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Kinetics of Processes Distributed in Activation Energy*†

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The kinetic behavior of systems in which processes occur which are distributed over a range of activation energies is considered. The effects produced by the initial distribution, the order of reaction, and the frequency factor are discussed. Imaginary and actual experimental situations are used to illustrate the large errors which can result when the distribution of the processes in activation energy is neglected. Some of the complications which can result from successive reactions and varying frequency factors are mentioned.

INTRODUCTION

Vand[1] introduced the concept of a group of processes distributed in activation energy in order to explain the kinetics of the irreversible resistance changes which take place in heating evaporated metal deposits. The same concept was used by Curie[2] and by Randall and Wilkins[3] to explain the decay of the long-period phosphorence. Neubert[4] used the concept to explain the annealing behavior of radiation damage. The merits of the alternative kinetic treatments considered by Brown,[5] Dienes and Parkins,[6] Bowen,[7] and others will not be discussed for it is the object here to consider in a general way some of the kinetic behavior resulting when processes are distributed in activation energy. Overhauser[8] studied the annealing of resistance changes in copper induced by high-energy deuterons and concluded the first part of the annealing could be explained by a distribution of processes over a range of activation energies followed by a single process in which the annealing proceeded by kinetics of order 2.5. Honig[9] considered the integral transformation of one of the equations arising in the kinetics of processes distributed in activation energy. These references furnished the background for the present paper and are not intended to represent an exhaustive survey.

The above investigations all involved solids which may be considered to be molecularly inhomogeneous in some sense. In the case of evaporated metal films, the crystal structure consists of random mosaic deposits; in the case of radiation damage by energetic particles, the stopping process is itself localized, the displaced atoms may be trapped at various points in the solid, or in varying groupings, and the solid may eventually break down into a mosaic structure; in the case of phosphors, the electron traps may have different depths. Thus the different activation energies would appear to be associated with different portions of the solid. If reactions of order other than one are considered, it may be necessary to introduce a local concentration in addition to the average volume concentration.

1. FORMAL THEORY OF THE KINETICS OF PROCESSES DISTRIBUTED IN ACTIVATION ENERGY; ISOTHERMAL ANNEALING AND TEMPERING

1.1. It has been customary to consider that in analogy with the kinetic processes in gases and in solution, the annealing processes obey a differential equation of the kind

$$-(dq/dt)=kq^n, \tag{1}$$

where q is the concentration of possible kinetic processes, t is the time, k is a constant, and n is the order of reaction (not restricted to integer values). In general, q cannot be measured directly. If a property is measured which is proportional to the number of processes which can occur, then for the processes which proceed at a particular value of the activation energy,

$$-(dp/dt)=kf(p/f)^n, \tag{2}$$

where f is the change in property accompanying the occurrence of a kinetic process (termed the importance factor) and p is a property or property change which can be used to measure the concentration of kinetic processes which can yet occur. It is usually assumed that the rate constant, k, can be equated to the Arrhenius expression for the activation energy. Then

$$-(dp/dt)=Afe^{-\epsilon/\tau}(p/f)^n, \tag{3}$$

where ϵ is the activation energy (units of ev will be used here), τ is the product of Boltzmann's constant and the temperature, and A is a constant having the dimensions of frequency when n is unity. In the case of isothermal annealing, this equation can be integrated to give

$$p=p_0[1-(1-n)At(f/p_0)^{(1-n)}e^{-\epsilon/\tau}]^{1/(1-n)} \tag{4}$$

$$=p_0[1-(1-n)Bte^{-\epsilon/\tau}]^{1/(1-n)}, \tag{5}$$

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[†] Enlarged from a manuscript submitted as a letter November 18, 1954.

[1] V. Vand, Proc. Phys. Soc. (London) **A55**, 222 (1943).

[2] M. Curie, Trans. Faraday Soc. **35**, 114 (1939).

[3] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 390 (1945).

[4] T. J. Neubert was probably the first to apply Vand's method to the annealing of radiation damage [work done at the Metallurgical Laboratory, 1944 (to be published)].

[5] F. W. Brown, North American Aviation Report NAA-SR-16, 1950 (unpublished).

[6] G. J. Dienes and W. E. Parkins, North American Aviation Report NAA-SR-60, 1950 (unpublished).

[7] D. Bowen, North American Aviation Report NAA-SR-41, 1950 (unpublished).

[8] A. W. Overhauser, Phys. Rev. **90**, 393 (1953).

[9] J. M. Honig, J. Chem. Phys. **22**, 1689 (1954).

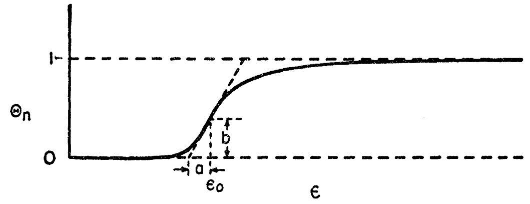

FIG. 1. The characteristic annealing function for isothermal annealing, $\Theta_n=[1-(1-n)Bte^{-\epsilon/\tau}]^{1/(1-n)}$, $a=n\tau$, $b=n^{1/(1-n)}$, $\epsilon_0=\tau\ln(Bt)$.

where p_0 is the value of p at $t=0$. The quantity B which is defined by Eqs. (4) and (5) has the dimensions of frequency for all orders of reaction. If the processes are distributed in activation energy, p and p_0 are distribution functions (the dependence of B and f on the activation energy will be disregarded in this section) and the measured value of the property is[10]

$$P=\int_0^\infty p_0[1-(1-n)Bte^{-\epsilon/\tau}]^{1/(1-n)}d\epsilon, \tag{6}$$

or

$$P(t)=\int_0^\infty p_0(\epsilon)\Theta_n(\epsilon,t)d\epsilon, \tag{7}$$

where P is the observed value of a suitable property. The function Θ defined by Eqs. (6) and (7) is termed the characteristic isothermal-annealing function. The distribution of processes over a range of activation energies is termed a spectrum.[11]

1.2. In dealing with a broad activation-energy spectrum, the annealing behavior is dominated by the exponential dependence on ϵ appearing in Θ_n, and the modifications introduced by p_0, the initial activation-energy spectrum, and the dependence of B and f on ϵ may be treated as perturbations of the gross behavior. The characteristic annealing function for isothermal annealing is shown schematically in Fig. 1. Solving for ϵ,

$$\epsilon=\tau\{\ln[(1-n)B]+\ln t-\ln[1-\theta^{(1-n)}]\}, \tag{8}$$

it is seen that as the isothermal annealing progresses, the curve is displaced along ϵ, but does not alter in shape. The point of inflection is termed here the characteristic activation energy and is designated ϵ_0. It is seen that

$$\epsilon_0=\tau\ln(Bt). \tag{9}$$

The rate of annealing is[10]

$$\begin{aligned}\frac{dP}{dt}&=\frac{d}{dt}\int_0^\infty p\,d\epsilon\\&=\int_0^\infty\left(-\frac{dp}{dt}\right)d\epsilon\\&=\int_0^\infty p_0\left(-\frac{d\Theta_n}{dt}\right)d\epsilon.\end{aligned} \tag{10}$$

Thus neglecting, for the moment, the effect of the initial activation energy spectrum, of the processes occurring simultaneously, those at the maximum of $d\Theta_n/dt$ make the maximum contribution. Since in isothermal annealing $d\Theta_n/dt$ and $d\Theta_n/d\epsilon$ (regarded as functions of ϵ) are proportional to each other (again neglecting any dependence of B and f on ϵ), they possess a maximum at the same value of ϵ, and hence the processes possessing the characteristic activation energy make the maximum contribution to those occurring simultaneously. However, because $(dp/dt)(\epsilon)$ is usually unsymmetrical about ϵ_0, the average activation energy of the processes undergoing simultaneous annealing is slightly displaced from ϵ_0, an effect which is small and which will be considered later. From the value and the slope of the characteristic annealing function at the characteristic activation energy

$$\Theta_n(\epsilon_0)=n^{1/(1-n)}, \tag{11}$$

$$\frac{d\Theta_n}{d\epsilon}(\epsilon_0)=\frac{n^{n/(1-n)}}{\tau}, \tag{12}$$

it is seen that for reasonable values of n, most of the processes occurring simultaneously lie in a narrow band of activation energies of the magnitude several times $n\tau$ (Fig. 1).

1.3. The presentation of the activation-energy spectrum as a function of time is a complete representation of the formal kinetic behavior of a suitable property for any kind of annealing program. Experimentally all that is observed is the integral of the activation-energy spectrum as a function of time. The customary kinetic interpretation of the data would consist of finding the initial activation-energy spectrum; and then through a proper choice of order and frequency factor (B), the activation-energy spectrum as a function of time would be given by the equations. If this could not be done, complications of kinetic behavior would be assumed. This matter is discussed later.

1.4. The kinetic behavior for isothermal annealing in the case of a broad activation-energy spectrum is easily visualized and is drawn schematically in Fig. 2. As time proceeds, the initial activation-energy spectrum is swept out as the characteristic annealing function advances in activation energy. If the initial activation-energy spectrum is very broad, many times $n\tau$, the

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[10] In applying limits to integrals involving the characteristic annealing functions it is necessary to exercise some care when the order is not unity. If the order is less than unity the characteristic annealing function is zero from $\epsilon=0$ to $\epsilon=\tau\ln[(1-n)Bt]$ while the functional form given is negative in this region, and thus integrals involving $\Theta_{n<1}$ or $d\Theta_{n<1}/dt$ should be taken from $\tau\ln[(1-n)Bt]$ as a lower limit when the functional form given is used. If the order is greater than 2, $-\int_0^\infty(d\Theta_n/dt)d\epsilon$ diverges and hence a finite upper limit must be employed with this integral.

[11] This term was introduced in the course of studies by Neubert (reference 4) in 1944 and has been in common use in the subject since then.

characteristic annealing function may be approximated by a step function. Then Eq. (7) becomes

$$P(t)\cong\int_{\epsilon_0}^{\infty} p_0(\epsilon)d\epsilon, \tag{13}$$

and

$$dP/dt\cong -p_0(\epsilon_0)(d\epsilon_0/dt). \tag{14}$$

From Eq. (9),

$$p_0[\tau\ln(Bt)]\cong -(t/\tau)(dP/dt). \tag{15}$$

1.5. The result Eq. (15) which gives the initial-activation-energy spectrum from the isothermal annealing data, was derived by Vand[1] for first-order processes, but is seen here to be quite general and applies to processes of any order. The order does not affect the initial activation energy spectrum (for it was present before annealing was started) but rather the shape of the changing portion of the activation-energy spectrum as the annealing proceeds. This shape was ignored when a step function was used to approximate the characteristic-annealing function, and hence the result applies to all orders. It is seen from Eq. (15) that the effect of the frequency factor in isothermal annealing is to cause a simple displacement along the activation energy axis. Thus the result gives the correct approximate shape for the initial activation-energy spectrum, but does not fix its location. For the usual range of times which can be realized in careful isothermal annealing, about three decades, it can be seen from Eq. (15) that the portion of the activation energy spectrum which is revealed is but several tenths of an electron volt, only a small portion of the several electron-volt wide activation energy spectra observed in disordered solids. If the whole spectrum is to be found by isothermal annealing, it is necessary to conduct isothermal annealings at a number of different temperatures. However, in this case the parts of the spectrum revealed at the different temperatures will not fit togther unless the frequency factor is correctly chosen (however, see paragraph 4.3) since the displacement along the activation energy axis involves a product of temperature and (logarithm of) frequency factor. If this is used as a method to obtain the frequency factor, it is important to fit the parts of the activation energy spectrum together rather than the observed property changes as is shown in paragraph 2.3.

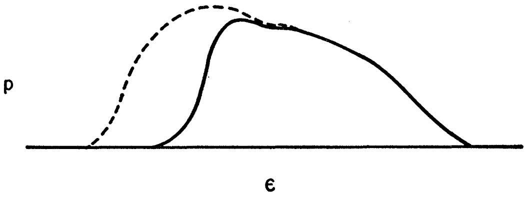

FIG. 2. An activation energy spectrum in isothermal annealing. The portion of the initial activation energy spectrum which has been annealed is shown as a dashed curve.

1.6. The treatment given here may be extended to the case of tempering, i.e., an annealing conducted by raising the temperature in a gradual manner. For a case in which the temperature of *the sample* is raised according to the law

$$t=c\tau, \tag{16}$$

when annealing a group of processes characterized by a discrete activation energy, the differential equations are

$$-(dq/cd\tau)=Ae^{-\epsilon/\tau}q^n, \tag{17}$$

$$-(dp/fcd\tau)=Ae^{-\epsilon/\tau}(p/f)^n, \tag{18}$$

for which the solution is

$$p=p_0[1-(1-n)Bc\tau\mathbf{E}_2(\epsilon/\tau)]^{1/(1-n)}. \tag{19}$$

If the processes are distributed in activation energy, p and p_0 are distribution functions, and the measured value of the property is

$$P=\int_0^{\infty} p_0[1-(1-n)Bc\tau\mathbf{E}_2(\epsilon/\tau)]^{1/(1-n)}d\epsilon, \tag{20}$$

or

$$P(\tau)=\int_0^{\infty} p_0(\epsilon)\Phi(\epsilon,\tau)d\epsilon, \tag{21}$$

where Φ is the characteristic annealing function in tempering.

The functions $\mathbf{E}_m(x)$ are defined as

$$\mathbf{E}_m(x)=x^{m-1}\int_x^{\infty} u^{-m}e^{-u}du, \tag{22}$$

and have been tabulated.[12] A property of interest is

$$d\mathbf{E}_m(x)/dx=-\mathbf{E}_{m-1}(x). \tag{23}$$

For the range of x of interest here (20–50), the first term of Blanch's asymptotic expansion,[12]

$$\mathbf{E}_m(x)\cong(x+m)^{-1}e^{-x}, \tag{24}$$

is a satisfactory approximation, and when used with the approximation

$$(x+a)(x+b)\simeq(x+j)(x+k), \tag{25}$$

where a, b, j, and k are small integers and

$$a+b=j+k, \tag{26}$$

the algebraic operations with these exponential integrals are greatly simplified while their identification is preserved. Often different expressions result from introducing the approximation at different stages of the algebraic operations; but because the values of x of interest here are so large, they do not differ significantly from each other numerically. Where alternative expressions were obtained, one convenient for the purpose at hand was chosen.

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[12] G. Placzek, National Research Council of Canada Report NRC-1547, 1946.

1.7. As in the case of isothermal annealing, the annealing behavior in tempering is dominated by the exponential dependence on ϵ appearing in Φ_n which is here termed the characteristic annealing function for tempering. It is sigmoid-shaped, somewhat like the curve drawn in Fig. 1, and varies from zero to one. Upon solving for ϵ using the approximation, Eq. (24),

$$\epsilon+\tau\ln[(\epsilon/\tau)+2] \cong\tau\{\ln[(1-n)B]+\ln(c\tau)-\ln(1-\Phi_n{}^{1-n})\}, \qquad (27)$$

it is thus seen that as the annealing proceeds (whether plotted in temperature as is customary, or in time), the sigmoid form of the characteristic annealing function advances in activation energy, and it also reclines instead of retaining its original form as it does in an isothermal annealing.

Using Eqs. (23)–(26), it is found that the point of inflection of the characteristic annealing function for linear tempering occurs at

$$\epsilon_0\cong\tau\{\ln(Bc\tau)-\ln[(\epsilon_0/\tau)+2]\}. \qquad (28)$$

The rate of annealing is

$$-dP/d\tau=\int_0^\infty p_0(-d\Phi_n/d\tau)d\epsilon. \qquad (29)$$

Neglecting, for the present, the effect of the initial activation-energy spectrum, the maximum contribution to the annealing at any moment is made by the processes occurring at the maximum of $-d\Phi_n/d\tau$ which does not occur at ϵ_0 but at ϵ_τ given by

$$\epsilon_\tau=\tau\{\ln Bc\tau-\ln[(\epsilon_\tau/\tau)+2] +\ln[(\epsilon_\tau/\tau)+n](\epsilon_\tau/\tau)^{-1}\}, \qquad (30)$$

which is at a slightly higher activation energy than the characteristic activation energy. Because $d\Phi_n/d\tau$ is unsymmetrical about its maximum, the average activation energy of the processes undergoing simultaneous annealing is even farther removed from the characteristic activation energy. However these displacements are usually small in comparison with the effects which the initial activation-energy spectrum can exert. At the characteristic activation energy, the characteristic function has the value

$$\Phi_n(\epsilon_0)=n^{1/(1-n)}. \qquad (31)$$

The slope of the characteristic annealing function is

$$\frac{d\Phi_n}{d\epsilon}(\epsilon_0)=\frac{1}{\tau}n^{n/(1-n)}\left(1+\frac{\tau}{\epsilon_0}\right), \qquad (32)$$

which in a typical case would be a few percent greater than in isothermal annealing. Thus, for reasonable values of n most of the processes occurring simultaneously in tempering also lie in a narrow band of activation energies, several times $n\tau$. Hence, the mathematical artifice used here, that of starting the tempering at $\tau=0$, does not introduce a serious restriction.

1.8. An approximate solution for the initial activation-energy spectrum can be obtained in the manner used previously. From Eq. (21),

$$P(\tau)\cong\int_{\epsilon_0}^\infty p_0d\epsilon, \qquad (33)$$

and taking the derivative with respect to τ,

$$p_0(\epsilon_0)=-\frac{1}{d\epsilon_0/d\tau}\frac{dP}{d\tau}. \qquad (34)$$

Writing y_0 for ϵ_0/τ, Eq. (28) becomes

$$y_0+\ln(y_0+2)=\ln(Bc\tau). \qquad (35)$$

Since the annealing takes place in a small range of y and since $y_0+\ln(y_0+2)$ is a very slowly varying function, it is quite permissible to take

$$y_0+\ln(y_0+2)\cong a+by_0, \qquad (36)$$

where a and b are constants appropriate to the range of y under consideration. Then writing ξ for $-a+\ln(Bc\tau)$,

$$\epsilon_0\cong\tau\xi/b, \qquad (37)$$

$$d\epsilon_0/d\tau\cong(\xi+1)/b\cong1+\xi/b \qquad (38)$$

(for b is close to unity), and

$$p_0\left(\tau\frac{\xi}{b}\right)\cong-\frac{dP}{d\tau}\frac{1}{(\xi/b)+1}. \qquad (39)$$

Since ξ/b varies only slowly with temperature, the initial activation energy spectrum is nearly proportional to the tempering curve which plots $(-dP/d\tau)$ against τ when the heating rate of the sample, $(1/c)$, has been constant. The resolution is several times $n\tau$ (see Vand[1]) and the method applies when the activation-energy spectrum is broad compared to $n\tau$ and to reasonable orders of reaction. Changing the frequency factor causes a displacement of the derived initial activation-energy spectrum along the activation energy axis as described for isothermal annealing in paragraph (1.5). However, since in tempering the temperature is continuously changing, a change in choice of frequency factor also causes a distortion of the derived spectrum. Choosing a larger frequency factor expands the spectrum along its abscissas (activation energy) and contracts its ordinates.

1.9. At n unity, the characteristic annealing functions converge to the exponential. Then some of the equations given previously can be written

$$p=p_0\exp(-Ate^{-\epsilon/\tau}), \qquad (4a), (5a)$$

$$P=\int_0^\infty p_0\exp(-Ate^{-\epsilon/\tau})d\epsilon, \qquad (6a)$$

$$\epsilon=\tau[\ln(At)-\ln_2(1/\Theta)], \qquad (8a)$$

$$\epsilon_0 = \tau \ln(At), \tag{9a}$$

$$\Theta(\epsilon_0) = e^{-1}, \tag{11a}$$

$$(d\Theta/d\epsilon)(\epsilon_0) = (\tau e)^{-1}, \tag{12a}$$

$$p_0(\tau \ln(At)) \cong -(t/\tau)(dP/dt), \tag{15a}$$

$$p = p_0 \exp[-Ac\tau \mathbf{E}_2(\epsilon/\tau)], \tag{19a}$$

$$P = \int_0^\infty p_0 \exp[-Ac\tau \mathbf{E}_2(\epsilon/\tau)] d\epsilon, \tag{20a}$$

$$\epsilon + \tau \ln[(\epsilon/\tau)+2] \cong \tau[\ln(Ac\tau) - \ln_2(1/\Phi)], \tag{27a}$$

$$\Phi(\epsilon_0) = e^{-1}, \tag{31a}$$

and

$$\frac{d\Phi}{d\epsilon}(\epsilon_0) = \frac{1+(\tau/\epsilon_0)}{\tau\epsilon}, \tag{32a}$$

where $\ln_2(x) \equiv \ln(\ln x)$.

1.10. In tempering, if the heating rate is given by the equation

$$t = c\tau^m, \tag{40}$$

where m is integral and greater than unity, the equations may be integrated by the methods given here, and it is found that the characteristic-annealing function involves the exponential integral $\mathbf{E}_{m+2}(\epsilon/\tau)$.

2. SOME EFFECTS PRODUCED BY THE INITIAL ACTIVATION ENERGY SPECTRUM

2.1. The exact mathematical inversion of the isothermal annealing data $P(t)$ to obtain $p_0(\epsilon)$ by means of a Laplace transform has been given by Honig.[9] In order to do this, it is necessary to know the function dP/dt sufficiently well analytically to determine its behavior over the whole of the complex plane. From the discussion in paragraph (1.5) it is obvious that this is impossible in practice. Honig's conclusion that a constant initial activation-energy spectrum cannot exist, while entirely correct, has no practical significance. Since, effectively, only the processes over a small range of activation energies occur simultaneously, and since only a small portion of the possible range of activation energies can be observed in an isothermal annealing, the portion of the initial activation-energy spectrum which for practical purposes can be considered to be involved in a particular experiment can be constant.[10] In this case the annealing behavior is essentially that of the characteristic annealing function. When the initial activation-energy spectrum is not constant, some care is needed in interpreting the data. This is especially true when attempting to find the frequency factor or the order of the reaction, for the effects which they produce and which are studied, occur in a range of activation energies of magnitude $\sim n\tau$, the range over which the processes are occurring simultaneously, and any variation of the initial activation-energy spectrum in this region will weight the processes occurring in some parts of this range with respect to those occurring in other parts of this range. Some of the effects which are observed are treated by giving two illustrations, one treating the analysis of isothermal data, and the other treating the analysis of step-annealing data.

2.2. It is useful here to introduce a comparison between the shape S_0 of the rapidly rising portion of the characteristic annealing function and the shape S_p of the portion of the activation-energy spectrum existing at that time in the same range of activation energies. The qualitative effect of a rising initial activation-energy spectrum is that S_p is steeper than S_0. Thus if it is not realized that p_0 is rising, it may be considered that the frequency factor is greater than its correct value. It may also be considered that the order is less than its correct value. However the point of inflection in S_p may not correspond to this latter interpretation for, in general, it will be higher than for S_0 corresponding to a greater order of reaction and would be lower than in S_0 only if p_0 although increasing possessed a negative radius of curvature, small compared to $n\tau$.

It is also readily seen by sketching some of the possible forms of initial activation-energy spectra and the S_p they yield that the maximum displacements of S_p with respect to S_0 can be of the magnitude $\sim n\tau$ for the most steeply rising initial activation-energy spectra. The reverse displacements will occur with falling initial activation-energy spectra. Accordingly, with the use of Eq. (14) or (39), processes occurring at a discrete activation energy will yield an approximate spectrum of width several times $n\tau$, and a smaller distortion will be found when the actual initial activation energy spectrum is less steep than a delta function.

2.3. In isothermal annealing, it is convenient, to plot the measured value of the property (P) against

$$\ln t \equiv x. \tag{41}$$

Then Eq. (15) may be written

$$p_0(\tau \ln B + \tau x) \cong -\tau^{-1}(dP/dx). \tag{42}$$

Over the small portion of the activation energy spectrum which is revealed, the distribution may change very little. Thus dP/dx will change very little, perhaps within the experimental error of the data. It is tempting to draw $P(x)$ as a straight line and thus miss the variations in the initial activation energy spectrum, p_0. It is necessary to be extremely cautious in interpreting isothermal annealing data extending from several minutes to several hours, but two decades in time.

If the data $P(x)$ for a number of independent isothermal annealings conducted at different temperatures are plotted, they will form a family of curves which are nearly straight lines, the higher temperature curves lying below the lower temperature ones. These curves are nearly parallel as can be shown by taking $\partial(dp/dx)/\partial\tau$ which is seen to be small when the relation $Bte^{-\epsilon/\tau} \sim 1$ [Eq. (9)] is inserted. If the temperatures are

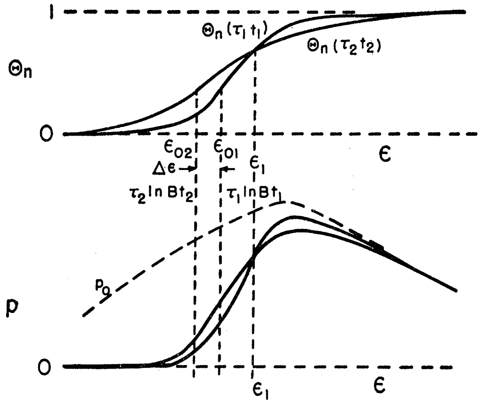

FIG. 3. The appearance of the characteristic annealing functions and the activation-energy spectra for two isothermal annealings conducted at different temperatures when the measured value of the property is the same.

sufficiently close together, the first measured values of the property at the beginning of one annealing will be greater than the last measured values at the end of the annealing performed at a lower temperature. Respective points on the two curves having the same measured values of the property are related kinetically as follows:

$$P=\int_0^\infty p_0\Theta_n(\tau_1,t_1,\epsilon)d\epsilon=\int_0^\infty p_0\Theta_n(\tau_2,t_2,\epsilon)d\epsilon. \qquad (43)$$

The approximation introduced in deriving Eq. (15) would lead to the result

$$\epsilon_0(\tau_1,t_1)\equiv\epsilon_{01}\cong\epsilon_{02}\equiv\epsilon_0(\tau_2,t_2), \qquad (44)$$

where ϵ_{01}, ϵ_{02} are the characteristic activation energies at the respective temperatures, and hence the approximate value of $\ln B$ is $\ln B'$, where

$$\ln(B')=(\tau_1x_1-\tau_2x_2)/(\tau_2-\tau_1). \qquad (45)$$

The behavior of $\ln(B')$ can be visualized with the aid of Fig. 3. The characteristic annealing functions for the two annealings will intersect at some activation energy, ϵ_1, and hence the activation energy spectra will also intersect at this activation energy. The condition Eq. (43) requires that when the measured value of the property is the same for the two annealings, the area between the activation-energy spectra to the left of ϵ_1 must be equal to the area between the two spectra to the right of ϵ_1. In general, the characteristic activation energies, ϵ_{01} and ϵ_{02} respectively, will not be at ϵ_1, and hence defining $\Delta\epsilon$ as

$$\Delta\epsilon=\epsilon_{01}-\epsilon_{02}, \qquad (46)$$

$$\ln B=\ln(B')-\Delta\epsilon/(\tau_2-\tau_1). \qquad (47)$$

For a rising initial activation-energy spectrum it is seen that ϵ_1 is advanced relative to ϵ_{01} and ϵ_{02} and hence $\Delta\epsilon$ is increased, and the reverse is true for a falling initial activation-energy spectrum. These variations in $\Delta\epsilon$ can be of the magnitude ($\sim n\tau$) since it is reasonable for the intersection of the characteristic annealing functions to occur over any part of their steep regions. Thus if τ_1 is about 0.05 and τ_2 is 0.055, B can differ from B' by factors ranging from $\sim 10^{-4n}$ to $\sim 10^{4n}$.

Even if the initial activation-energy spectrum is constant in the region of activation energies which are annealing, B must, in general, differ from B'. It is readily seen that with a constant initial spectrum, if the region of the initial spectrum undergoing annealing is not too close to the end of the initial spectrum, the condition of equality of areas between the activation-energy spectra on either side of their intersection requires the ordinate of the intersection decrease for pairs of points at greater times; accordingly $\Delta\epsilon$ decreases and from Eq. (47), $\ln B'$ also decreases. The same reasoning requires that $\ln B'$ increase when the region of the initial spectrum undergoing annealing is close to its end. These effects are several orders of magnitude smaller than the possible effects of the rising and falling regions of the initial spectrum.

2.4. For two successive stages of step-annealing, if the processes occur at a discrete activation energy, then

$$-(dp/dt)_1=Afe^{-\epsilon/\tau_1}(p/f)^n, \qquad (48)$$

$$-(dp/dt)_2=Afe^{-\epsilon/\tau_2}(p/f)^n. \qquad (49)$$

At the beginning of the second stage, the value of the property is the same as at the end of the first stage. Designating the ratio of the rates at the two temperatures at this point as R and $\tau_1\tau_2/(\tau_1-\tau_2)$ as ζ, it is seen that

$$\epsilon=\zeta\ln R, \qquad (50)$$

a relation pointed out by Overhauser.[8] When the processes are distributed in activation energy, it is obvious that this relation can at best hold only approximately since different distributions of processes are taking place at the two temperatures. The number which is obtained in this case upon introducing the experimentally determined rates and temperatures into Eq. (50) will be designated E and its meaning is investigated here.

If the first of the two particular stages of step-annealing considered has been conducted for a time t_1 sufficiently long to advance the characteristic annealing function at least several $n\tau_1$, the activation-energy spectrum will have become

$$p_1=p_0[1-(1-n)Bt_1e^{-\epsilon/\tau_1}]^{1/(1-n)}, \qquad (51)$$

or, for $n=1$,

$$p_1=p_0\exp(-At_1e^{-\epsilon/\tau_1}). \qquad (51a)$$

If at this point another annealing is started, the rate at which the property changes is

$$\frac{dP}{dt}=\int_0^\infty p_0[1-(1-n)Bt_1e^{-\epsilon/\tau_1}]^{1/(1-n)} \times[1-(1-n)Bte^{-\epsilon/\tau_2}]^{n/(1-n)}Be^{-\epsilon/\tau_2}d\epsilon.$$

At the beginning of the second annealing $t=0$, and hence[10]

$$-\left(\frac{dP}{dt}\right)_0=\int_0^\infty p_0[1-(1-n)Bt_1e^{-\epsilon/\tau_1}]^{1/(1-n)}Be^{-\epsilon/\tau_2}d\epsilon, \tag{52}$$

and for first-order processes

$$-\left(\frac{dP}{dt}\right)_0=\int_0^\infty p_0\exp(-At_1e^{-\epsilon/\tau_1})Ae^{-\epsilon/\tau_2}d\epsilon. \tag{52a}$$

The integrals, Eqs. (52) and (52a), are various forms of the Euler integrals. If the initial activation-energy spectrum is constant, then for first-order processes, upon setting $z=At_1e^{-\epsilon/\tau_1}$ and $\sigma=\tau_1/\tau_2$, Eq. (52a) becomes

$$-\left(\frac{dP}{dt}\right)_0=p_0\frac{\tau_1}{t_1}(At_1)^{(1-\sigma)}\int_0^{At_1}e^{-z}z^{(\sigma-1)}dz. \tag{53}$$

Since At_1 is a very large number, the upper limit may be taken to be infinite. Hence,

$$-\left(\frac{dP}{dt}\right)_0=p_0\frac{\tau_1}{t_1}(At_1)^{(1-\sigma)}\Gamma(\sigma), \tag{54}$$

where Γ is the gamma function. The rate at the end of the first annealing stage is obtained by setting $\sigma=1$. As before, designating the ratio of the rate at the beginning of the second stage to that at the end of the first stage as R,

$$R=(At_1)^{1-\sigma}\Gamma(\sigma), \tag{55}$$

and

$$(1-\sigma)\ln(At_1)=\ln[R/\Gamma(\sigma)]. \tag{56}$$

If it is assumed that the processes which are annealing simultaneously may be characterized by the characteristic activation energy at the end of the annealing at the lower temperature, from Eq. (9a),

$$\epsilon_0=\zeta\ln[R/\Gamma(\sigma)]. \tag{57}$$

Usually $0.9<\sigma<1$, hence $\Gamma(\sigma)$ is near unity, and the result may seem to be insignificantly different from Eq. (50). However, this small correction is but one of a number which it will be seen are quite important in interpreting the kinetic significance of the annealing data. If the order is less than unity, and the initial activation-energy spectrum is constant, by setting $Bt_1e^{-\epsilon/\tau_1}=y$, Eq. (52) may be written[10]

$$-\left(\frac{dP}{dt}\right)_0=p_0\frac{\tau_1}{t_1}(Bt_1)^{1-\sigma}$$

$$\times\int_0^{1/(1-n)}[1-(1-n)y]^{1/(1-n)}y^{\sigma-1}dy \tag{58}$$

$$=p_0\frac{\tau_1}{t_1}(Bt_1)^{1-\sigma}(1-n)^{-\sigma}\beta\left(\sigma,\frac{2-n}{1-n}\right), \tag{59}$$

where β is the beta function; and hence

$$R=(1+\alpha_2)(Bt_1)^{1-\sigma}\Gamma(\sigma), \tag{60}$$

where

$$1+\alpha_2\equiv(1-n)^{1-\sigma}$$

$$\times\Gamma[1+(2-n)/(1-n)]/\Gamma[\sigma+(2-n)/(1-n)]. \tag{61}$$

The respective values of α_2 for $n=\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, are 0.056, 0.040, and 0.032. The same treatment can be employed for orders $1<n<2$, and then Eq. (52) becomes

$$-\left(\frac{dP}{dt}\right)_0=p_0\frac{\tau}{t_1}(Bt_1)^{1-\sigma}\int_0^{Bt_1}\frac{y^{\sigma-1}dy}{[1+(n-1)y]^{1/(n-1)}},$$

and since Bt_1 is a large number, upon marking the upper limit infinite, this becomes

$$-\left(\frac{dP}{dt}\right)_0=p_0\frac{\tau}{t_1}(Bt_1)^{1-\sigma}(n-1)^{-\sigma}\beta\left(\sigma,\frac{1}{n-1}-\sigma\right), \tag{63}$$

and hence

$$R=(1-\alpha_3)(Bt_1)^{1-\sigma}\Gamma(\sigma), \tag{64}$$

where

$$1-\alpha_3\equiv(n-1)^{1-\sigma}\Gamma\left(\frac{1}{n-1}-\sigma\right)\Big/\Gamma\left(\frac{1}{n-1}-1\right). \tag{65}$$

The respective values of α_3 for orders $n=1.5$, 1.9, and 1.99 are about 0.133, 0.497, and 0.9142. Part of the large correction α_3 for large values of the order arises in the region of large values of ϵ which in practice would not exist, while part of the smaller correction in the region of ϵ of significance would be partially compensated for by the displacement of the average activation energy of the processes undergoing simultaneous annealing from the characteristic activation energy. If the order is 2 or greater, it is necessary to limit the extent of the initial activation-energy spectrum in order to perform the integrations. However, it is seen that the deviations of the behavior of processes distributed in activation energy from Eq. (50) can all be cast into the same form. The deviations will be estimated here for several kinds of initial activation-energy spectra for processes following first-order kinetics. The same kind of corrections would apply when the order differs from unity, but the magnitudes of the corrections would, in general, differ somewhat. The corrections to be considered are those arising from the first of two consecutive stages of step-annealing being insufficiently protracted and from rising and falling regions in the initial activation-energy spectrum. To indicate the magnitude of the corrections, the results will be applied to the step-annealing data published by Overhauser.[8]

(*a*) *Length of the steps in step-annealing.*—It was shown (Fig. 1) that most of the rising part of the first-order-characteristic-annealing function lies in a range of activation energies $\sim3\tau$. Hence for first-order processes, if one of the stages of a step-annealing is conducted for a time sufficient to advance the characteristic-annealing function about 3τ, practically none of the activation-energy spectrum lies under portions formed in previous stages of annealing, and hence the spectrum is practically that which would have arisen if the final annealing were the only annealing which had been performed. Since in isothermal annealing, the characteristic-annealing function moves to higher activation energies without altering its shape, its motion may be followed by choosing any point on it; and in the present case the characteristic-activation energy is a convenient point. Then the length of successive stages of step annealing should be determined from

$$\epsilon_{02}=\epsilon_{01}+3\tau_1, \tag{66}$$

or

$$\tau_2\ln(At_2)=\tau_1\ln(At_1)+3\tau_1, \tag{67}$$

and hence

$$t_2=t_1e^{3\sigma}(At_1)^{\sigma-1}\equiv\lambda t_1. \tag{68}$$

If At_1 were about 10^{13}, a number which seems reasonable for Overhauser's data (V.I.), and if it were desired to conduct each stage of step-annealing for the same length of time, σ should be about 0.91. Actually for most of his annealings $\sigma\cong0.94$ and Eq. (68) suggests each stage should have been three times as long as the previous one; i.e., $\lambda=3$. Since it has not been, a residue of the spectrum of the previous annealing remains and hence Eq. (52a) is altered to

$$-\left(\frac{dP}{dt}\right)_{03}=\int_0^\infty p_0\exp(-At_1e^{-\epsilon/\tau_1}-At_2e^{-\epsilon/\tau_2})Ae^{-\epsilon/\tau_3}d\epsilon. \tag{69}$$

Letting $\sigma_1=\tau_2/\tau_1$, $\sigma=\tau_3/\tau_2$, $r=At_1/At_2$, $z=At_2e^{-\epsilon/\tau_2}$, and $\beta=r(At_1)^{1-\rho}z^{\rho-1}$,

$$-\left(\frac{dP}{dt}\right)_{03}=\frac{\tau_2}{t_2}(At_2)^{1-\sigma}\int_0^{At_2}p_0e^{-z(1+\beta)}z^{\sigma-1}dz. \tag{70}$$

Now β is small, and regarding it as constant gives a somewhat greater effect than it actually exerts. For a constant activation-energy spectrum it is approximately true that

$$-\left(\frac{dP}{dt}\right)_{03}=p_0\frac{\tau_2}{t_2}(At_2)^{1-\sigma}\Gamma(\sigma)(1+\beta)^{-\sigma}, \tag{71}$$

and hence, upon altering the subscript on t to correspond to the nomenclature of Eq. (55),

$$R=(At_1)^{1-\sigma}\Gamma(\sigma)(1+\beta)^{1-\sigma}. \tag{72}$$

Since $\Gamma(\sigma)$ is nearly unity, this can be written

$$R=(At_1)^{1-\sigma}[1+\alpha+(1-\sigma)\beta], \tag{73}$$

where α is a small number.

For Overhauser's conditions, $(1-\sigma)\beta$ is about 0.002 to 0.010 which, it will be seen, is small compared to the value of α.

(*b*) *The effect of rising regions in the initial activation energy spectrum.*—These can be easily investigated by setting p_0 proportional to powers of ϵ or to negative powers of $e^{-\epsilon/\tau_1}$. Two effects are produced: a correction factor equivalent to increasing α is obtained, and the average activation energy of the processes undergoing simultaneous annealing is altered relative to the characteristic-activation energy.

If the initial activation-energy spectrum in the region is rising proportionately to an integral power (μ) of ϵ,

$$p_0=k\epsilon^\mu, \tag{74}$$

and hence

$$-\left(\frac{dP}{dt}\right)_0=k\frac{\tau_1{}^{\mu+1}}{t_1}(At_1)^{1-\sigma}\int_0^{At_1}e^{-z}z^{\sigma-1}\times[\ln(At_1)-\ln z]^\mu d\epsilon, \tag{75}$$

which is seen to consist of a sum of products of gamma and polygamma functions.[13] The result can be cast into the form of Eq. (73) but α is now greater. Typically, when approaching a peak in the initial activation-energy spectrum, the spectrum rises so rapidly that it is best expressed by an exponential as

$$p_0=ke^{\nu\epsilon/\tau_1}, \tag{76}$$

where k and ν are constants. Hence

$$-\left(\frac{dP}{dt}\right)_0=k\frac{\tau_1}{t_1}(At_1)^{1-\sigma}\int_0^{At_1}e^{-z}z^{\sigma-\nu-1}dz, \tag{77}$$

and therefore

$$R=(At_1)^{1-\sigma}\Gamma(\sigma-\nu)/\Gamma(\nu). \tag{78}$$

Since $\Gamma(\sigma-\nu)/\Gamma(\nu)$ is nearly unity but is greater than $\Gamma(\sigma)$, Eq. (78) can be written in the form of Eq. (73) and hence the effect of the exponentially rising distribution is to increase α. The average activation energy $\bar{\epsilon}$ of the processes annealing simultaneously is

$$\bar{\epsilon}=\int(dp/dt)\epsilon d\epsilon\bigg/\int(dp/dt)d\epsilon. \tag{79}$$

For spectra rising as powers of ϵ [Eq. (74)], the integrals in Eq. (79) are like those of Eq. (75) and are easily evaluated with the aid of tables of gamma and polygamma functions.[13] It is found that while the activation energy at which the processes annealing simultaneously possess the maximum rate of annealing is about

$$(1+10^{-3}\mu)\tau_1\ln(At_1), \tag{80}$$

the average activation energy of the processes annealing simultaneously is about

$$(1.017+2\mu\,10^{-3})\tau_1\ln(At_1) \tag{81}$$

for small integral values of μ. For exponentially rising

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[13] H. T. Davis, *Tables of Higher Mathematical Functions* (Principia Press, Bloomington, 1933), Vol. 2.

spectra, Eq. (76), Eq. (79) becomes

$$\bar{\epsilon}=\frac{(\tau_1{}^2/t_1)(At_1)^{\nu-1}\int_0^{At_1}e^{-z}z^{1-\nu-1}[\ln(At_1)-\ln z]dz}{(\tau_1/t_1)(At_1)^{\nu-1}\int_0^{At_1}e^{-z}z^{1-\nu-1}dz} \tag{82}$$

$$=[1-\Psi(1-\nu)/\ln(At_1)]\tau_1\ln(At_1). \tag{83}$$

where Ψ is the logarithmic derivation of the gamma function. The quantity $\Psi(1-\nu)/\ln(At_1)$ is a small negative number; and hence, as found for spectra rising as powers of ϵ, $\bar{\epsilon}$ can be expressed as

$$\bar{\epsilon}=\epsilon_0(1+\delta), \tag{84}$$

and for a constant activation-energy spectrum ($\nu=0$), $\delta\cong0.02$ as before. For a falling initial activation-energy spectrum δ and α will assume values less than their values with a constant initial activation-energy spectrum in about the same proportion as for rising initial spectra. Thus, taking into account the effects of the lengths of the annealing stages, Eq. (72), the effects of the initial activation-energy spectrum Eqs. (75) and (78), and the nomenclature of Eqs. (73) and (84), Eq. (57) may be written

$$\epsilon_0=\zeta\ln\{R/[1+\alpha+(1-\sigma)\beta]\}, \tag{85}$$

and the average activation energy of the processes undergoing annealing simultaneously is therefore

$$\bar{\epsilon}=(1+\delta)\ln\{R/[1+\alpha+(1-\sigma)\beta]\}, \tag{86}$$

and hence

$$E\cong(1-\delta)\bar{\epsilon}+[\alpha+(1-\sigma)\beta]\zeta. \tag{87}$$

The corrections α, β, δ are to be considered approximate and maximal since the finite character of each type of behavior has not been taken into consideration. From Eqs. (84) and (9a), it is seen that the average activation energy of the processes occurring simultaneously $\bar{\epsilon}$ at equal values of At_1 in a region in which the initial activation-energy spectrum is constant is proportional to the absolute temperature at which the annealing is conducted. When the initial activation-energy spectrum is rising, this average activation energy is above this line; and when the initial activation-energy spectrum is falling, this average activation energy is below this line. Since α increases nearly proportionately to δ, the effect of the initial activation-energy spectrum on E is less than its effect on this average activation energy. In Overhauser's case, ζ was about $\bar{\epsilon}/2$ and hence in this case the deviations of E from a linear dependence on τ would be about half as great as the deviations of $\bar{\epsilon}$ from a linear dependence on τ and opposite in sign.

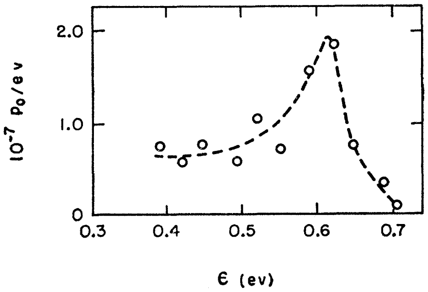

FIG. 4. The approximate activation energy spectrum from Overhauser's isothermal annealing data assuming first-order kinetics and a frequency factor 10^9.

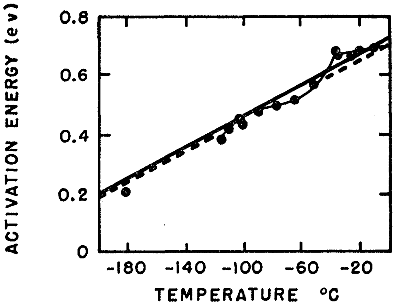

FIG. 5. The behavior of E (plotted points) and 1.02ϵ_0 (solid line) as a function of temperature.

The results published by Overhauser[8] illustrate the effects shown here. An approximate value of A may be obtained from the slope of the curve E as a function of temperature given in Fig. 5, taken from Overhauser's Fig. 4, and is about 10^9. The approximate initial activation-energy spectrum obtained by introducing the slopes at the end of his stages of step-annealing (his Fig. 3) into Eq. (14), no correction being made for previous stages of annealing, is shown in Fig. 4. The sharp peak is readily apparent; and from the discussion in paragraph (2.2), the actual peak must be somewhat sharper. The peak in Fig. 4 rises about as $r^{10\epsilon}$ (or $e^{0.2\epsilon/\tau_1}$), changing α and δ by *ca* 0.02; and falls about as $e^{-20\epsilon}$, changing α and δ by *ca* -0.04. Now ζ can be written

$$\zeta=\tau_1/(1-\sigma), \tag{88}$$

and since for these experiments $\sigma\cong0.94$, $\zeta\cong1/5$. Thus, since $\bar{\epsilon}\cong0.6$, the deviation of E from a straight line should be about -0.01 ev just before the peak and should be about $+0.02$ ev just following the peak. This expected deviation is readily apparent in Fig. 5 when the straight line (solid line) is drawn at slightly greater slope than was done by Overhauser (dashed line). Thus the data shown in Fig. 5 cannot be taken as proof of a 2.5 order; they can be as easily explained by first-order kinetics. Within the precision of the data and of the approximations of the theory, the results could be explained by any order of reaction over quite a range of orders. The data given by Overhauser are affected mainly by the initial activation-energy spectrum, and as was shown in Sec. 1, such data is rather insensitive to order or frequency factor. That short isothermal annealings in the region of the peak can be fitted by kinetics of order 2.3 using a discrete activation energy is but an expression of the fact that the peak obtained by inserting isothermal annealing rates into Eq. (14) is of width several times 2.3τ. Since $\tau \cong 1/30$ ev in the region in which the peak anneals, the expected width is shown in Fig. 4. It is evident that the rates in short isothermal annealings in this region could equally well be explained by any order $0<n<2.3$ if one assumes the processes to be properly distributed over a range of activation energies several times $2.3\ \tau/n$. It would seem that the method of step-annealing used by Overhauser might be more useful for evaluating the frequency factor than the order.

3. DETERMINATION OF THE ORDER BY A COMBINATION OF ISOTHERMAL ANNEALING AND TEMPERING

3.1. A possible method for determining the order of a group of processes which occur over a range of activation energies is suggested by the physical picture presented in paragraphs 1.3 and 1.4. The method is best applied when it is found that the initial activation-energy spectrum is quite constant over a sufficient range of activation energies. This fact can be easily ascertained, for then the approximation, Eq. (39), is quite good. If a sample of a substance possessing such an initial activation-energy spectrum is subjected to an isothermal annealing at a suitable temperature for a sufficient length of time, the rising portion of the resultant activation-energy spectrum has the form of the corresponding portion of the characteristic annealing function. If a tempering experiment is now conducted on the isothermally annealed sample, the nature of the characteristic isothermal annealing function is revealed. The portion of the tempering curve of interest is that resulting from the steeply rising portion of the isothermal annealing curve. Here the approximation of Eq. (39) is useless. However, since the original initial activation-energy spectrum was constant (here designated p_a), the equations can be integrated directly. The tempering rate if the processes are first order is

$$-\frac{dP}{dt}=p_a\int_0^\infty Ac \times\exp[-At_1e^{-\epsilon/t_1}-Ac\tau\mathbf{E}_2(\epsilon/\tau)-\epsilon/\tau]d\epsilon, \quad (89)$$

where the isothermal annealing has been conducted for a time t_1 at a temperature τ_1. When the isothermal annealing has been conducted for a long time, at the initial part of the tempering curve the condition $t_1 \gg c\tau/(y+2)$ where $y=\epsilon/\tau$ maintains. Letting $\rho=\tau_1/\tau$, Eq. (89) becomes

$$-\frac{dP}{d\tau}\cong p_a\int_0^\infty Ac\tau\exp[-At_1e^{-y/\rho}-y]dy, \quad (90)$$

which is seen to be

$$-\frac{dP}{d\tau}\cong p_a\left(\frac{c\tau}{t_1}\right)^\rho (Ac\tau)^{1-\rho}\rho\Gamma(\rho). \quad (91)$$

Equation (91) is useful for values of Θ up to $\sim\frac{1}{2}$ in practice.

Similarly, when the order is not unity,

$$-\frac{dP}{d\tau}=p_a\int_0^\infty [1-(1-n)Bt_1e^{-y/\rho}]^{1/(1-n)} \times[1-(1-n)Bc\tau\mathbf{E}_2(y)]^{n/(1-n)}Bc\tau e^{-y}dy, \quad (92)$$

and when $t_1 \gg c\tau/(y+2)$,

$$-\frac{dP}{d\tau}\cong p_a\int_0^\infty [1-(1-n)Bt_1e^{-y/\rho}]^{1/(1-n)}Bc\tau e^{-y}dy, \quad (93)$$

which, for the particular case of orders between 1 and 2, is

$$-\frac{dP}{d\tau}\cong p_a\left(\frac{c\tau}{t_1}\right)^\rho (Bc\tau)^{1-\rho}\rho\Gamma(\rho) \times\left[(n-1)^{-\rho}\Gamma\left(\frac{1}{n-1}-\rho\right)\Big/\Gamma\left(\frac{1}{n-1}\right)\right]. \quad (94)$$

The quantity in the brackets approaches unity when n approaches unity and increases when n increases over the range 1–2. Since the expression refers to the beginning of the rising portion of the tempering curve, that on the low-temperature side of the inflection point, it is in accord with the physical picture that the tempering curve is nearly proportional to the initial activation-energy spectrum, and that the slope of the rising portion of the isothermal annealing curve decreases with increasing order. Because the frequency factor affects the characteristic annealing function and the characteristic tempering function differently, it is necessary to choose a correct frequency factor (and indeed is a useful method of determining the frequency factor). If the frequency factor has been established, a comparison of the actual tempering curve with the results which are expected for first-order processes can be a method for investigating the actual order of the processes. The method is not necessarily confined to the initial portion of the tempering curve or to the simple experimental conditions chosen here if graphical integration is resorted to. It may then be possible to determine both frequency factor and order from the same experiment since they affect the functions differently.

3.2. *Experimental use of tempering rates.*—For significant kinetic studies, it is essential that the temperature of the sample be raised strictly in accordance with a known law. Since thermal changes whose temperature derivatives are of the order of magnitude of the heat capacity often accompany annealing, it may be insufficient to raise the ambient temperature according to the known law, the customary procedure. The effects of not raising the temperature of a sample according to a known law are qualitatively the same for the kinetic systems considered here; they are easily demonstrated for processes obeying first-order kinetics and possessing a constant initial activation-energy spectrum. Then

$$-\frac{dP}{d\tau}=p_0Ac\tau\int_0^\infty \exp[-y-Ac\tau\mathbf{E}_2(y)]dy, \tag{95}$$

where $y=\epsilon/\tau$. From Eq. (24):

$$-\frac{dP}{d\tau}\cong p_0Ac\tau\int_0^\infty \exp[-y-Ac\tau e^{-y}/(y+2)]dy. \tag{96}$$

Let $v=\exp[-Ac\tau e^{-y}/(y+2)]$; then, using the approximation Eq. (36),

$$y+\ln(y+2)=\ln(Ac\tau)-\ln_2(1/v)\cong a+by, \tag{97}$$

and hence

$$y=(1/b)[\ln(Ac\tau)-\ln_2(1/v)-a]. \tag{98}$$

Over the effective range of y, the variable v ranges from nearly zero to nearly one; hence

$$\begin{aligned}-\frac{dP}{d\tau}&\cong p_0Ac\tau\int_0^1 e^{-y}vdv/bv\ln(1/v)\\&=p_0Ac\tau\int_0^1 \exp[-\ln(Ac\tau)+\ln_2(1/v)\\&\qquad\qquad+\ln(y+2)]dv/b\ln(1/v)\\&=(p_0/b)\int_0^1 (y+2)dv\\&=(p_0/b^2)\int_0^1[\ln(Ac\tau)-\ln_2(1/b)-a+2b]dv\\&=(p_0/b^2)[\ln(Ac\tau)+\gamma-a+2b],\end{aligned} \tag{99}$$

where $\gamma=0.577\cdots$.

The quantity $-dP/d\tau$, which will be called the annealing rate, is greater the lower the tempering rate, for c is the inverse tempering rate. This is to be expected, for the lower the tempering rate, the longer the sample remains at any temperature. If the tempering rate is not constant, but starts changing, an exaggerated effect is observed. The qualitative nature of the effect is easily shown for an increasing tempering rate such as that governed by the law of Eq. (40). The annealing rate corresponding to Eq. (99) is then

$$-(dP/d\tau)=(p_0/s^2)[\ln(Amc\tau^m)+\gamma-r+(m+1)s], \tag{100}$$

where $\ln(y+m+1)\cong r+sy$ [see Eq. (36)]. Since r and s have nearly the same values as a and b, the major effect is due to the power of the temperature appearing in the logarithm term. For a typical case at a temperature several hundred degrees centigrade, if the tempering rate were parabolic ($m=2$), the annealing rate would be about 10% less than if the tempering rate were constant. However, if the tempering rate were originally constant, and were to change to a parabolic one at some particular temperature, the decline in annealing rate would obviously be greater than the difference between the annealing rates for the two powers m because the activation-energy spectrum at the particular temperature for the constant tempering rate is smaller than for the parabolic one. Such an increase in tempering rate is common at the beginning of a tempering experiment, and since the tempering curve is usually interpreted as if the tempering rate were constant, it may be said that the initial portion of the tempering curve is depressed. As the constant tempering rate is approached, the tempering rate is declining, and here the tempering curve is elevated. The same effect frequently occurs at the end of the tempering range where a declining tempering rate is common. The result of these variations in tempering rate is the introduction of "false peaks" into the tempering curve. When thermal changes accompany annealing even more severe effects can occur.[14]

4. COMPLICATIONS

4.1. The treatment given here has considered the behavior of processes distributed in activation energy when the frequency factor and order are constant. The physical justification of this treatment is that the experimentally observed range of activation energies affects the gross kinetic behavior more severely than the range of expected orders and frequency factors. Despite the lack of any detailed kinetic investigations, it is worth noting some of the effects which may be treated as variations of order and frequency factor.

4.2. *Variations in order due to the property chosen for investigation.*—It was pointed out by Brown[5] that if a property is proportional to a power of the number of processes which can occur,

$$p=fq^\nu, \tag{102}$$

then the property will obey kinetics of order n/ν.

4.3. *Variations in frequency factor.*—The results which were derived here were based upon a slow variation of frequency factor with activation energy. This may seem a rather severe restriction, especially when the order is not unity and the frequency factor contains a concentration. However, this concentration is the original concentration, that given by the initial activation-energy spectrum. Since the annealing which is observed is due mainly to processes for which

$$[\tau\ln(Bt)-\epsilon]\sim 0, \tag{103}$$

the variations in B needed to affect the results are variations orders of magnitude larger than the ranges of ϵ being considered. Such variations in concentration have already been excluded in many of the results given

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[14] W. Primak (to be published).

here by the requirement that the initial activation-energy spectrum be broad compared to several times $n\tau$. However some physical circumstances might give rise to large variations in frequency factor and perhaps diffusion controlled processes might be so treated.

From Eq. (103) it is seen that if B changed greatly enough to affect $\ln B$ to an extent comparable to the ranges of ϵ under study, the processes with the changed B would be attributed to some other activation energy, despite the fact that they occur with the same activation energy. Then when an isothermal annealing is performed at another temperature, the processes would be attributed to still another activation energy. Thus when the frequency factor shows marked variations and it is assumed constant, the initial activation-energy spectrum seems to be different at different temperatures. The effect is easily seen by considering a case in which the activation energy is constant but there is a distribution of frequency factors and is illustrated here for processes obeying first-order kinetics.

In an isothermal annealing of processes of one activation energy distributed in frequency factor and obeying first-order kinetics, the annealing rate is

$$-\frac{dP}{dt}=\int_0^\infty p_0(A)\exp(-Ate^{-\epsilon/\tau})dA, \qquad (104)$$

and taking as a specific example one in which the distribution $p_0(A)$ is a constant p_a over a range A_1 to A_2 and zero elsewhere,

$$-\frac{dP}{dt}=p_a\int_{A_1}^{A_2}\exp(-Ate^{-\epsilon/\tau})dA, \qquad (105)$$

$$-\frac{dP}{dt}=\frac{p_a\tau}{t^2e^{-\epsilon/\tau}}[(1+A_1te^{-\epsilon/\tau})\exp(-A_1te^{-\epsilon/\tau}) - (1-A_2te^{-\epsilon/\tau})\exp(-A_2te^{-\epsilon/\tau})]. \qquad (106)$$

From Eq. (105), it is seen that at the instant the annealing starts, the rate is $p_a(A_2-A_1)$. However, after any appreciable time, since A_1 will be greater than A_2 by orders of magnitude, the annealing rate becomes

$$-\frac{dP}{dt}=\frac{p_a\tau}{t^2e^{-\epsilon/\tau}}(1+A_1te^{-\epsilon/\tau})\exp(-A_1te^{-\epsilon/\tau}). \qquad (107)$$

If it is erroneously assumed that the system consists of processes possessing a single frequency factor A_1, but distributed in activation energy, then $A_1t=e^{-\epsilon_0/\tau}$ and inserting Eq. (107) into Eq. (15a) there is obtained

$$p_0(\epsilon_0)=p_aA_1(1+e^{-(\epsilon-\epsilon_0)/\tau})\exp(-e^{-(\epsilon-\epsilon_0)/\tau}). \qquad (108)$$

In Eq. (108), ϵ is fixed and ϵ_0 is the variable. The fictitious activation-energy spectrum given by this equation resembles the form of a characteristic-annealing function because both are dominated by the negative exponential of a negative exponential. For the fictitious activation-energy spectrum: the point of inflection occurs at $\epsilon_0=\epsilon+\tau\ln 2$ where the slope is $p_0A_1 4e^{-2}/\tau$; most of the rise occurs over a small range of ϵ_0 several times τ; no change takes place in time since it is an initial spectrum; and the ordinate $2p_0A_1/e$ remains fixed at $\epsilon_0=\epsilon$ for all temperatures. Thus the segments of the fictitious activation-energy spectrum obtained by isothermal annealings at different temperatures do not join. For a series of segments obtained with successively higher temperatures, points obtained at higher temperatures will lie above points having the same value of ϵ_0 obtained at lower temperatures when $\epsilon_0<2p_0A_1/e$. When $\epsilon_0>2p_0A_1/e$, the higher temperature points will lie below the lower temperature points of the same ϵ_0. It should be noted that the lower values of the frequency factor dominate the kinetic behavior.

The effect of using a higher frequency factor in Eqs. (15) and (15a) is to displace the derived initial-activation-energy spectrum to higher energies, and in Eq. (39) to displace the spectrum, to reduce its height, and to spread it over a greater range of activation energies. A twofold distribution of processes in frequency factor and activation energy could be represented in Cartesian space, and its projection on a vertical plane parallel to the activation energy axis would be a band. If the experimental rates of isothermal annealing at various temperatures are inserted into Eqs. (15) and (15a), there results an effect similar to that obtained in considering a distribution in frequency factor alone: the segments of the fictitious initial activation-energy spectrum obtained at various temperatures do not form a continuous curve; and for an appropriate mean frequency factor fall within the band.

4.4. *Successive reactions.*[15]—Successive reactions are possible for the systems considered here. The effect is the occurrence of a process which involves a property change and which thereby generates another process which will occur at a higher activation energy. The appearance of such additional property change at activation energies close to those at which the original process occurred would steepen the activation-energy spectra in these regions; and if the data were analyzed by the methods given here, an apparent order lower than the actual order and/or a frequency factor higher than the actual frequency factor would be derived.

4.5. *Experimental eludication of the kinetics.*—It is seen that once the kinetics of annealing is admitted to have complexities as great as a distribution of activation energies, other complexities of behavior can be excluded only by experimental evidence. It is necessary (1) to ascertain that the property measured is a suitable one, (2) to exclude or ascertain successive reactions, (3) to ascertain the frequency factor, and (4) to ascertain the

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[15] This possibility was suggested by others in the course of radiation damage studies at the Metallurgical Laboratory and the Argonne National Laboratory, among whom are Simpson, Neubert, and Hennig.

order of reaction. Each of these requirements must be met by suitably planned sets of annealings or combinations of annealings over the whole of the temperature range to be investigated. The writer is not familiar with any investigation sufficiently detailed to meet these requirements. Since much of the complexity commonly results from the fact that the properties which are studied do not identify particular chemical species in particular environments (an analogy which could be taken in chemical kinetics would be the measurement of pressure in the pyrolysis of a gaseous mixture of organic compounds which was not simultaneously subjected to chemical analysis), it may be hoped that when suitable properties or combination of properties are studied much of the complexity of a particular system can be removed.

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Exciton Absorption in Cuprous Oxide

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The exciton absorption spectrum of Cu_2O has been measured at low temperatures. As reported by Gross, the observed lines fit a hydrogen-like series formula. The wavelength shift of the position of the optical absorption band edge has also been measured as a function of temperature. The dependence is approximately quadratic.

INTRODUCTION

In a series of papers, Gross and his collaborators[1] have reported on the exciton absorption in crystals of Cu_2O. This absorption appears as a series of lines near the main optical absorption edge which occurs in the red end of the visible region. The observation is made at low temperatures (77°K or lower) and with thin crystal slabs (of the order of 10 to 50 microns thickness). The observed lines may be empirically fitted to a hydrogen-like series formula with astonishing accuracy.

Wannier,[2] in 1937, postulated the existence of the corresponding energy levels, and proposed the following as a model. When an electron in an otherwise perfect dielectric crystal is raised to an excited state, it may be thought of as belonging to the crystal as a whole rather than to any particular atom. If its energy is insufficient to raise it to the conduction band, then it will remain within the Coulomb influence of the positive hole which it has left behind in the lattice. This electron-hole system may exist in stationary states, and will behave with respect to the remainder of the crystal as if embedded in a dielectric medium. The system is, however, free to migrate within the crystal.

The expected energy levels, measured from the ionization continuum (the conduction band), will be given by the Bohr expression:

$$W_k = -\mu e^4/4\pi\epsilon^2 k^2 c\hbar^3,$$

where $\mu = m_h^* m_e^*/(m_h^* + m_e^*)$, the reduced mass of the electron-hole system; ϵ is the dielectric constant of the dielectric material; k is the ordinal number of the level and takes on integral values. The other symbols have their usual meaning. The radii of the Bohr orbits will be given by

$$a = k^2 \epsilon\hbar/\mu e^2.$$

These expressions for the energy and the radius differ from those obtained in the Bohr theory for atomic hydrogen only in that the value for the reduced mass is much different, and that a dielectric constant has been introduced into the force equation. It should be noted also that the "ground state" for this system is the recombined state in which the electron has collapsed into its hole. This occurs at an energy W_g (the width of the forbidden energy gap) below the conduction band. Consequently the series formula for the expected lines will be given by

$$\nu = W_g - W_k/k^2,\ k = 1, 2, 3, \cdots.$$

EXPERIMENTAL

We have repeated the earlier measurements of Gross *et al.*, using the apparatus shown diagrammatically in Fig. 1. The spectrograph was a three-meter concave grating machine having a dispersion of roughly five angstroms per millimeter. The source was a tungsten filament. A water cell was placed between source and

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[1] Ye. F. Gross and N. A. Karryev, Doklady Akad. Nauk S.S.S.R. **84**, 261 (1952); **84**, 471 (1952); Ye. F. Gross and B. P. Zakharchenya Doklady Akad. Nauk S.S.S.R. **90**, 745 (1953); Gross, Zakharchenya, and Reinov, Doklady Akad Nauk S.S.S.R. **92**, 265 (1953).

[2] G. Wannier, Phys. Rev. **52**, 191 (1937).