beta \epsilon_b)$].

It frequently happens that the Arrhenius plots of different members of a family of reactions are straight lines with different slopes, which (when extrapolated if necessary) intersect at a common point, at least approximately. The temperature coordinate of this point is called the compensation temperature, or the isokinetic temperature T_c . Such behavior is described phenomenologically by writing $A = A_0 \exp(\beta_c \epsilon_b)$; evidently, this gives $k = A_0 \exp[-(\beta - \beta_c) \epsilon_b]$, i.e., a compensation effect with isokinetic temperature $1/k_B \beta_c$. When the effect is present, a plot of $\ln A$ versus the different ϵ_b 's of the family members gives a straight line of slope β_c . The compensation effect was first reported by Constable¹ almost sixty years ago in relation to dehydrogenation of ethanol on a copper catalyst. At first, the effect was thought to be limited to heterogeneous catalysis²⁻⁴ but subsequently it was found in other thermally activated rate processes as well.

Varying the surface treatment of the copper catalyst, Constable found a variation of ϵ_b from 20 to 24 kcal/mol, accompanied by a change in A by a factor of 10, and a compensation temperature of 875 K. An important review is that of Cramer² who listed many examples and also discussed a statistical distribution in the properties of catalytically

active centers as a possible theoretical explanation. This model fails to explain cases in which the substrate is fixed and the reactants are different, as is the case, for example, in the decomposition of ethanol, *n*-propanol, and *n*-butanol on Nd_2O_3 (Ref. 5), or in the dissociative adsorption reactions of methane, ethane, and propane on nickel.³

Another example of the compensation effect is ethane hydrogenolysis on silica-supported metals.⁶ In this case the reaction rate is measured at fixed partial pressure of ethane and hydrogen. The reported results show activation energies between 21.4 and 58 kcal/mol, and prefactors between 4.5×10^{20} and 3.7×10^{33} mole/sec cm². The metals cobalt, nickel, and rhenium displayed a compensation temperature of 1255 K, while ruthenium, rhodium, palladium, osmium, iridium, and platinum had a T_c of 380 K. It is important to observe that the experimental measurements were made at temperatures between 400 and 600 K. Thus measurements were taken at temperatures lower than the compensation temperature in one case, and at temperatures higher than T_c in the other. The compensation temperatures (as in most cases) had to be found by extrapolation.

The compensation effect was also reported in thermally activated rate processes other than heterogeneous catalysis. In 1937 Meyer and Nedel⁷ reported a compensation effect for the activated electron conductivity of oxide semiconductors (WO_3 , Al_2O_3 , Ta_2O_5 , and Fe_2O_3). For this reason the effect is often called the Meyer-Nedel rule. Another example is the electrical conductivity of a single crystal of Cu_2O ,⁸ where measurements at temperatures between 380 and 555 K are in agreement with the Meyer-Nedel rule. The activation energies varied from 0.3 eV up to 0.5 eV, and a T_c of 815 K was reported. The effect is also seen for NiO exposed to different oxygen pressures (1.2×10^{-1} up to 1 atm), with an observed T_c of 1500 K.⁹ Also, organic semiconductors show the compensation effect.¹⁰ For example, oxidized cholesterol complexes

yield a T_c of 500 K and activation energies between 0.8 and 3 eV.¹¹ The effect has also been reported for complex biophysical systems. When Sindibis virus is heated at temperatures between 317 and 320 K in different concentrations of Na_2HPO_4 and MgSO_4 the corresponding death-rate—temperature plots show compensation temperatures of 330 K for MgSO_4 and 329 K for Na_2HPO_4 .¹² Denaturation of proteins such as hemoglobin, egg albumin, invertase, and other biopolymers at different¹³ pH shows the effect, as does the complex process of the thermal death of bacteria and of yeast.¹⁴ *Pseudomonas fragi*, *Staphylococcus aureus*, and two strains of salmonella show a compensation temperature of 331 K.

Returning to more ordinary cases, the effect is also observed in homogeneous phase reactions¹⁵ in solutions, e.g., decomposition of triethylsulfonium in hydroxylic solvents, thermal decomposition, e.g., manganese (II) carbonates prepared in the presence of metal ions¹⁶ like Al^{3+} and Na^+ ; thermal dissociation of solids under different pressures of selected gases,¹⁷ e.g., carbonates under CO_2 , etc. In most cases, the energy transfer from the heat bath to the reactants can be regarded as absorption, by the reactants, of elementary excitations of the heat bath. Perhaps the most obvious example is desorption of an adatom from the surface of an insulator. Here the heat bath is the solid, and the elementary excitations are the phonons. In reactions over certain metal surfaces on the other hand, the dominant excitations might be the hole-electron pairs of the substrate, though phonons may also play an important role. In a homogeneous phase reaction in a liquid, sound waves may qualify as excitations.

The total probability of a reaction is evidently the sum of the probabilities that the reactants absorb one, two, three, etc., excitations with a total energy exceeding the barrier energy. The probability for absorption of exactly n excitations with energy ϵ is the square of the T -matrix element for this process, multiplied by $\rho_n(\epsilon)$, the density of states of n excitations with total energy ϵ . We shall show that the sum over all n tends to behave like $e^{-(\beta-\beta_c)\epsilon}$, where $\beta=1/k_B T$, k_B is Boltzmann's constant, and T is the absolute temperature. $\beta_c=1/k_B T_c$ is a function of a suitable coupling parameter (not necessarily the coupling strength itself), and a function of the way the single-excitation density $\rho_1(\epsilon)$ depends on ϵ . In addition, β_c (or T_c) may be weakly dependent on ϵ . Thus we propose that the compensation effect may be regarded as resulting from a kind of "dynamical" entropy of the heat bath. It results from counting the number of ways in which the heat bath

can furnish the energy needed to overcome the barrier. The qualifying adjective is needed because the various ways are weighted by transition matrix elements. We shall see, however, that this weighting does not have a major influence on the proposed explanation.

II. GENERAL FORMALISM

The probability of escape over the barrier may be written as a sum of all possible processes leading to escape. We first arrange that sum so as to take maximum advantage of any helpful features that the transition matrix elements may possess. The general formula for the transition rate per unit time is

$$\frac{2\pi}{\hbar} \sum_{f,i} |\langle f|T|i\rangle|^2 \frac{e^{-BE_i}}{Z} \delta(E_f - E_i), \quad (2.1)$$

where $\{i\}$ is the complete set of quantum numbers of the system in the reactant well and $\{f\}$ is the set of quantum numbers of the reacted system. $\langle f|T|i\rangle$ is the T -matrix element. Z is the reactant-plus-bath partition function. Formula (2.1) assumes that the conditions for the validity of absolute rate theory are met, i.e., that quasiequilibrium conditions prevail during the reaction. Thus we suppose that thermal equilibration among the reactants levels is very much faster than the rate of transition to the reaction products. When this is not the case, the relation between prefactor- and T -matrix elements is less direct.

In the present case we take $|i\rangle$ and $|f\rangle$ to be direct products of reactant states and bath excitation states. The latter are either inherently Boson excitations (e.g., phonons) or behave very nearly as such (e.g., hole-electron pairs, magnons, etc.). Thus we may write

$$\begin{aligned} |i\rangle &= |E_i^0, \{n_k + m_k\}\rangle, \quad |f\rangle = |E_f^0, \{m_k\}\rangle, \\ E_i &= E_i^0 + \sum_k (m_k + n_k)\epsilon_k, \\ E_f &= E_f^0 + \sum_k m_k\epsilon_k, \end{aligned}$$

where the bath in its initial and final states is characterized by the excitation number sets $\{m_k + n_k\}$ and $\{n_k\}$, respectively, where E_i^0 is the reactant energy in a bound state of the reactant well and where E_f^0 is the energy of the reaction products. k labels the excitations, and ϵ_k labels the energy of the k th of these. Neglecting tunneling, we have $E_i^0 < \epsilon_b$ and $E_f^0 > \epsilon_b$, where ϵ_b is the barrier energy. The transition occurs by absorption of the excess n_k

excitations.

The nature of the bath-reactant coupling is normally such that:

(a) $|\langle f|T|i\rangle|^2$ depends on E_i^0, E_f^0 , and the sets $\{n_k\}, \{m_k\}$.

(b) Because of the way we shall arrange the order of summation in (2.1), $|\langle f|T|i\rangle|^2$ will depend on $\{n_k\}$ mainly through the sum $n = \sum_k n_k$. Related to this is the fact that it does not depend much on k . This is particularly clear when \vec{k} is considered to be a wave number, and the reactant-bath coupling is highly localized. The strongest dependence on n is through the appropriate coupling parameter (see example below), which is raised to the n th power. Any residual dependence of T on the individual distribution of the m_k 's (rather than on just $\sum m_k$) can be expressed as a minor modification of the simple excitation state density.

(c) Except in the Born approximation for T , $|\langle f|T|i\rangle|^2$ will also depend on $\sum \epsilon_k n_k = E_f^0 - E_i^0 = \epsilon$. Evidently, this quantity occurs in the energy denominator of all higher terms in the perturbation series for T . However, this dependence is not strong, and in cases where the absorption of n quanta appears only beyond the Born term, the integration over intermediate states will tend to reduce the ϵ dependence to simple logarithmic.

The sum (2.1) is therefore adequately represented by

$$\frac{2\pi}{\hbar} \sum_i \int_{\epsilon_b - E_i^0}^{\epsilon_c} d\epsilon e^{-\beta\epsilon} R_f(E_i^0 + \epsilon) \times \sum_{\text{all } \{n_k\}} |T(E_i^0, n, \epsilon)|^2 \frac{e^{-\beta E_i^0}}{Z_r} \times \delta \left(\epsilon - \sum_k n_k \epsilon_k \right) \quad (2.2)$$

where Z_r is the partition function of the reactants alone. In this formula $R_f(E)$ is the final-state density of the reaction products at energy E . ϵ_c is a cutoff to be discussed later.

As we shall see, summing over the n_k is best done in the order

$$\sum_{\{n_k\}} = \sum_n \sum_{\sum n_k = n} .$$

We then have

$$\sum_{n_1} \cdots \sum_{n_s} \delta \left(\epsilon - \sum_k \epsilon_k n_k \right) = \rho_n(\epsilon),$$

which is the density of states of n independent excitations of total energy ϵ , or in other words, the convolution of n single-excitation densities of state:

$$\rho_n(\epsilon) = \int_{\sum_i \epsilon_i = \epsilon} \rho(\epsilon_1) \rho(\epsilon_2) \cdots \rho(\epsilon_n) \times d\epsilon_1 \cdots d\epsilon_n .$$

For simplicity, consider only one bound state in the well, choosing its energy to be zero. Then the result for the rate R

$$R = \frac{2\pi}{\hbar} \int_{\epsilon_b}^{\epsilon_c} d\epsilon e^{-\beta\epsilon} R_f(\epsilon) \times \sum_n |T(n, \epsilon)|^2 \rho_n(\epsilon) . \quad (2.3)$$

Let

$$\tilde{\rho}_1(p) = \int_0^\infty e^{-p\epsilon} \rho_1(\epsilon) d\epsilon .$$

Then the Laplace transform of $\rho_n(\epsilon)$ is $[\rho_1(p)]^n$. Therefore, the rate is

$$R = \frac{1}{i\hbar} \int_{\epsilon_b}^{\epsilon_c} d\epsilon e^{-\beta\epsilon} R_f(\epsilon) \times \int_{c-i\infty}^{c+i\infty} dp e^{p\epsilon} \times \sum_{n=1}^{\infty} |T(n, \epsilon)|^2 [\tilde{\rho}_1(p)]^n \quad (2.4)$$

where the integration contour runs to the right of all singularities of the integrand.

A. Compensation effect and radius of convergence

Consider the sum

$$\sum_{n=1}^{\infty} |T(n, \epsilon)|^2 \tilde{\rho}_1^n \quad (2.5)$$

as a function of the complex variable $\tilde{\rho}_1$ (not p). Its radius of convergence in the $\tilde{\rho}_1$ plane is

$$\mathcal{R}(\epsilon) = \lim_{n \rightarrow \infty} |T(n, \epsilon)|^{-2/n},$$

a weakly varying function of ϵ . We shall assume that \mathcal{R} is finite (and at least in the example discussed in Sec. V, it indeed is). Since the $|T(n, \epsilon)|^2$ are positive, the point $\tilde{\rho}_1 = \mathcal{R}(\epsilon)$ in the $\tilde{\rho}_1$ plane is a singularity of the sum (2.5) (see Ref. 18). We shall assume it to be a simple pole. There may be other singularities on the circle of convergence, all of which map into corresponding singularities in the p

plane. However, we shall see presently that for a large class of $\rho_1(\epsilon)$, the singularity $\tilde{\rho}_1 = \mathcal{R}(\epsilon)$ maps into a *real* positive singularity in the p plane, which is further to the right in the p plane than all the others. It therefore dominates the contour integral in Eq. (2.4), for sufficiently large ϵ . If it is a simple pole at

$$p = \beta_c(\epsilon),$$

it yields a residue proportional to $e^{\epsilon\beta_c(\epsilon)}$. The dependence of β_c on ϵ is generally negligible, particularly at large values of ϵ . If $R_f(E)$ in Eq. (2.4) is also slowly varying with E , the result of the integration is very nearly, for $\beta \gg \beta_c$,

$$R = \mathcal{P} e^{-(\beta - \beta_c)\epsilon_b} \quad (2.6)$$

where the preexponential factor is $\mathcal{P} = (2\pi/\hbar)\bar{R}_f$ times a nonexponential function of β_c . The upper cutoff in the integral (2.4) may be neglected for $\beta > \beta_c$. Formula (2.6) shows that there will be a compensation effect for any family of reactions in which ϵ_b varies from one member to another, while the effective coupling to the bath remains the same for all members. "Effective coupling" here does not necessarily mean the coupling *strength*. In the example of Sec. V, it is the *shape* of the interaction that must be the same, not the strength, and even the shape enters only weakly, as we shall see. Likewise, in the case of weak coupling to conduction electrons, the metal substrate must stay the same, not the coupling strength (see Sec. VI).

The singularities in the p plane are given by

$$\mathcal{R} = \int_0^\infty e^{-p\epsilon} \rho_1(\epsilon) d\epsilon = \tilde{\rho}_1(p). \quad (2.7)$$

Suppose that

$$\tilde{\rho}_1(0) = \int_0^\infty \rho_1(\epsilon) d\epsilon > \mathcal{R}$$

and that $\rho_1(\epsilon)$ increases less rapidly with ϵ than an exponential does. Then $\tilde{\rho}_1(p)$ decreases steadily, with increasing real p yielding a singularity on the real p axis, at p_0 for example. Furthermore, its value is greater than the real value of other possible singularities on the boundary of convergence. Suppose there were a root of Eq. (2.7) at $p = p' + ip''$. Then

$$\begin{aligned} \mathcal{R} &= \int e^{-p'\epsilon} \cos(p''\epsilon) \rho_1(\epsilon) d\epsilon \\ &= \int e^{-p_0\epsilon} \rho_1(\epsilon) d\epsilon. \end{aligned} \quad (2.8)$$

But

$$\int e^{-p'\epsilon} \cos(p''\epsilon) \rho_1(\epsilon) d\epsilon < \int e^{-p_0\epsilon} \rho_1(\epsilon) d\epsilon.$$

Hence p' must be less than p_0 if (2.8) is to hold. For a $\rho_1(\epsilon)$ for which

$$\mathcal{R} > \int_0^\infty \rho(\epsilon) d\epsilon,$$

there are no real singularities, but the complex ones occur in complex conjugate pairs. The pair with the largest positive real part then dominates. If that pair is $\beta'_c \pm i\beta''_c$, the rate still has the form (2.6), with β'_c replacing β_c . For cases in which $\rho_1(\epsilon)$ has an upper cutoff energy (e.g., the Debye energy in the case of phonons) β'_c could, in principle, turn out negative. The extrapolated Arrhenius plots for various ϵ_b would then intersect at a negative temperature. No observations of such an "anticompensation effect" have, however, been reported in the literature.

Note that the form of the result (2.6) would be the same if the dominant singularity were a higher-order pole or even a branch point. In the latter case, the integral along the edges of the cut is still dominated by the value of the integrand at the branch point. Our method will fail only if the circle of convergence of the series (2.5), in the ρ_1 plane, is a natural boundary of the function represented by (2.5). We doubt if physical examples of this case can be constructed.

Finally, we note that these results change very little when the reactant well has several bound states. In fact, if the dependence of the T matrix on E_i^0 is neglected, formulas (2.2)–(2.4) remain unchanged. (The sum over i then just cancels Z_r .)

III. DEPENDENCE OF T_c ON THE FORM OF $\rho_1(\epsilon)$

For the common case of a power law of $\rho_1(\epsilon)$ [sound waves in fluids $\rho_1(\epsilon) \sim \epsilon^2$, electron-hole pairs $\rho_1(\epsilon) \sim \epsilon$, magnons in a continuum theory $\rho_1 \sim \sqrt{\epsilon}$] we have

$$\tilde{\rho}_1(p) = \frac{\Gamma(\nu+1)}{\epsilon_0^{\nu+1}} \frac{1}{p^{\nu+1}}$$

where Γ is the gamma function, $\rho_1(\epsilon) = \epsilon^\nu / \epsilon_0^{\nu+1}$, and ϵ_0 sets the energy scale (for sound waves $\epsilon_0 \approx \hbar v R^{1/3}$, v is the sound velocity, and R is the density; for hole-electron pairs, ϵ_0 is approximately equal to Fermi energy, and for magnons ϵ_0 is approximately equal to the exchange integral). Consequently, the dominant pole is $[\Gamma(\nu+1)]^{1/\nu+1} \epsilon_0^{-1}$, and so

$$T_c = \frac{\epsilon_0}{k[\Gamma(\nu+1)]^{\nu+1}}.$$

For the case of $\rho_1(\epsilon)$ with an upper cutoff ϵ_u

(e.g., phonons or magnons in ordered solids) the inequality $\tilde{\rho}_1(0) > \mathcal{R}$ will not hold for too small a value of $\rho_1(\epsilon)$, or too small a radius of convergence. In fact, if at fixed \mathcal{R} the cutoff is steadily reduced from a large value, the dominant pole moves steadily towards the origin along the real axis, attaining 0 (infinite T_c) when

$$\mathcal{R} = \int_0^{\epsilon_u} \rho_1(\epsilon) d\epsilon.$$

As ϵ_u is further decreased, the dominant pole splits into a complex conjugate pair $\beta'_c \pm i\beta''_c$, and (if $\beta'_c > 0$) again gives a finite $T_c = 1/\beta'_c$. In particular, for the case of Debye spectrum with cutoff energy ϵ_d we have $\rho_1(\epsilon) = 3N\epsilon^2/\epsilon_d^3$, where in the simplest approximation the numerical factor N is 3. For large N , we get $kT_c \approx \epsilon_d/(6N)^{1/3}$. As N decreases, kT_c increases, reaching ∞ at $N=1$, in the manner

$kT_c \approx \frac{3}{4}\epsilon_d/(N-1)$. We have not pursued kT_c into the complex plane for this case.

IV. GENERAL BEHAVIOR

In Eq. (2.4) we have a cutoff energy ϵ_c . This is defined as the energy at which other reaction channels open up at the expense of the one under study. For the case where β is less than or of the same order as β_c , the cutoff energy is important. We can no longer neglect its contribution to the rate as we did in the case $\beta \gg \beta_c$. For all β we get, from (2.4),

$$R = \frac{2\pi}{\hbar} A(\beta_c) \int_{\epsilon_b}^{\epsilon_c} R_f(\epsilon) e^{-(\beta-\beta_c)\epsilon} d\epsilon$$

where $A(\beta_c)$ is the residue of the function represented by (2.5) at the pole β_c . For example, if the final state is a "free" state of reaction products, $R_f(\epsilon) \sim \beta\sqrt{\epsilon-\epsilon_b}$, we get

$$R = \frac{C\sqrt{\epsilon_c-\epsilon_b}}{\beta-\beta_c} \left[\frac{\sqrt{\pi} \operatorname{erf}\{[(\epsilon_c-\epsilon_b)(\beta-\beta_c)]^{1/2}\}}{2 [(\epsilon_c-\epsilon_b)(\beta-\beta_c)]^{1/2}} e^{-(\beta-\beta_c)\epsilon_b} - e^{-(\beta-\beta_c)\epsilon_c} \right]$$

where $c = A(\beta_c)B$ and $\operatorname{erf}(x)$ is the error function. Using its asymptotic behaviors¹⁹ we get

$$R_{>} = \frac{C}{\beta} e^{-(\beta-\beta_c)\epsilon_b},$$

$$R_{<} = \frac{C\sqrt{\epsilon_c-\epsilon_b}}{\beta_c} e^{(\beta_c-\beta)\epsilon_c},$$

$$R_{=} = C \frac{2}{3} \sqrt{\epsilon_c-\epsilon_b} \left[\frac{e^{-(\beta-\beta_c)\epsilon_b} - e^{-(\beta-\beta_c)\epsilon_c}}{\beta-\beta_c} \right]$$

for $\beta \gg \beta_c$, $\beta \ll \beta_c$, and $\beta \simeq \beta_c$.

In the case of β_c being the complex pole with the largest real part, we sum the contribution of such a pole and its complex conjugate. The expression for the rate becomes

$$R = \frac{4\pi}{\hbar} |A(\beta_c)| \int_{\epsilon_b}^{\epsilon_c} R_f(\epsilon) e^{-(\beta-\beta'_c)\epsilon} \cos(\varphi - \beta''_c\epsilon) d\epsilon$$

where

$$\beta_c \equiv \beta'_c \pm i\beta''_c$$

and

$$\varphi = \tan^{-1}[\operatorname{Im}A(\beta_c)/\operatorname{Re}A(\beta_c)].$$

To illustrate the changes let us consider $R_f(\epsilon) = B_1(\epsilon - \epsilon_b)$. We get,²⁰ for all β , the expression

$$R = \frac{4\pi}{\hbar} |A(\beta_c)| B_1 [f_1(\beta, \beta'_c, \beta''_c; \epsilon_b) e^{-(\beta-\beta'_c)\epsilon_b} - g_1(\beta, \beta'_c, \beta''_c; \epsilon_b, \epsilon_c) e^{-(\beta-\beta_c)\epsilon_c}]$$

where

$$f_1(\beta; \beta'_c, \beta''_c; \epsilon_b) = \frac{(\beta - \beta'_c)^2 - \beta''_c \cos(\varphi - \beta''_c\epsilon_b) - 2\beta''_c(\beta - \beta''_c) \sin(\varphi - \beta''_c\epsilon_b)}{[(\beta - \beta'_c)^2 + \beta''_c^2]^2}$$

and

$$g_1(\beta; \beta'_c, \beta''_c; \epsilon_b, \epsilon_c) = \frac{(\beta - \beta'_c)(\epsilon_c - \epsilon_b) \cos(\varphi - \beta''_c \epsilon_c) + \beta''_c(\epsilon_c - \epsilon_b) \sin(\varphi - \epsilon_c \beta''_c)}{(\beta - \beta'_c)^2 + \beta''_c{}^2} + f_1(\beta', \beta'_c, \beta''_c; \epsilon_c).$$

If we compare these results with the case where β_c is real, we notice that the only change in the rate is a factor of $\cos(\varphi - \beta''_c \epsilon_c)$ for $\beta \ll \beta'_c$, and a factor $\cos(\varphi - \beta''_c \epsilon_b)$ for $\beta \gg \beta'_c$ ($\beta' \gg \beta''_c$).

We have considered, up to now, only one energy level in the reactant well. For the multilevel case, we need to add the contribution coming from each of the levels multiplied by a proper weight factor. In the case of a Boltzmann population we obtain

$$R = F(\beta; \beta'_c, \beta''_c; \epsilon_b) e^{-(\beta - \beta'_c) \epsilon_b} - G(\beta; \beta'_c, \beta''_c; \epsilon_c, \epsilon_b) e^{-(\beta - \beta'_c) \epsilon_c}$$

where

$$F(\beta; \beta'_c, \beta''_c; \epsilon_b) = \frac{1}{Z_R} \sum_j e^{-\beta'_c \epsilon_j} f(\beta; \beta'_c, \beta''_c; \epsilon_b, \epsilon_j),$$

$$G(\beta; \beta'_c, \beta''_c; \epsilon_b, \epsilon_c) = \frac{1}{Z_R} \sum_j e^{-\beta \epsilon_j} g(\beta; \beta'_c, \beta''_c; \epsilon_c, \epsilon_b, \epsilon_j),$$

f and g are functions resulting from the integration of

$$R_f(\epsilon) e^{-(\beta - \beta'_c) \epsilon} \cos(\varphi - \epsilon \beta''_c)$$

between $\epsilon_b - \epsilon_j$ and ϵ_c , and Z_R is the partition function of the reactants in the well. In contrast to the case of a real dominant pole, we here have some sensitivity to the number and the character of states in the reactant well.

Figure 1 depicts the simplest case when $R_f(\epsilon)$ is a constant, $\rho_1(\epsilon)$ is linear in energy, there is one ener-

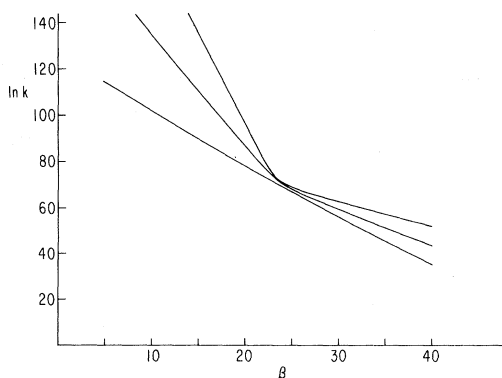


FIG. 1. Calculated \ln (reaction rate) vs $\beta = 1/k_B T$ for various values of the activation and cutoff energies and the same heat bath.

gy level, and the reactants are coupled with the same strength to any number of heat-bath excitations. Typical experimental values needed in the rate expression were taken from Ref. 6 and the values of ϵ_b, ϵ_c varied from 1 to 8 eV.

V. PHYSICAL MODEL

In this section, we will calculate the sum of probabilities due to absorption of all possible numbers of excitations. Let us consider desorption of an adatom A at position \vec{r} , weakly coupled through a potential $V(\vec{r} - \vec{u})$ to just one surface atom displaced from its equilibrium at the origin by an amount \vec{u} due to phonon agitation. The Hamiltonian is

$$H = H_{\text{host}} + K + V(\vec{r} - \vec{u})$$

where H_{host} is the Hamiltonian of the substrate and K is the kinetic energy of the adatom. The transition matrix element, for desorption of A by absorption of a particular set of n_j , in the Born approximation^{21,22} is

$$T(n, \epsilon, \alpha; n_j; m_j) \equiv \langle \alpha' | \hat{V} \hat{O} | \alpha \rangle \quad (5.1)$$

where

$$| \alpha \rangle = \prod_{r=1}^l \frac{(\hat{a}_{q_r}^\dagger)^{m_r}}{\sqrt{m_r!}} | g \rangle \varphi_\alpha,$$

$$\hat{O} = \prod_{j=1}^l b_j \frac{(\hat{a}_{q_j}^\dagger)^{n_j}}{\sqrt{n_j!}}.$$

The a_q 's are phonon operators, $| g \rangle$ is the substrate ground state, φ_α is A 's wave function, and $b_j = [n_j! m_j! / (n_j + m_j)!]^{1/2}$.²³ $| \alpha' \rangle$ is a state with A desorbed, and with only the set $\{m_k\}$ left in the substrate.

Retaining only longitudinal phonons we have

$$\vec{u} = \sum_q \gamma_q \hat{q} (\hat{a}_q^\dagger + \hat{a}_q)$$

where $\gamma_q = (\hbar/2MN\omega_q)^{1/2}$, MN the total mass of the N host atoms, and $\hat{q} = \vec{q}/q$. Representing $V(\vec{r} - \vec{u})$ by a Fourier integral and using the Baker-Hausdorff formula, (5.1) simplifies into

$$T_{\alpha\alpha'}(n, \epsilon, n_j, m_j) = \int \frac{d\vec{k}}{(2\pi)^{3/2}} V_k e^{-k^2 a^2/2} \times \prod_{j=1} \left[\frac{m_j! n_j!}{(m_j + n_j)!} \right]^{1/2} \left\langle \alpha' \left| e^{i\vec{k} \cdot \vec{r}} \exp \left[-i \sum_q \gamma_q \vec{k} \cdot \hat{q} \hat{a}_q^\dagger \right] \exp \left[-i \sum_q \gamma_q \vec{k} \cdot \hat{q} \hat{a}_q \right] \hat{O} \right| \alpha \right\rangle \quad (5.2)$$

where $a^2 = \langle 0 | [\vec{k} \cdot \vec{u}(0)]^2 | 0 \rangle$. To lowest order in γ_q we reduce Eq. (5.2) to

$$T_{\alpha\alpha'}(n, \epsilon, n_j, m_j) = \left\langle \alpha' \left| \prod_{j=1} \frac{(-\gamma_{q_j})^{n_j}}{\sqrt{n_j!}} \left[\frac{(m_j + n_j)!}{n_j! m_j!} \right]^{1/2} (\hat{q}_j \cdot \vec{\nabla})^{n_j} \mathcal{V}(\vec{r}) \right| \alpha \right\rangle. \quad (5.3)$$

here $\mathcal{V}(\vec{r})$ is a smeared potential

$$\mathcal{V}(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^{3/2}} e^{i\vec{k} \cdot \vec{r}} V_k e^{-a^2 k^2/2}. \quad (5.4)$$

The expression given by (5.3) is used to calculate the rate given by Eq. (2.1). We assume that $E_i = \sum_j (m_j + n_j) \epsilon_j$ and $E_f = \sum_j n_j \epsilon_j + \epsilon$. The sum over initial states translates to unrestricted sums over the m_j 's, and over all n_j restricted by $\sum_i n_i = n$. For one energy level in the reactant well and using Ref. 24 we get for the transition rate per unit time

$$\frac{2\pi}{\hbar} \sum_f e^{-\beta \epsilon} \rho_n(\epsilon) D_{\alpha\alpha'}(\epsilon, n)$$

where

$$D_{\alpha\alpha'}(n, \epsilon) = \frac{a^{2n}}{n!} \int \int \varphi_\alpha^*(\vec{r}') \varphi_{\alpha'}^*(\vec{r}) [(\vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}'})^n \mathcal{V}(\vec{r}) \mathcal{V}(\vec{r}')] \varphi_\alpha(\vec{r}) \varphi_{\alpha'}(\vec{r}') d\vec{r} d\vec{r}',$$

and where $\rho_n(\epsilon)$ has a Laplace transform given by $[\tilde{\rho}_1(p)]^n$ with

$$\tilde{\rho}_1(p, \beta) = \frac{1}{3a^2} \sum_i \frac{\gamma_{q_i}^2 e^{-p\epsilon_i}}{1 - e^{-\beta\epsilon_i}}.$$

[We see that $\rho_n(\epsilon)$ is a state density weighted in favor of long wavelengths.] Its Laplace transform depends on β . But the position of the dominant pole in the p plane will depend only weakly on β . The total rate is given by

$$R = \frac{2\pi}{\hbar} \int_{\epsilon_b}^{\epsilon} R_f(\epsilon) e^{-\beta\epsilon} \left\{ \frac{1}{2\pi i} \int_C e^{p\epsilon} \left[\sum_n \left[\sum_{\alpha'} D_{\alpha\alpha'}(\epsilon, n) \right] [\tilde{\rho}_1(p)]^n \right] dp \right\} d\epsilon. \quad (5.5)$$

Virtual phonons effects are neglected in the wave function $\varphi_\alpha(\vec{r}) = \langle \alpha | \vec{r} \rangle$ and this wave function varies with energy as $\exp\{i[2m(\epsilon - \epsilon_b)/\hbar]^{1/2}\}$ for α' states. Notice that the double integral, compared with the remaining terms, varies slowly with ϵ , and so does the sum over α' . Closure may therefore be applied, and if there is only one bound state α , we get

$$\sum_{\alpha'} D_{\alpha\alpha'}(\epsilon, n) = \frac{a^{2n}}{n!} \{ \langle \alpha | [(\vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}'})^n \mathcal{V}(\vec{r}) \mathcal{V}(\vec{r}')]]_{\vec{r}=\vec{r}'} | \alpha \rangle - D_{\alpha\alpha}(\epsilon) \}. \quad (5.6)$$

The expression $(\vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}'})^n \mathcal{V}(\vec{r}) \mathcal{V}(\vec{r}')$ appearing in (5.6) is better handled if we recall $\mathcal{V}(\vec{r})$ from (5.4),

$$\mathcal{V}(\vec{r}) = \int \int \frac{V(\vec{\rho})}{(2\pi)^3} e^{i\vec{k} \cdot (\vec{r} - \vec{\rho}) - (1/2)k^2 a^2} d\vec{k} d\vec{\rho}.$$

The behavior of the series, over n , in Eq. (5.5) is governed by the large n terms. This fact facilitates an approximation of the integral over the polar angle in the k space. We used the steepest-descent method to ap-

proximate integrals, and Stirling's formula to get the following expression for large n :

$$(\vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}'})^n \mathcal{Y}(\vec{r}) \mathcal{Y}(\vec{r}') = \frac{(-1)^n n!}{a^{2n}} \frac{1}{a^4 \pi} \left[\frac{2}{\pi(n+2)} \right]^{1/2} \left[\int_0^\infty \rho V(\rho) \sin \left[\sqrt{n+2} \frac{\rho}{a} \right] d\rho \right]^2$$

$$\times \left[\frac{\sin \left[\frac{\sqrt{n+2} r_s}{a} \right]}{\frac{\sqrt{n+2} r_s}{a}} + (-1)^n \frac{\sin \left[\frac{\sqrt{n+2} r_d}{a} \right]}{\frac{\sqrt{n+2} r_d}{a}} \right] \quad (5.7)$$

where $r_s \equiv |\vec{r} + \vec{r}'|$ and $r_d \equiv |\vec{r} - \vec{r}'|$. Equation (5.7) reduces the sum over α' , given by (5.6) into

$$\sum_{\alpha'} D_{\alpha\alpha'}(n, \epsilon) = \frac{\sqrt{2}}{a^2 [\pi(n+2)]^{3/2}} \left[\int_0^\infty x V \left[\frac{ax}{\sqrt{n+2}} \right] \sin x dx \right]^2$$

$$\times \left[1 + (-1)^n \int |\varphi_\alpha(\vec{r})|^2 \frac{\sin \left[\frac{\sqrt{n+2}}{a} 2r \right]}{\frac{\sqrt{n+2}}{a} 2r} d\vec{r} \right.$$

$$\left. - (-1)^n \int \int |\varphi_\alpha(\vec{r})|^2 |\varphi_\alpha(\vec{r}')|^2 \left[\frac{\sin \left[\frac{\sqrt{n+2}}{a} r_s \right]}{\frac{\sqrt{n+2}}{a} r_s} \right. \right.$$

$$\left. \left. + (-1)^n \frac{\sin \left[\frac{\sqrt{n+2}}{a} r_d \right]}{\frac{\sqrt{n+2}}{a} r_d} \right] d\vec{r} d\vec{r}' \right].$$

The radius of convergence for the sum over n in (5.5) is given by

$$\mathcal{R} = \lim_{n \rightarrow \infty} \left| \sum_{\alpha'} D_{\alpha\alpha'}(n, \epsilon) \right|^{-2/n}$$

and is equal to unity. Thus although the expansion (5.6) was based on the notion of slow spatial variation of \mathcal{Y} , the radius of convergence of (5.5) ultimately does not depend on the details of that variation.

VI. DISCUSSION

In Sec. V the Born approximation has been used with respect to coupling strength, but the shape of the coupling function has been taken into account to all orders in the number of possible excitations. The n th term in the series does not involve an n th power of any of the physical variables; therefore, in this approximation at least, we have extreme universality, and the compensation effect should be very marked in the desorption of very weakly cou-

pled adatoms. A similar exponential result of summation of phonon processes to all orders was noted by Sham and Sparks²⁵ in their discussion of energy transfer of laser radiation to an insulating solid.

By contrast, for strong but weakly curved potentials, n phonons will be absorbed only in n th-order perturbation theory, so that the radius of convergence of (2.1) would be proportional to $\bar{\epsilon}/\lambda$, where λ is the coupling strength and $\bar{\epsilon}$ a typical intermediate-state energy. Thus for stronger coupling, a sharp compensation effect will be observed only for families with members having equal λ and various ϵ_b . This dependence on λ is, however, weakened by renormalization (due to emission and reabsorption of intermediate-state phonons), which causes $\bar{\epsilon}$ to be λ dependent in such a way as to weaken the dependence of $\bar{\epsilon}/\lambda$ on λ .

Another example, to be discussed fully in a later publication, is that of reactants coupled to a metal catalyst. In that case the coupling to the conduction electron density $n(\vec{r})$ has the form $\gamma = \int V(\vec{R} - \vec{r}) n(\vec{r}) d\vec{r}$, seemingly involving only

one electron-hole pair at a time. However, the residual shielded Coulomb interaction of the electron taken to n th order, together with γ taken only to first order effectively couples the reactants to $n + 1$ electron-hole pairs. The dominant pole is then modified roughly by the ratio (Coulomb energy to kinetic energy)^{1/2}, but remains independent of γ . The analogous result holds for a weak linear coupling W to phonons of a significantly anharmonic solid. Interaction between the lattice phonons taken to n th order, together with W taken to first order gives an effective coupling to $3n + 1$ phonons; once

again the sum $\sum \rho_n(\epsilon)$ is essentially exponential, yielding a compensation effect independent of W .

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$$|\beta\rangle = \prod_i b_i \frac{(\hat{a}_{q_i}^\dagger)^{n_i}}{\sqrt{n_i!}} |\alpha\rangle,$$

with $n = \sum_i n_i$, is the "infinitely sharp" limit of an asymptotic wave-packet eigenstate $|\tilde{\beta}\rangle$ of H , with energy excess $\epsilon = \sum_i n_i \omega_{q_i}$ over E_α , the energy of $|\alpha\rangle$.

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$$\sum_{m_j=0}^{\infty} \frac{X^{m_j} (n_j + m_j)!}{m_j! n_j!} = \frac{1}{(1-X)^{n_j+1}},$$

$$\sum_{n_1} \cdots \sum_{n_s} \prod_{i=1}^s \frac{n_i!}{n_i!} X_i^{n_i} = \left(\sum_{i=1}^s X_i \right)^n,$$

$$\sum_{i=1}^s n_i = n$$

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