

Book Chapter

A SET Approach to the Interplay of Catalysts and Reactants

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Abstract

Research within the area of selective energy transfer (SET) on how resonance develops between a specific vibration within a catalyst system and a corresponding vibration within a reacting system that resonates with it is discussed here. The catalyst system is assumed to donate one or more vibrational quanta to the reacting system. The term 'specific vibration' refers to vibration of a type involving bending or stretching that, when transferred resonantly to the reacting system, serves to drive the reactant molecules involved to assume the basic structure of the molecules of the catalyst system. Regardless of whether the catalyst is a pure metal surface or a complex polymolecular system (an enzyme), its role is seen to be that of transferring energy to corresponding vibrations of the reactant system. Examples are here presented of vibrators of various types that can act as catalysts.

Keywords

Catalysis; SET; Selective Energy Transfer; Vibrational Resonance; Isokinetic Temperature

Introduction

During the last few decades, work on developing and exploring a new conception of catalysis, selective energy transfer (SET), has been underway. This assumes there to be a resonant interplay between molecular vibrations of a catalyst and of a reactant, the vibrations of the reactant and of the catalyst being equal or nearly equal in frequency, and the reactions this involves being initiated when sufficient amounts of vibrational quanta from the catalyst have been transferred to the reactant-to-be. The rate of energy transfer of this type, when damped and coupled oscillations are involved, is dealt with in classical physics (see e.g., Ref. [1]). The classical formula for the power absorption of the system, P , i.e., the energy transfer per unit of time, is

$$P = P_{\text{res}} \times (\omega^2/\tau^2)/[(\nu^2 - \omega^2)^2 + (\omega^2/\tau^2)] \quad (1)$$

where P_{res} is the power absorption at resonance, i.e., when $\nu = \omega$.

In these expressions, ν is the energy-accepting vibration frequency and ω is the energydonating vibration frequency.

For results reported in classical physics, the problems of interest here have come about in part through the use of concepts employed in quantum physics [2]. Results of relevance obtained there are then used in such a manner that the rate of the chemical reaction taking place is set equal to the rate of energy transfer this provides [2,3].

In deducing the most appropriate formula to use to predict the rate of a catalytic reaction, one takes account of two distinctly different types of energy dissipation. The one type, “*Case a*”, concerns a variety of similar but slightly differing ways in which a reacting molecule that is activated can lose its energy; the other type, “*Case b*”, involving only one way for this energy to be dissipated [2].

In the formulae presented below, and in others of the same or similar type that are employed, the frequency of the relevant vibration of the reacting molecule is denoted as ν and the frequency of the active vibration of the catalyst as ω . The route of the energy dissipation of the reactant is referred to as Q , this being regarded as the ‘quality factor’ [1], τ being the relaxation time.

$$Q = \nu \tau \quad (2)$$

The first of the two types of energy dissipation referred to above, which represents the usual conditions for heterogeneous catalysis, contains a large number of differing possibilities for the energy stored in the reactant molecule being lost. This problem can be resolved by integrating over all possible values of Q , from infinity to $Q = 1/2$, which results in formula (3), taken from one of the early SET papers [2]. Here Z refers to contributions to the reaction rate that are not related to the resonance effect, such as the collision number if this is relevant.

$Q = 1/2$ defines the border line between under damped vibrations ($Q > 1/2$) and over damped vibrations ($Q < 1/2$), [1].

$$\ln k = \ln Z + \frac{\omega}{v^2 - \omega^2} (\pm \pi / 2 - \arctg \frac{v\omega}{2(v^2 - \omega^2)}) \sum \Delta E_i / hc - E / RT \quad (3)$$

Here, $\Delta E_i = h c (v_i - v_{i-1})$.

This enables one then to identify $N \sum \Delta E_i$, the activation energy needed for exciting one mole of the reactant. Here $\sum \Delta E_i$ stands for the absolute value of the energy difference between one vibrational level ($i + 1$) and the one below it (i).

$$N \cdot \sum_{i=1}^{i=n} \Delta E_i = E \quad (4)$$

It can be difficult in many cases to ascertain the reaction rate in absolute terms. One can then consider instead the effect that the Arrhenius lines show, when the lines of a series of related reactions intersect at one and the same point; the abscissa there indicating a temperature wherein all the systems involved have the same reaction rate. This temperature is termed the isokinetic temperature, T_{iso} . In previous work [2], Equation (3) was compared with the formal expression for designating an isokinetic temperature, as given in Equation (5):

$$\ln k = \ln Z + E / R(1/T_{iso} - 1/T) \quad (5)$$

Combining Equations (3) and (5) enables one to obtain an expression for the isokinetic temperature, T_{iso} :

$$T_{iso} = \frac{Nhc}{R} \cdot \frac{v^2 - \omega^2}{\omega} \cdot \frac{1}{\pm \pi / 2 - \arctg \frac{v\omega}{2(v^2 - \omega^2)}} \quad (6)$$

This statement is in direct contrast to previous thoughts about the isokinetic effect [4].

For the ideal case of resonance [2], in which $v = \omega$, the limiting value of T_{iso} is:

$$T_{\text{iso}} = Nhc\nu/2R \quad (7)$$

One might note that the dimension of the factor Nhc/R is

$$[Nhc/R] = \text{mol}^{-1} \text{ J s cm s}^{-1}/\text{J mol}^{-1} \text{ K}^{-1} = \text{cm K} \quad (8)$$

and that this entity turns into temperature when multiplied by a frequency (cm^{-1}).

If ν is expressed in cm^{-1} and T_{iso} in degrees Kelvin, Equation (7) turns into

$$T_{\text{iso}} = 0.719 \nu \quad (9)$$

Regarding the other extreme for the energy dissipation of an excited molecule, viz. when there is one route for energy loss that is completely dominating, there is no point to integrating over all possible values of Q , so that, as was done in [2,3], one can consider the reaction conditions to be

$$\ln k = \ln Z + \sum v_i \frac{v\omega^2}{(v^2 - \omega^2)^2 Q^2 + \omega^2 v^2} - E/RT \quad (10)$$

Here, the summation $\sum v_i$ represents the sum of the vibrational quantum levels of just that vibration mode that is exciting the reactant up to the activation energy.

It is the term for the dissipation of energy, Q , that plays the single, dominant role.

Combining this Equation (10) with Equation (5) provides an expression of the isokinetic temperature:

$$T_{\text{iso}} = \frac{(v^2 - \omega^2)^2 Q^2 + \omega^2 v^2}{v\omega^2 R} \cdot Nhc \quad (11)$$

If $Q = 0$, or $\nu = \omega$, one obtains

$$T_{\text{iso}} = Nhc \nu/R = 1.44 \nu \quad (12)$$

In the sections that follow, I illustrate the use and the utility of the deductions referred to above, using real examples; in most cases, ones in which I have taken part. One can start with the simplest case, in which an integration over many different ways in which energy dissipation can be employed was performed. Besides these examples, some results from previous investigations on the SET theory, or leading towards SET, are presented to the reader [5–17].

Isokinetic Effects on Solid State Catalysts

The example of the type to be dealt with here, reported in an article about 10 years ago [18], reflects calculations on the catalytic hydrodechlorination of chlorobenzene that I carried out on data from experiments in prof. Keane's laboratory. Indeed, an isokinetic effect was observed. In varying the carrier of a particular catalyst material, metallic nickel (see Figure 1), the following isokinetic temperature was obtained:

$$T_{\text{iso}} = 669 \pm 2 \text{ K} \quad (13)$$

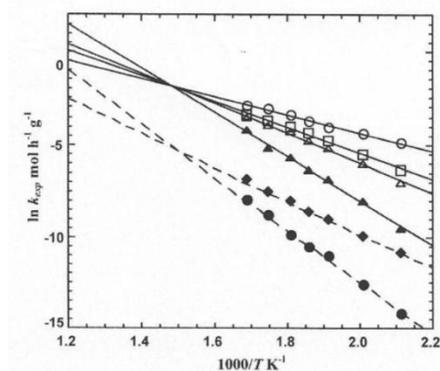


Figure 1: Arrhenius lines describing the hydrodechlorination of chlorobenzene over supported nickel. The upper four systems result in an isokinetic temperature of $669 \pm 2 \text{ K}$. The symbols there are arranged in the following order downwards from the highest to the lowest level: Ni/AC; Ni/SiO₂; Ni/MgO; Ni-Ta₂O₃. The lines of the two remaining systems, Ni/Al₂O₃ and Ni/graphite, have been shifted downwards by 3 ordinate units (for purposes of clarity). Since there are only two lines that intersect, this crossing point is regarded as being less accurate than the upper one. (Figure 1 is from Figure 5 in Ref. [18].)

In testing Equation (6), the following values were used for the vibration frequencies of the reacting (ν) and the catalytic (ω) molecules, respectively:

$$\nu = 740 \text{ cm}^{-1} \text{ and } \omega = 940 \text{ cm}^{-1} \quad (14)$$

These frequency values (14), were derived from an earlier investigation [19], in which a series of chloro- (and bromo-) substituted arenes likewise showed signs of isokinetic behavior, with use of differing reactants but of the same catalyst each time (Ni/SiO₂).

The vibration $\omega = 940 \text{ cm}^{-1}$ was the only one of the Ni-H vibrations that agreed well with formula (6) (the other frequencies giving values for the calculated T_{iso} result that were too high), whereas the $\nu = 740 \text{ cm}^{-1}$ vibration result represents one of several possible C–H out-of-plane bending vibrations [20]. In fact, in the first investigation [19], it was found best to use what Varanyi [20] terms the “17b” vibration (at 902 cm^{-1}). Yet, here [18], when the variation that resulted in an isokinetic state was on the catalyst support, Keane and I found it better to make use of the ‘umbrella vibration’ at 740 cm^{-1} . The result obtained, Equation (15), based on the use of Equation (6), agreed closely with the experimental results reported in Equation (13). Thus, use of formulae based on the classical concept of vibrational resonance appears to “work well”.

$$T_{\text{iso}} = 669.2 \text{ K} \quad (15)$$

Gas Phase Interactions

There are extreme cases of reactions that do not fit with the calculations described in Section 2. For example, about two decades ago, Campell [21] discovered and described the reaction between carbon dioxide and lanthanide atoms that occur in free space. Although Campell [21] considered the reaction products to be MO and CO, calculations appear to indicate the primary product to be an insertion compound, OM (CO); see e.g., Ref. [22] for elements as heavy as U and Th, and Ref. [23] for Nb. In a later paper, Larsson and Mascetti [24] also adapted this view to

the lanthanides. Since Campbell et al. [21] had obtained data characterizing the Arrhenius lines for the systems they investigated, it was easy to check on whether or not an isokinetic effect could be noted. We found [24] that for the elements in the middle of the lanthanide row there was in fact such an effect (Figure 2), whereas for the first elements as well as for the latter ones the Arrhenius lines crossed at one point, at $1/T = 0$, i.e., at infinite temperatures.

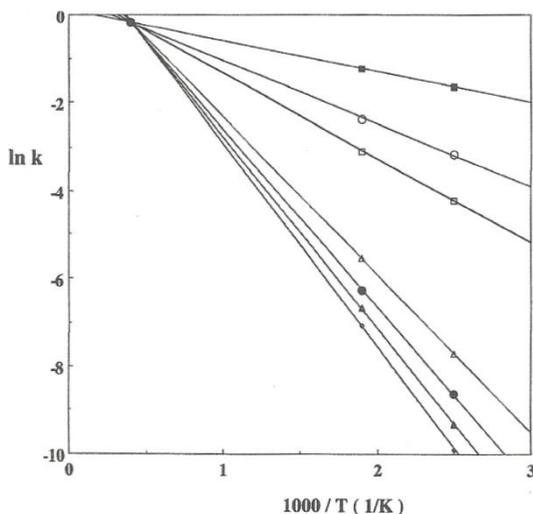


Figure 2: Arrhenius lines for the reaction between carbon dioxide and lanthanide atoms. This relationship [24] holds for the seven elements from samarium up to and including erbium.

Experimental Data and Indications of a Reaction Route

For the elements located in the middle of the lanthanide row, we found a finite value of $1/T$ to apply, which resulted in an isokinetic temperature of $T_{\text{iso}} = 2500 \pm 330$ K. Such a temperature usually indicates the presence and the actions of a catalyst [3]. Since in the present case there are only two acting partner substances, one needs to accept there being one of these species that has taken on the role of being a catalyst. As was found earlier [24], the magnitude of the isokinetic temperature makes it appear unreasonable to suppose that what has been termed ‘case a’ in this article is operating here, accordingly, one

can conclude that *case b* is operating as depicted in Equation (11).

The parameters of importance here are:

Q; dimensionless.

The wave number of the reactant; $\nu = 1933.5 \text{ cm}^{-1}$, reported by Adel and Dennison [25] and confirmed by Herzberg [26], as given in Table 1. Here, as well as in continued calculations, the high accuracy value of $1933,5 \text{ cm}^{-1}$ is abbreviated to 1933 and 1934, respectively.

The wave number of the catalyst; $\omega = 667.5 \text{ cm}^{-1}$ was reported by Herzberg [26]. We found it more reasonable to put $\omega = 1934 \text{ cm}^{-1}$ in full resonance with the same vibration in the reactant. If the system is excited by some newly incoming vibrational quantum from the catalyst, the angle between the two C-O bonds would become still greater.

Standard constants $Nhc/R = 1.43 \text{ cm K}$.

Table 1: Designation of the quantum states of the 1933 cm^{-1} band in the CO_2 IR spectrum.

Denotation	Calc.	Observed	Reference
V1 V2 V3			
0 3 0	1933.2	1933.5	[25]
0 3 0	1931.0	1943.5	[26]
0 1 0		667.5	[26]

Suggested Mechanisms

The attempt will be made now to sketch a possible route for the energy transfer that occurs, namely the following: First, the CO_2 molecule that is to react by engaging a vibration ν combines loosely with a lanthanide atom. Thereafter, another CO_2 molecule—the catalyst—associates with the previous LnCO_2 compound and delivers a quantum of vibrational energy (ω) to the LnCO_2 compound. In this way, energy is pressed into the first CO_2 molecule. This means that this new stroke of excitation

of an O-C-O bending is operating on the first CO₂ unit. In this way the O-C-O angle becomes opened up to allow the lanthanide atom to approach the inner space of the O-C-O angle and to thus make it possible for the lanthanide atom to approach one of the C-O bonds from the inside. At the same time, the energy needed to open this gap, i.e., ω , is liberated—as the Ln atom now makes the job of keeping the C–O bonds separate—and radiates out into space. This means the conditions for *case b* being fulfilled.

With the purpose of using the ν data, both larger and smaller than the reported value [25], 1934 cm⁻¹, to make this critical frequency a safely established one, the following construction was made:

$$\Delta = \nu^2 - (1934)^2 \quad (16)$$

These values are plotted in Figure 3, and one finds a linear relation with an ordinate value for the abscissa = 0 to be 1930.5 cm⁻¹. As this experiment has been assigned as a ‘*case b*’ type, one can calculate $T_{\text{iso}} = 1.43 \times 1930.5 \text{ K} = 2761 \text{ K}$. As the experimental value of T_{iso} is $2500 \pm 330 \text{ K}$, one finds a reasonable agreement between calculated and experimental values of the isokinetic temperature.

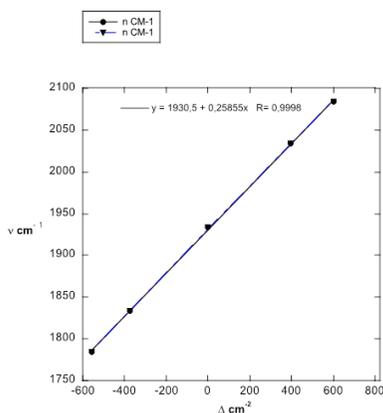


Figure 3: Plot of the data of Table 2, showing a correlation coefficient very close to $R = 1$.

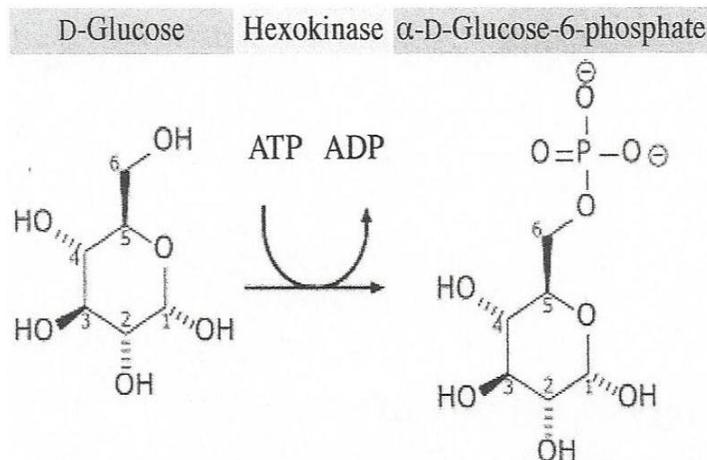
Table 2: Calculated values of Δ (cm^{-2}) for a series of vibrations ν (cm^{-1}).

ν cm^{-1}	1784	1834	1934	2034	2084
Δ cm^{-2}	-557	-376	0	397	603

Enzymes

An enzyme is a highly complex system of high molecular weight. One could well imagine there to be a large number of highly adequate energy suppliers for virtually any need. The specificity of a given enzyme system depends, however, on the construction of the active center, which obtains its energy supply from the molecular structure of the enzyme surrounding it.

As an example of this, one can consider the phosphorylation reaction between ATP and glucose to form glucose 6-phosphate. This reaction, as illustrated in Figure 4, is catalyzed in nature by the enzyme hexokinase, and in higher animals by the enzyme glucokinase.

**Figure 4:** Schematic view of the phosphorylation of glucose (Wikipedia) [27].

It is of interest in this context to note that there is a close similarity in value between one of the strongest PO_4 stretches of phosphates to be found in nature and the C (6)-O-H vibration that can take place in glucose; see Table 3.

If an appropriate enzyme/catalyst is present, there is thus a sound basis for a phosphate assimilation of the sugar that is present. Such a reaction is important for maintaining the energy balance in nature since it keeps the 'energy-rich' glucose within the boundaries of the cell.

The O–H group of the glucose becomes activated by close resonance with the HO_4P^{2-} unit, a water molecule then being set free, facilitating the combining of C(6)-O and O_3P . In this process, a combination of the sugar and the phosphate, described in Figure 4, $\omega/\nu = 1:1$. This reaction scheme also presumes that there is a pH of approximately 7, enabling two protons bind to the phosphate group.

The adenosine triphosphate is a small molecule, its having a molecular weight of 507, yet it is the center of a major enzyme. Within the SET framework, one can assume or suppose that the energy that excites the outermost PO_4 group (in a line of three) is obtained from vibrations of the protein groups surrounding it.

Table 3: IR data (cm^{-1}) concerning vibrations of solid state phosphates and glucose C(6)-O-H. The descriptions of the vibrations in column 1 are those of the authors of respective papers.

Assignment	Glucose	Phosphate	References
$\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ asym str		1044	[28]
C-O-H	1047		[29]
$\nu\text{CO} + \nu\text{CC}$	1050		[30]
$\text{CO}(79\%)+\text{CC}(19\%)$ PED	1047		[31]
PO_4^{3-} asym str.		1046	[32]

On the basis of what has been said above, one can conclude that the set of formulae that was presented in the first part of this paper fulfills its duty, so to speak. Without this information as a background, it would be difficult to understand how the various products of the catalyzed reactions that take place come about. Sometimes—as in Section 4—it is necessary to work with a 1:1 ratio of the vibrational quanta to the catalyst and to the reacting molecule. In other cases, such as in Section 2, there is a ratio of 4:5 that carries the reaction forward.

All of this is in line with the SET model of catalysis.

Indeed, it is what gives us a promise accuracy when comparing calculated and experimental values; e.g., Equations (13) and (15) above.

In 'case b', Section 3, on the other hand, the comparison of calculated and experimental data is less promising. A better estimation of experimental precision might improve the interpretation. The calculations cited here have not been published before.

In both cases, however, the formulae used are derived from classical physics and adapted to the SET model of catalysis.

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