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Origin and information content of the compensation effect*

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An attempt is made to assess: (i) The conditions under which a compensation effect should be observable. (ii) The associated physical properties affected by such compensation. (iii) The nature of the information which can be gleaned from studies of compensation. Specific attention is given to simple desorption processes and the main conclusion is that the compensation law in adsorption indicates a phenomenon involving many molecules. However the Meyer-Neldel rule in semiconductors is also embraced, as well as observations of the compensation effect in liquids.

Key words: Desorption—Compensation—Phase transitions

1. Introduction

The compensation effect has a long, and controversial history, going back at least to Constable [1] and Schwab [2]. In most thermally activated processes, one has for the reaction rate k the form:

$$\ln k = \ln A - \beta\varepsilon_b : \beta = (k_B T)^{-1}. \tag{1.1}$$

It is found empirically that the Arrhenius plots of different members of a family of reactions are frequently straight lines with different slopes, which intersect at a common point. The temperature associated with this point is the so-called compensation temperature T_c. The term isokinetic temperature is also used as in the work of Peacock-Lopez and Suhl [3]. Phenomenologically one writes the pre-exponential factor A as

$$A = A_0 \exp(\beta_c \varepsilon_b) : \beta_c = (k_B T_c)^{-1}. \tag{1.2}$$

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

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In the presence of compensation, the fingerprint is the linearity of ln A versus activation energy ε_b of the different members of the family of reactions. The compensation effect was thought initially to be limited to heterogeneous catalysis [4–6], but it was later exposed in other thermally activated rate processes, e.g. the activated electronic conductivity of oxide semiconductors [7, 8].

In the present work, we attempt to delineate the conditions under which compensation should be observable, to refer to some associated physical properties it should influence, and to discuss its information content. Thus, Sect. 2 considers first principles and phenomenological treatments of compensation: reference being made to adsorption, taken up in more detail later. Section 3 deal with bulk compensation effects: the oxide semiconductors [7] plus liquid state reactions [9]. Section 4 treats compensation as it manifests itself in the rate of desorption as a function of coverage. Section 5 constitutes a brief discussion and summary.

2. Phenomenological and first-principles treatments exhibiting compensation effect

Clark [10] and Schwab [11] review theories of compensation. One group of models starts from the fact that for a reaction proceeding in quasi-equilibrium the rate is given by

$$k \propto \exp(\Delta S/k_B)\exp(-\Delta H/k_B T). \tag{2.1}$$

One then seeks physical reasons why in a particular group of reactions $\Delta H \sim T\,\Delta S$ [12], or why the chemical potential should remain constant. The latter is, e.g. the case if the reaction proceeds in the presence of a phase transition (cf. Sect. 3.1.1). Two explanations for this kind of compensation may also be cited here:

(i) In biopolymers, as in [12], Benzinger [13] points out that these (as well as smaller molecules) have many conformations in equilibrium, with equilibrium constants near unity. Any perturbation changing the distribution of conformational isomers is likely to produce thermodynamics leading to compensation.

(ii) Ben-Naim [14] and Grunwald [15] consider the perturbation of the liquid water network by solutes. By a thermodynamic proof, this produces no effect on the partial molar free energy of the solute. Therefore enthalpy and entropy show compensation.

Other more elaborate models have been reviewed by Clark [10]. Schwab already suggested in 1929 that heterogeneities might lead to compensation, i.e. one assumes that ΔH is not constant throughout the system but has a certain statistical distribution. In averaging Eq. (2.1), e.g. with an exponential distribution, one readily obtains a compensation effect. Schwab [11] quotes experimental evidence against this model, which on the other hand is at the heart of work of Dyre [8].

Beyond this phenomenology, there have recently been two attempts by Peacock-López and Suhl [3] and by Sommer and Kreuzer [16] to show that compensation might arise as a result of dynamics. In [3] the compensation effect is 'explained' by counting the ways in which the heat bath can furnish the energy necessary to surmount the barriers. It is argued that, in most thermally activated processes, the energy transfer from the heat bath to the reactants can be regarded as absorption, by the reactants, of elementary excitations of the heat bath. One example to cite is desorption of an adatom from an insulating surface: the solid being the heat bath and the elementary excitations the phonons. With a metal surface, both phonons and hole-electron pairs might be involved. Or in a homogeneous phase reaction in a liquid [3], sound waves may be the appropriate excitations (cf. Sect. 3.2.2). Compensation may be viewed as resulting from the "dynamical entropy of the heat bath".

The study of [16], concerned with helium on a metal or on graphite, leads to the prediction of a compensation effect in physisorption. A novel feature here is the prediction for weakly coupled systems of a transition from first-order desorption at low coverage to zero-order evaporation at higher coverage, with a rate of desorption which is then independent of coverage. The compensation effect here has a microscopic explanation via the mean-field binding of an adsorbed particle, particularly around monolayer coverage, to the solid surface and the other adsorbed particles and in the weakening of the effective adsorbate-phonon coupling.

Turning to the information content, it seems clear that compensation temperatures can involve at least three sorts of information:

(i) The strength and range of lateral interactions between adsorbates on solid surfaces. In the work of [16] for He on graphite, there is only compensation as the coverage is increased.

(ii) The magnitude of the basic parameter ε_0 characterizing the collective excitations, related to T_c by $k_B T_c \sim \varepsilon_0$ [3]. An attempt will be made in Sec. 3.2 to correlate compensation temperatures in liquids [9], with $\varepsilon_0 = \hbar v_s \rho^{1/3}$, v_s being the velocity of sound and ρ the density.

(iii) The temperature at which a phase transition occurs, Dyre ([8], cf. Sec. 3.1) terms this the 'glass transition' and this temperature T_g he equates to T_c. In the treatment of Estrup et al. [18], T_c is characterized by the surface phase transition temperature.

3. Bulk compensation effects

3.1. Averaging and Meyer-Neldel rule

Considering the time evolution of the number N of particles participating in a particular process: namely

$$\frac{dN}{dt} = r_d f(N) \tag{3.1}$$

and assume the reaction rate to have the form

$$r_d = \nu \exp(-Q/k_B T). \tag{3.2}$$

Let us examine the case when Q has some distribution, e.g. in an amorphous or inhomogeneous material: a suggestion made 60 years ago and re-discovered by Dyre [8] in his discussion of the Meyer-Neldel rule. For the number of particles N_i attempting barrier Q_i we write Eqs. (3.1) and (3.2) with $N \rightarrow N_i$ and $Q \rightarrow Q_i$, where now

$$N = \sum_i N_i. \tag{3.3}$$

The other situation is where a given particle has the option of surmounting any one of a number of barriers to escape. In that case

$$\frac{dN}{dt} = \sum_i f_i \nu_i \exp(-Q_i/k_B T) f(N). \tag{3.4}$$

for some barrier distribution f_i.

This implies that in the local environment of one particle all these barriers exist simultaneously. Returning to Eqn (3.1) one has to specify $f(N_i)$ to make further progress. If the process is zero order, like evaporation, then $f(N_i) = f_i$ and one finds

$$\frac{dN_i}{dt} = f_i \nu_i \exp(-Q_i/k_B T) \tag{3.5}$$

or

$$\frac{dN}{dt} = \sum_i f_i \nu_i \exp(-Q_i/k_B T). \tag{3.6}$$

It is to be noted that, in desorption kinetics, a compensation effect is usually found in zero order processes; but not due to a distribution of Q_i but because the chemical potential remains constant.

In the case of a first-order process, with $f(N_i) = -N_i$, the rate equation for N_i can be integrated, and then the summation over i taken, to yield

$$N(t) = \sum_i N_i(t) = \sum_i N_i(0) \exp(-\nu_i t \exp(-Q_i/k_B T)). \tag{3.7}$$

One can then show that for $N_i(0)$ chosen to be of Gaussian or exponential form:

$$N(t) \sim \exp(-at^{\alpha}) \tag{3.8}$$

where $\alpha \neq 1$. For $\alpha < 1$, we get a stretched exponential-like Kohlrausch's law.

Returning to zero-order desorption, we can write for the coverage θ the rate equation

$$\frac{d\theta}{dt} = \nu(\theta) \exp(-Q(\theta)/k_B T). \tag{3.9}$$

Zero order means that for $T = \text{const}$, $d\theta/dt = \text{const.}$ over a range of θ. But if $Q = Q(\theta)$ Eq. (3.9) immediately implies

$$\frac{d\theta}{dt} = \text{const.} => \nu(\theta) = \text{const.} \exp\{Q(\theta)/k_B T\} \tag{3.10}$$

i.e. absolute compensation implying that zero order cannot have $Q = Q(\theta)$. Thus within the regime of zero order, the activation energy must be constant.

On the other hand, experiments show zero order and compensation [19]-[23] from which one concludes that Eq. (3.10) cannot be the whole story[1]. The first option is to take

$$\frac{d\theta}{dt} = \sum_i f_i \nu_i(\zeta)\, e^{-Q_i(\zeta)/k_B T} \tag{3.11}$$

with an exponential barrier distribution, f_i. Secondly, the process is not strictly zero order.

We again draw attention to Schwab's [11] evidence against such heterogeneous effects.

3.1.1. Phase transitions and compensation. As mentioned above, a compensation effect is likely to occur if the system undergoes a phase transition during a reaction. Suppose in a certain range of T and coverage, two 2-dimensional phases of an adsorbate co-exist. If the processes of equilibrium between these two phases are faster than the desorption process, then the chemical potential will remain constant (at constant T) during desorption implying that $T\,\Delta S \sim \Delta H$.

Though the suggestion that compensation arises because of a phase transition has been made [1, 18], this idea, we believe, cannot have general applicability, e.g. compensation in the liquid state [9] (see also below) where such a model is inappropriate. In Dyre's work on the Meyer-Neldel rule, T_c is then identified with the "glass transition", at which "thermal disorder" is frozen out. In the context of our emphasis on surface examples, Estrup et al. [18] point out that a compensation effect follows from the equality on the chemical potentials of two phases at a transition.

3.2. Liquid state reactions: enthalpy and entropy under solvent changes

Solvent changes frequently alter the enthalpy and entropy of activation of a reaction. Following Leffler [9], one notes that:

(i) If solvents in a series perform closely similar roles in the reaction, enthalpy is a linear function of entropy.
(ii) In some reactions, solvents fall into two different classes.

Leffler's study [9] contrast the decomposition of triethylsulfonium bromide in (a) hydroxylic and (b) non-hydroxylic solvents (cf. Fig. 4 of [9]). To explain this "discontinuous" solvent effect, a mechanism similar to that of steric hindrance is possible: either the ground or transition state has a double potential energy minimum.

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[1] Reference should be made here to the alternative definition of compensation in [18] and [20]. Compensation as defined there has been explained in [21] and [22] by an approach different from the one embodied in Eq. (3.11) below

The fact that the dielectric constant is T-dependent is an obvious source of variation in enthalpy and entropy under solvent changes; having relevance where dipoles or charges are generated or destroyed. Purely electrostatic differences in solvents will lead to a linear relationship between electrostatic parts of ΔH and ΔS [9]. But numerous polar reactions have different rates in different solvent mixtures of equal dielectric constant: chemical effects must play a part. Other solvation effects can contribute: according to the statistical thermodynamic treatment of Rice [24] (see also Münster [25]), energies and entropies due to the mutual orientation of solute and solvent molecules will be linearly related. Also, empirically, heat and entropies of solution often are linearly related as well as heat and entropies of reaction.

One must note here that hydrogen bonding and similar specific solvent effects can be more important than the dielectric constant or other macroscopic properties of the solvent.

3.2.1. Gross regularities among reactions exhibiting isokinetic relationships. Leffler tabulates some 80 reactions exhibiting isokinetic relationships. Some facts deduced from his Table 1 are:

(i) The isokinetic temperature, though between 1320 K and 70 K, is such that it lies between 300 and 500 K for some 50 reactions: only 7 have $T_c > 700$ K and only 4 have $T_c < 200$ K.

(ii) Many reactions have T_c values according with collective excitation (sound wave) energies (see the Appendix also). But T_c is also affected by solute-solvent interactions.

(iii) Compensation in liquid-state reactions in organic chemistry is widespread: it is difficult to understand interpretations of T_c here as a phase transition.

4. Desorption processes and compensation

There are many instances where a pronounced compensation effect shows up in the rate of desorption as a function of coverage; recent examples have been given by Bauer et al. [19] and Menzel et al. [20]. For these, rather strongly bound, chemisorbed adsorbates, it can be safely assumed that the system remains in quasi-equilibrium during desorption and that transition state theory can be applied to calculate the desorption rate constant. This has been done with some success by Leuthauser [21] and Zhdanov [22] by calculating ΔS and ΔH for a lattice gas in the quasi-chemical approximation. This suggests that many-body effects are important to produce a compensation effect in addition to dynamic coupling effects. A heuristic argument that a single-particle picture is more likely not sufficient to understand the compensation effect can be constructed from the master equation treatment of desorption (see, for example, Kreuzer and Gortel [26]) but we omit the detail. Rather, we develop in the following section a nonequilibrium thermodynamic approach to compensation.

4.1. *Nonequilibrium thermodynamic approach to compensation*

We want to outline briefly that an apparent compensation effect can show up under non-isothermal conditions, although we feel that it is by far smaller than what is usually observed experimentally. Nevertheless it seems worthwhile to explore this avenue further.

Define extensive variables $X_1 = N_a$, $X_i = N_g$, $X_3 = N_s$ as the numbers of particles in adsorbate, gas, and solid, and $X_4 = U_a$, $X_s = U_g$, $X_0 = U_s$ as the internal energies in adsorbate, gas, and solid.

Following Onsager's approach to nonequilibrium thermodynamics we derive the rate equations

$$\frac{dX_i}{dt} = \sum_j L_{ij} \frac{\partial S}{\partial X_j}\bigg|_{V_j N_j U} \tag{4.1}$$

where

$$\begin{aligned} &N = N_a + N_g + N_s = \text{const.} \\ &U = U_a + U_g + U_s = \text{const} \\ &L_{ij} = L_{ji}. \end{aligned} \tag{4.2}$$

We further assume that $N_s = \text{const}$ and $N_a + N_g = \text{const}$. Consider the special case when $T_a = T_g = T$.
Then one has

$$\frac{dN_a}{dt} = -\frac{dN_g}{dt} = -\frac{L_{11}}{T}(\mu_a - \mu_g) + L_{16}\left(\frac{1}{T_s} - \frac{1}{T}\right) \tag{4.3}$$

$$\begin{aligned} \frac{dU_s}{dt} &= -\frac{L_{16}}{T}(\mu_a - \mu_g) + L_{66}\left(\frac{1}{T_s} - \frac{1}{T}\right) \\ &= -\frac{d}{dt}(U_a + U_g) \end{aligned} \tag{4.4}$$

In the isothermal situation, $T_s = T$, each desorbing particle carries roughly, the activation energy Q with it.

Thus we get from (4.4):

$$\frac{dU_s}{dt} = -\frac{L_{16}}{T}(\mu_a - \mu_g) = Q\frac{dN_a}{dt} = -Q\frac{L_{11}}{T}(\mu_a - \mu_g) \tag{4.5}$$

so that

$$L_{16} = L_{11}Q. \tag{4.6}$$

For $T_s > T$

$$\frac{dU_s}{dt} = (Q + \delta q)\frac{dN_a}{dt} \tag{4.7}$$

in the steady state. It follows from Eq. (4.3) that

$$\delta q \frac{dN_a}{dt} = L_{66}\left(\frac{1}{T_s} - \frac{1}{T}\right) \tag{4.8}$$

and from Eqs. (4.8 and 4.3):

$$\begin{aligned} \frac{dN_a}{dt} &= -\frac{1 - Q^2 L_{11}/L_{66}}{1 - Q^2 L_{11}/L_{66} - Q\delta q L_{11}/L_{66}} (\mu_a - \mu_g) \\ &\approx -\frac{L_{11}}{T} \exp\left(\frac{L_{11} Q}{L_{66} - Q^2 L_{11}} \delta q\right) (\mu_a - \mu_g) \\ &= \underline{-Sv\, e^{-Q/k_B T} \exp\left(\frac{L_{11} Q}{L_{66} - Q^2 L_{11}} \delta q\right)} N_a. \end{aligned} \tag{4.9}$$

The bracketed piece is the effective desorption rate constant.

The apparent compensation effect arises from the fact that during desorption isothermal conditions cannot be maintained because the substrate gets cooled by desorbing particles carrying energy away. This cooling effect has been estimated by Gortel and Kreuzer [31] to be very small under normal experimental desorption conditions.

We point out that non-equilibrium thermodynamics has recently been used extensively by Payne and Kreuzer [32] to study the adsorption-desorption kinetics of two-phase adsorbates. In particular, they employed the Bragg-Williams and quasichemical approximations to the lattice gas model with nearest neighbour interactions to evaluate the chemical potentials in the rate equations (similar to (4.3)) for the mole numbers in the two adsorbed phases. Plotting the desorption rates for constant coverage against increase temperature one obtains straight lines from which desorption energies and pre-exponential factors can be obtained. It is found that the desorption kinetics of two-phase adsorbates show perfect compensation, even outside the co-existence region, due to collective many-body effects. These results will be discussed at length elsewhere [32].

5. Discussion and summary

Compensation appears to be widespread. Yet the physical mechanisms involved are clearly diverse. What then are the underlying features required for systems to exhibit compensation?

First, we have argued here that it is a genuine many-particle effect. This is in accord with the first-principles theories of Peacock-López and Suhl [3] and of Summor and Kreuzer [16]. However, since the compensation temperature of the former workers is dominated by the collective excitations of the heat bath, there is some assumption of "linear response" involved and their theory does not contain within itself conditions under which a compensation effect can arise.

Secondly, the order of the reaction appears important. In Dyre's phenomenological model, compensation arises in the framework of a zero-order reaction.

Thirdly, we have demonstrated by a more detailed study of this aspect of desorption than made hitherto that non-equilibrium thermodynamic treatments can lead to effects "mimicing" compensation and we have proposed a temperature programmed desorption experiment as a test.

It is relevant at this point to return briefly to the explanation of compensation offered by Ben-Naim [14] and Grunwald [15], intended to apply to added solutes in water. It appears possible that a slight modification of this argument will apply to adsorption. All that one needs to invoke in this latter case is that adsorbed molecules perturb the atomic mesh of the surface.

Turning to information content, while T_c seems to involve in an important way collective excitations of the heat bath, as discussed above, reactant-solvent interaction is clearly important in many liquid-state reactions, as becomes evident from an analysis of the work of Leffler [9]. For the future, attempts to explain compensation or isokinetic temperature in terms of a phase or a "glass" type transition seem promising, though they do not appear to be capable of embracing the liquid states reactions. Various other physical properties are related to compensation: one example being the AC conductivity in oxide semiconductors. While, as one of us has emphasized recently [33], general arguments lead to power-law AC conductivity of the form $\sigma^{\alpha}\omega^{s}$, the exponent s has a specific form $(1-T/T_c)$ for compensation [8], which should eventually prove a valuable fingerprint.

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Appendix

Estimates of compensation temperature for various mechanisms

We think it of interest, in the present context, to make some observations on the work in [3].

(1) Taking the example of phonon-mediated desorption, the authors assume that only longitudinal phonons contribute. We know that in a bulk Debye model, employed for desportion kinetics, longitudinal phonons contribute about 6% to all desorption events, whereas 94% are aided by transverse phonons. If one were to use a full treatment of surface phonons, one would find that some 64% are initiated by Rayleigh phonons, see [26] for details.

(2) Estimates of isokinetic energies T_c seem somewhat curious:
(a) for phonons, $T_c \sim$ fraction of Debye temperature θ.
(b) for electron-hole pairs, $T_c \sim$ fraction of the Fermi temperature T_F.
The work of Gunnarsson and Schonhammer [34] and of Norskov [35] indicates that electron-hole pairs are far less important for desorption than had been initially supposed. Thus the estimate $T_c \lesssim \theta$ would be appropriate [3]. In contrast, for metals (Au, Ag, Cu/Mo, W), T_c is found experimentally $\sim 10^3$ K.

(3) Estimates to T_c should invoke not only static properties (density of states) but, more importantly, coupling effects, i.e. energy transfers rather than energy minimization. This seems then to require that one transcends the analysis of Peacock-López and Suhl.

(4) Further, the treatment of these workers is restricted to one bound state in the holding potential. In such a case, desorption, for example, would have to proceed via absorption of n coherent phonons. On the other hand, a realistic surface potential has many (for heavy ad-particles, a quasi-continuum of) bound states and desorption proceeds predominantly via cascades involving many incoherent events.

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