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Dyre, J. C.

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A PHENOMENOLOGICAL MODEL FOR THE MEYER-NELDEL RULE

Jeppe C. Dyre

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ROSKILDE UNIVERSITETSCENTER
INSTITUT FOR STUDIET AF MATEMATIK OG FYSIK SAMT DERES
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Abstract

In this paper it is argued that the generality of the Meyer-Neldel rule compels one to adopt a phenomenological approach if a universally valid model is aimed at. It is shown that there exists only one possible phenomenological model. This model is based on an exponential probability distribution of energy barriers. The model predicts a power-law frequency-dependence of the a.c. conductivity with the exponent s given by $s = 1 - T/T_0$ where T_0 is the characteristic temperature of the Meyer-Neldel rule. It is conjectured that the exponential energy barrier distribution derives from a "glass transition" at T_0 . The generalization of the model to account for the compensation effect is briefly discussed exemplified by the case of heterogeneous catalysis.

1. Introduction

Semiconductors are characterized by the temperature-dependence of their electrical conductivity. If $\sigma(0)$ denotes the d.c. conductivity one usually writes

$$\sigma(0) = A e^{-\Delta E/kT} \quad (1)$$

where ΔE is the activation energy, k is the Boltzmann constant, T is the temperature, and A is the so-called preexponential factor. Almost 50 years ago, Meyer and Neldel (1937) found for some oxide semiconductors that when the semiconductor is prepared or annealed under different conditions, the activation energy varies and that A depends exponentially on ΔE . Their discovery has become known as the Meyer-Neldel (MN-) rule. It states that the d.c. conductivity is given by

$$\sigma(0) = \sigma_{00} e^{\Delta E/kT_0} e^{-\Delta E/kT} \quad (2)$$

where σ_{00} and T_0 are constants within a class of related semiconductors.

The MN-rule is an empirical relation which has been observed in very many different semiconductors. These include single-crystal and polycrystalline semiconductors, amorphous semiconductors, organic semiconductors, and even ionically conducting crystals and glasses (Rosenberg, Bhowmik, Harder and Postow 1968, Roberts 1971, Carlson and Wronski 1979, Dosdale and Brook 1983). The rule applies to chemically closely related semiconductors or to a single semiconductor prepared in various

ways. For instance one may vary the degree of non-stoichiometry, the dopant concentration, the oxygen partial pressure at annealing, etc. The MN-rule seems to be an almost universal characteristic of semiconductors which have in common only the property of being inhomogeneous from some point of view (Irsigler, Wagner and Dunstan 1983). But the relation is even more general than that. In a number of rate processes it is found that the preexponential factor A of the reaction rate depends itself exponentially on the activation energy: $A \propto \exp(\Delta E/kT_0)$, just as in eqn. (2). This phenomenon is usually referred to as the compensation effect, but it has also been called the Constable law, the isokinetic relationship or the θ -rule (Exner 1964, Khait 1983). A thoroughly studied example is the compensation effect in heterogeneous catalysis which has been reviewed by Galwey (1977). The compensation effect has also been observed by e.g. thermionic emission of electrons from a metal (Vanselow 1985), diffusion in solids (Shinar, Davidov and Shaltiel 1984), annealing time of irradiated silicon (Fang 1969), viscosity of aqueous solutions (Good and Stone 1972), decomposition of solids (Zsako, Varhelyi, Varhelyi and Liptay 1981), and a number of biophysical, biochemical and biological systems (Rosenberg, Kemeny, Switzer and Hamilton 1971, Tomlinson 1983).

In this paper the starting point is the observation that one is forced to adopt a phenomenological approach if the many occurrences of the MN-rule are believed to have a single common origin. The occurrence of the compensation effect in other contexts even more emphasizes the need for a phenomenological approach. While the paper is almost exclusively about the MN-rule in semiconductors, the model to be proposed can be generalized immediately to deal with the compensation effect in other

rate processes, as will be briefly commented upon in sec. 6.

The paper is organized as follows. Section 2 argues for the need for a phenomenological model and derives the basic feature of such a model, an exponential probability distribution of energy barriers. In section 3 the simple mathematics of the model is developed. It will be shown that the model predicts a correlation between the MN-rule and the a.c. properties of the semiconductors. In section 4 the model predictions are compared to experiments. In section 5 it is conjectured that the exponential energy barrier distribution is a consequence of a glass transition. Section 6 deals with the generalization of the model to deal with the compensation effect in other rate processes, exemplified by the case of heterogeneous catalysis. A final discussion is given in section 7.

2. The need for a phenomenological approach

Several models have been proposed to explain the MN-rule. Busch (1950) suggested that the MN-rule in extrinsic broad band semiconductors is due to a freezing of the donor concentration during cooling after the preparation. The MN-rule in amorphous or polycrystalline semiconductors may derive from an exponential tailing of the majority band states as suggested by Roberts (1971), or it may be due to a long-ranged electrostatic random potential (Overhof 1984). As regards the MN-rule in organic semiconductors, Kemeny and Rosenberg (1970) proposed a model where electrons or polarons tunnel through intermolecular barriers from activated energy states of the organic molecu-

les. For ionic conductors it has been argued that the MN-rule is an approximate relation valid for ionic crystals with either Frenkel, Schottky or interstitial disorder (Dosdale and Brook 1983). It has even been suggested that the MN-rule may be a spurious effect due to a thin rectifying layer at the electrode-solid interface (Roberts 1971).

It is of course perfectly possible that the MN-rule has many different explanations, each valid for only a limited class of solids. But in view of the generality of the phenomenon it seems more likely that there is a single, general explanation. However, if a single model of the MN-rule is to be universally valid, it can not relate directly to the microscopic details of the conduction process; it must be a phenomenological model. This is an important, though obvious, conclusion. It will be shown below that once the phenomenological approach is accepted there is only one possible model.

Proceeding now to derive the basic feature of a phenomenological model for the MN-rule, we remind that the rule has been observed in both electronically, polaronically and ionically conducting solids. The only way to describe these different cases by a single model is to use a hopping model, i. e. to regard the conduction process as mediated by hopping of localized charge carriers ("quasiparticles"). The single common feature of the many occurrences of the MN-rule is an element of disorder from some point of view (Dewsberry 1975, Irsigler et al. 1983). Disorder can easily be built into a hopping model via a probability distribution $p(\tau)$ of waiting times τ at each quasiparticle site (Scher and Lax 1973). It is known from a. c. conductivity measurements that there is always a maximum waiting time τ_{\max} , corresponding to the frequency

below which the conductivity becomes frequency-independent. On the other hand, there is no minimum waiting time τ_{\min} of any relevance to this problem (i.e. $\tau_{\min} \cong 10^{-12}$ s). Thus, in the phenomenological model a solid is completely characterized by the two entities: $p(\tau)$ and τ_{\max} . Now, a class of MN-related solids must have something in common. It is physically obvious that the d.c. conductivity depends strongly on τ_{\max} so the common entity must be $p(\tau)$.

Having reached the conclusion that different MN-related solids have the same $p(\tau)$ but different τ_{\max} , the next step is to ask what can be learned about $p(\tau)$ from eqn. (2) - the Meyer-Neldel rule. The d.c. conductivity is proportional to the diffusion constant which by Einsteins equation is proportional to the mean-square displacement per unit time of a quasiparticle. The d.c. conductivity is thus proportional to $\lim_{N \rightarrow \infty} N / \tau_N$ where τ_N is the time taken for N jumps, that is

$$\sigma(0) \propto \langle \tau \rangle^{-1} \quad (3)$$

where $\langle \rangle$ denotes an average over $p(\tau)$ (all jump-jump correlations are ignored). The quasiparticle jumps are thermally activated so τ is determined by an energy barrier $\Delta E'$:

$$\tau = \tau_0 e^{\Delta E' / kT} \quad (4)$$

where τ_0 is a microscopic time ($\tau_0 \cong 10^{-12}$ s). The maximum waiting time τ_{\max} corresponds to a maximum energy barrier ΔE_{τ} , while the minimum energy barrier is approximately equal to zero because $\tau_{\min} \cong \tau_0$. If the distribution of energy barriers corresponding to $p(\tau)$ is denoted by

$p(\Delta E')$ we now find by combining eqns. (2), (3) and (4)

$$e^{-\Delta E/kT_0} e^{\Delta E/kT} \propto \int_0^{\Delta E_T} e^{\Delta E'/kT} p(\Delta E') d(\Delta E') \quad (5)$$

which is valid for each sample, i.e. for varying ΔE .

Taking the derivative of this equation with respect to ΔE one obtains

$$e^{-\Delta E/kT_0} e^{\Delta E/kT} \propto e^{\Delta E_T/kT} p(\Delta E_T) \frac{d\Delta E_T}{d\Delta E} \quad (6)$$

The constant of proportionality depends weakly on T and ΔE_T but this is unimportant compared to the exponentials and it will be ignored. By considering the temperature-dependence of both sides of eqn. (6), one finds that $\Delta E = \Delta E_T$. This is a manifestation of the above mentioned fact that $\sigma(0)$ and τ_{\max} are strongly correlated. Equation (6) now becomes

$$p(\Delta E') \propto e^{-\Delta E'/kT_0} \quad (7)$$

Thus, once the phenomenological approach is accepted one is led to a unique model for the MN-rule based on an exponential distribution of energy barriers. It is not surprising that the mathematics involved is very similar to the derivation of the MN-rule from the assumption of exponential band tails (Roberts 1971, Cohen, Economou and Soukoulis 1984), here we have essentially just reversed their argumentation.

3. The model

It is easy to see that variations in quasiparticle jump distance are of little importance compared to the large variations in waiting times. This fact may be built into the model by adopting the Scher-Lax approach (1973) and regard the disordered semiconductor as a regular lattice with randomly varying jump frequencies, and this approach is adopted here. It is convenient to speak of jump frequencies γ instead of waiting times, these two quantities are related by $\gamma = \tau^{-1}$ so the jump frequency is given by

$$\gamma = \gamma_0 e^{-\Delta E'/kT} \quad (8)$$

where γ_0 is the attempt frequency ($\approx 10^{12} \text{ s}^{-1}$) and $\Delta E'$ is the energy barrier.

As mentioned, the MN-rule is observed in disordered semiconductors. This is the same class of solids that is known to show strong frequency dispersion of the conductivity, and therefore it is of interest to evaluate the entire frequency-dependent conductivity of the model, $\sigma(\omega)$. This quantity can be calculated by the CTRW approximation, the simplest possible non-trivial mean-field approximation. In the CTRW $\sigma(\omega)$ is given by (Scher and Lax 1973, Odagaki and Lax 1981)

$$\sigma(\omega) = \frac{C}{T} \left[-i\omega + \left\langle \frac{1}{\gamma + i\omega} \right\rangle^{-1} \right] \quad (9)$$

where $\langle \rangle$ denotes an average over the jump frequency probability distribution $p(\gamma)$; and C is a constant depending on the quasiparticle concentration, average jump distance, etc.

The jump frequency distribution is really a probability density: $p(\gamma) \equiv d\tilde{p}/d\gamma$. From this we find by means of eqns. (7) and (8)

$$p(\gamma) = \frac{d\tilde{p}}{d\gamma} = \frac{d\tilde{p}}{d\Delta E'} \frac{1}{\frac{d\gamma}{d\Delta E'}} \propto e^{-\Delta E'/kT_0} \frac{1}{\gamma} \propto \gamma^{-s} \quad (10)$$

where

$$s = 1 - T/T_0. \quad (11)$$

The maximum jump frequency is γ_0 (corresponding to $\Delta E'_{\min} = 0$) while the minimum jump frequency is given by

$$\gamma_{\min} = \gamma_0 e^{-\Delta E'/kT} \quad (12)$$

where ΔE as in sec. 2 is the maximum energy barrier. The normalized jump frequency distribution is given by

$$p(\gamma) = \frac{1-s}{\gamma_0} \left(\frac{\gamma}{\gamma_0} \right)^{-s} \quad (13)$$

Here it has been assumed that $\gamma_{\min} \ll \gamma_0$ which is valid in all cases of interest and will be assumed throughout the paper.

Proceeding now to calculate the conductivity we find for the d.c. conductivity

$$\sigma(0) = \frac{C}{T} \langle \gamma^{-1} \rangle^{-1} = \frac{C}{T} \frac{s}{1-s} \gamma_0 \left(\frac{\gamma_{\min}}{\gamma_0} \right)^s \quad (14)$$

or

$$\sigma(0) = \frac{C}{T} \frac{s}{1-s} \gamma_0 e^{\Delta E'/kT_0} e^{-\Delta E'/kT} \quad (15)$$

As expected we recover the MN-rule. There is a factor of T^2 in the denominator differing from eqn. (2), but this is almost unobservable compared to the strong temperature-dependence of the Boltzmann factor. The a.c. conductivity is independent of frequency for $\omega \ll \gamma_{\min}$ and equal to $\sigma(0)$. For frequencies around γ_{\min} the conductivity begins to increase. In the limit $\omega \gg \gamma_{\min}$ (but still $\omega \ll \gamma_0$) it is easy to calculate $\sigma(\omega)$. In this regime one finds

$$\left\langle \frac{1}{\gamma + i\omega} \right\rangle \approx \frac{1-s}{\gamma_0} \int_0^{\infty} \frac{(\gamma/\gamma_0)^{-s}}{\gamma + i\omega} d\gamma = \frac{1}{\gamma_0} \frac{(1-s)\pi}{\sin(s\pi)} \left(\frac{i\omega}{\gamma_0} \right)^{-s} \quad (16)$$

and since the $i\omega$ -term of eqn. (9) is negligible, $\sigma(\omega)$ is simply given by

$$\sigma(\omega) = \frac{C}{T} \gamma_0 \frac{\sin(s\pi)}{(1-s)\pi} \left(\frac{i\omega}{\gamma_0} \right)^s, \quad \gamma_{\min} \ll \omega \ll \gamma_0. \quad (17)$$

Thus a power-law frequency-dependence of the conductivity results, with the exponent $s = 1 - T/T_0$. It must be emphasized, however, that $\sigma(\omega) \propto \omega^s$ with $s = 1 - T/T_0$ is a direct consequence of eqn. (13); the CTRW approximation enters only in the calculation of the constant of proportionality.

4. The phenomenological model and the experimental situation

As shown above, the phenomenological model implies a power-law frequency-dependence of the a.c. conductivity. This is a striking prediction which can be easily checked experimentally, it seems. And indeed, all disordered semiconductors exhibits an ω^s -behaviour of the a.c. conductivity where s is always

less than one and always goes to one as T goes to zero (Jon-
scher 1977, Long 1982). Still, these experimental findings can
not be taken as evidence for the model. The reason is the fol-
lowing. For most solids $\Delta E/T_0$ is not very much larger than
one and therefore it is necessary to go to temperatures much
below T_0 in order to observe a power-law behaviour of $\sigma(\omega)$
covering a wide frequency range. But at low temperatures, the
above model is hard to distinguish from another phenomenological
model which has nothing to do with the MN-rule. This model,
which formally corresponds to the $T_0 \rightarrow \infty$ limit of the above
model, predicts that (Dyre 1985a)

$$\sigma(\omega) = \sigma(0) \frac{i\omega\tau}{\ln(1+i\omega\tau)} \quad (18)$$

This formula implies an a.c. conductivity which is very close
to a power-law ω^s where s at low temperatures is given by
(Dyre 1985b)

$$s = 1 - T / \frac{1}{2} \Delta E \quad (19)$$

Here ΔE as usual denotes the activation energy of $\sigma(0)$.
Obviously, accurate measurements of the a.c. conductivity are
necessary in order to distinguish the MN-phenomenological
model from the model behind eqn. (18). To make things even worse,
it seems that no measurements at all of $\sigma(\omega)$ has been carried
out on the same samples that has been reported to obey the
MN-rule.

The superionic conductor Na β -alumina is a promising candi-
date for the verification of the phenomenological model.
Although the MN-rule has not been observed in Na β -alumina, we

expect the MN-rule to apply at low temperatures with T_0 around 250 K. This prediction is based on the a.c. conductivity measurements of Almond and West (1981). Their data has been carefully analysed by Macdonald and Cook (1984) and they find values of s between 0,35 and 0,72 which turn out to obey eqn. (11) with $T_0 \cong 250$ K. A search for the MN-rule in the low-temperature d.c. conductivity of Na β -alumina samples would be very interesting.

5. The Meyer-Neldel rule as a consequence of a glass transition

In this section the origin of the MN-rule is discussed. First one may ask whether T_0 is to be interpreted as a real physical temperature or whether kT_0 is just a characteristic energy. The latter point of view is held by the workers postulating exponential band tails (Roberts 1971, Adler 1982, Cohen et al. 1984) and by Kemeny and Rosenberg (1970) who link T_0 to the Debye temperature which really is an energy scale. Here, we shall suggest that T_0 is a real physical temperature, namely a glass transition temperature.

Remember that the MN-rule implies that the d.c. conductivity at $T = T_0$ is independent of ΔE . According to the phenomenological model, as T rises towards T_0 the deepest energy minima become less important for the determination of $\sigma(0)$ and right at $T = T_0$ they are not important at all. This is reflected by the fact that $p(\gamma) \propto \gamma^{-5}$ becomes $p(\gamma) = \text{const.}$ at $T = T_0$. When the deepest energy minima lose their importance it is obvious that $\sigma(0)$ becomes independent of ΔE , the maximum

energy barrier. In the $\Delta E' \rightarrow 0$ limit, energy maxima and energy minima are indistinguishable so the population of energy maxima becomes non-vanishing at $T = T_0$. This means that the picture of activated conductivity breaks down in the setting of an exponential energy barrier distribution, so that the model does not apply for $T > T_0$.

What happens at T_0 is hinted at by the exponential energy barrier distribution itself. Since on the average $\Delta E' = \text{const.} - E'$, where E' is the energy of the state which has the barrier $\Delta E'$ to its surrounding states, we find immediately from eqn. (7)

$$n(E') \propto e^{E'/kT_0} \quad (20)$$

where $n(E')$ is the density of energy levels. It must be emphasized that eqn. (20) refer to the quasiparticle-lattice interaction energy and does not include any quasiparticle "kinetic energy". A macroscopic system with the density of energy levels given by eqn. (20) undergoes a phase transistion at $T = T_0$ to a state of zero entropy (a Gibbs-DiMarzio glass transistion (1958)). The system is "frozen". A quasiparticle is only a microscopic system, but still eqn. (20) implies that the quasiparticle energy fluctuations decrease drastically below T_0 . It is an obvious guess that what happens at T_0 is that the relevant lattice degrees of freedom freeze, so that the quasiparticles for $T < T_0$ are unable to exchange potential energy with the lattice. By freezing is not meant the crystallization of the liquid state, of course, but the freezing-in of the various kinds of lattice defects that determine the quasiparticle energy. When the lattice freezes, the quasiparticle-lattice interaction energy E' becomes a function of the quasiparticle coordinates only. This function is more or less random in space and eqn. (20) then just expresses the pro-

bability of finding energy E' at a given quasiparticle position. In summary, it is conjectured that the MN-rule and eqn. (20) are consequences of a frustration of thermal equilibrium at T_0 . The frustration takes place on cooling at the sample preparation. If this picture is correct, the element of disorder common to all occurrences of the MN-rule simply derives from a freezing of thermal disorder at T_0 .

A frustration of thermal equilibrium can be referred to as a glass transition. The concept is here used in a generalized sense, often one only speaks of a glass transition in connection with the solidification of supercooled liquids. The idea that the MN-rule is due to a glass transition, is not new. Busch (1950) suggested that the MN-rule for extrinsic semiconductors derives from a freezing of the donor concentration during cooling after the sample preparation (Metselaar and Oversluizen 1984). This idea has been generalized here to the conjecture that the MN-rule universally is a consequence of a glass transition.

6. Generalization of the model. A model for the compensation effect in heterogeneous catalysis.

The topic of this section is the generalization of the phenomenological model to deal with the compensation effect in other contexts than electrical conductivity. By the compensation effect is meant the phenomenon that the reaction rate K for a class of related rate processes is given by

$$K = \text{const.} \cdot e^{\frac{\Delta E}{kT_0}} e^{-\frac{\Delta E}{kT}} \quad (21)$$

In this more general setting T_0 is often referred to as the isokinetic temperature. To be specific we shall discuss only the compensation effect in heterogeneous catalysis (Cremer 1955, Sinfelt 1969, Galwey 1977), but it is straightforward to

generalize the below considerations to deal with other cases.

In the present model heterogeneous catalysis is regarded as the result of many possible reaction sequences, each sequence consisting of many intermediate steps. The intermediate states are situated at local energy minima in the abstract reaction coordinate space and an intermediate reaction is a thermally activated "jump" between two adjacent minima. This is analogous to quasiparticle jumps in ordinary space and the overall reaction rate K becomes the analogue of $\sigma(0)$. Because of the complexity in the model, a statistical approach is needed for the calculation of K . Analogously to the MN-rule case it can now be shown that an exponential energy barrier distribution implies eqn. (21). As in sec.5, the exponential distribution is conjectured to derive from a glass transition at T_0 . The glass transition is here the freezing of the relevant catalyst surface degrees of freedom - they determine the energy function in reaction coordinate space.

If this model is correct there is no such thing as the mechanism of a heterogeneous catalytic reaction. Many different reaction sequences contribute to the overall reaction, and the whole thing is so complex that a statistical approach is necessary. Actually, the complexity of heterogeneous catalysis is commonly recognized to the extent that the mechanism of catalysis is often referred to as "black magic". Once the statistical approach is accepted, however, the argumentation of sec. 2 applies from which it can be concluded that the model is unique in the sense that only an exponential energy barrier distribution is possible if the compensation effect is to be reproduced (assuming $\Delta E'_{\min} = 0$).

The model implies that interesting time-dependent phenomena

must be present in connection with the compensation effect. As a consequence of the exponential barrier distribution, it is predicted that power-law time- or frequency-dependence should be observed in chemical relaxation experiments with an exponent s given by eqn. (11). Further discussion of this point will appear elsewhere.

7. Summary and discussion

The MN-rule is a quite universal phenomenon and this fact emphasizes the need for a phenomenological model. As shown in sec. 2, once the phenomenological approach is accepted there is only one possible model, namely that based on an exponential distribution of energy barriers. The exponential barrier distribution is well-known. It has been used e.g. for describing a.c. conductivity of hollandite (Bernasconi, Beyeler, Strässler and Alexander 1979), dispersive transport in a-Si:H (Hvam and Brodsky 1981), structural relaxation of amorphous germanium (Olsen), dielectric polarisation phenomena in glasses (Thurzo, Barančok, Doupovec, Mariani and Janči 1975), and, in the form of exponential band tails, to explain the MN-rule (Roberts 1971, Cohen et al. 1984). A thorough study of the exponential energy barrier distribution was given by Macdonald (1963). The phenomenological model thus contains few new ideas, it is just an attempt to present a coherent picture of conductivity in MN-semiconductors. Though the model was constructed to explain the d.c. properties, it implies a perhaps surprising prediction of a correlation between the MN-rule and the a.c.

properties: $\sigma(\omega) \propto \omega^s$ where $s = 1 - T/T_0$ (sec. 3).

The experimental situation is complex and there exists no conclusive evidence in favour of the model. The MN-rule is observed in disordered semiconductors, exactly the same class of solids that is known to show a power-law frequency-dependence of the a.c. conductivity. This, and the fact that the exponent s always obeys $s < 1$ and $s \rightarrow 1$ for $T \rightarrow 0$, is in agreement with model predictions, but it can not be taken as evidence for the model as discussed in sec. 4. Careful experiments are needed, for instance measuring $s(T)$ as $T \rightarrow 0$. In one case, for the important semiconductor a-Si:H, observed values of s close to one at $T \cong 300$ K (Shimakawa, Watanabe, Yano and Kondo 1983) do not agree with the model because the various reported values of T_0 for this solid are all below 1000 K (Fritzsche 1980).

In sec. 5 it was suggested that the MN-rule is a consequence of a glass transition. It was conjectured that the exponential barrier distribution follows from a freezing-in of the lattice degrees of freedom defining the quasiparticle energy, i.e. of the various relevant lattice defects. In this picture both the MN-rule and the conductivity dispersion are ultimately consequences of broken ergodicity (Palmer 1982).

At $T = T_0$ the phenomenological model breaks down and a kind of phase transition is expected. In particular, the conductivity becomes frequency-independent at this temperature. Usually, it is not possible to measure at this high temperature. Some experiments at T_0 have been carried out, though, and there are signs of something happening at T_0 as signalled by a discontinuous change of activation energy (fig. 1 of Weichman and Kužel (1970), fig. 1 of Irsigler et al. (1983)). Further experiments near T_0 would be very interesting.

The MN-rule is only one manifestation of the very general compensation effect. The need for a universal explanation is increasingly realized, and this problem has been addressed by several authors recently suggesting various modifications of rate theory (Conner 1982, Peacock-López and Suhl 1982, Khait 1983, McCoy 1984). In this paper rate theory has been assumed to apply. It is straightforward to generalize the phenomenological model to deal with the compensation effect in general, as was discussed in sec. 6 exemplified by the case of heterogeneous catalysis. Quasiparticle jumps in ordinary space are replaced by reactions in the abstract reaction coordinate space, but the exponential energy barrier distribution remains unchanged. The basic assumptions of the generalized model are: 1) the existence of an element of disorder, and 2) that the overall reaction is the result of many reaction sequences acting in parallel, each sequence involving many intermediate steps. If these assumptions are accepted, the overall reaction rate becomes the analogue of the d.c. conductivity of the MN-rule, and the uniqueness of the generalized model can be proved just as in sec. 2.

As in sec. 5 it may be argued that a glass transition at T_0 is the origin of the exponential energy barrier distribution of the generalized model. It is interesting that the compensation effect almost always involves solids. These solids must contain an element of disorder deriving from a freezing of thermal disorder at T_0 , if the ideas of sec. 5 are correct. As regards the observation of the compensation effect in liquid solutions (Leffler 1955), it is hard to see how the glass transition ideas can apply, though.

The generalized model predicts a power-law time-dependence of chemical relaxation experiments and also that a kind of

phase transistion must occur at T_0 . Further discussion of the phenomenological model in this more general setting is the subject of a future publication.

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