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On the isokinetic effect for reactions of carbon dioxide with metal surfaces

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Kinetics data for the reaction $CO_{2(g)} \rightarrow CO_{(g)} + O_{(ads)}$ at metal surfaces are used to illustrate a previously developed model for the isokinetic effect. From this, it is concluded that the bending mode of an adsorbed, slightly bent CO_2 molecule is the one which must be activated for the reaction to occur.

Keywords: isokinetic temperature, carbon dioxide, adsorption, metal surface, bending modes

1. Introduction

Using radioisotope labelling, Grabke [1] could successfully measure the rate of the decomposition reaction of CO_2 on metal surfaces, i.e. $CO_{2(g)} \rightarrow CO_g + O_{(ads)}$. It was the ambition of the author [1] to establish a relation between the catalytic properties of various metals for this reaction and the chemical properties of the metals, especially if the adsorption step, the surface reaction or the desorption step was rate determining. The reactions were followed at high temperatures $\lesssim 1300$ K, in most cases just below the melting points of the metals; Ag 1234 K, Pd 1828 K, Au 1338 K, Ni 1555 K and Cu 1356 K. The result of the investigation could be expressed as

$$\text{rate} = kAa_O^{-m}p(CO_2)\,, \qquad (1)$$

where A is the surface area of the metal, a_O is the activity of oxygen on the surface, m is an exponent, $p(CO_2)$ is the partial pressure of carbon dioxide and k is the rate constant. Grabke [1] analyzed these data and suggested that the surface reaction, $CO_{2(ads)} \rightarrow CO_{(ads)} + O_{(ads)}$, was the rate-determining step and that furthermore the reacting species, CO_2, CO and O, were adsorbed in a “mobile” condition.

Analysis of k for a series of temperatures gave the Arrhenius parameters, the activation energy E_a and the pre-exponential factor k_0, for a series of metals – noble and base. It was later pointed out by Boudart et al. [2] that these data were exhibiting what is known as the compensation effect [3], i.e., a linear relation was found between the logarithm of the pre-exponential factor, k_0, and the observed activation energy:

$$\ln k_0 = a + bE_a\,, \qquad (2)$$

where

$$b = 1/RT_{iso} \qquad (3)$$

and T_{iso} denotes the so-called isokinetic temperature.

In view of the above-mentioned deductions of Grabke, it was regarded important to attempt an analysis of T_{iso} by the method of selective energy transfer [4] and to combine this with present-day knowledge of the vibrational spectra of adsorbed and coordinated carbon dioxide [5], to obtain information on the mechanism of the reaction.

2. Treatment of data

Boudart et al. [2] used slightly recalculated values of the pre-exponential factor in a discussion of the “sticking coefficient”. In order to better emphasize the implications of the observation of Boudart et al. [2], i.e. the compensation phenomenon, we will, however, use the original data as presented by Grabke [1]. These data are recorded in table 1. In figure 1a we have plotted $\ln k_0$ versus E_a as is conventionally done when describing the compensation effect. It is seen that the data do conform to the requirements of the compensation effect, a linear relation between $\ln k_0$ and E_a. We have only included metals that showed a non-dependence on the oxygen activity. The latter quantity is measured [1] by the ratio between the partial pressures of CO_2 and CO; $a_O = p(CO_2)/p(CO)$. Metals with high oxygen affinity were found to have a non-zero exponent of a_O in the expression (1). As we did not know the temperature dependence of the adsorption equilibrium governing the amount of oxygen on the

Table 1
Experimental data, relevant for this paper, of Grabke [1] on the reaction $CO_{2(g)} \rightarrow CO_{(g)} + O_{(ads)}$, where m is the exponent for the oxygen activity, a_O, in the rate expression (1). 1 kcal/mol = 4.184 kJ/mol

Metal	k_0 (mol/(s cm^2 atm))	m	E (kcal/mol)	a_O
Au	0.6	0	49.5 ± 3	–
Ag	1.7	0	52.3 ± 3	8.8×10^8
Pd	2.1×10^3	0	62.6 ± 1	2.7×10^7
Cu	4.8×10^3	0	60.6 ± 0.3	8.2×10^3
Ni	3.6×10^4	0	61.2 ± 0.3	144
Co	3.0×10^2	0.3	45.6 ± 1	12.8
Fe	1.2×10^2	0.3	44.3 ± 1	0.40
W	–	1	–	0.48

surface, we could not easily use the data for Fe, Co and W.

We find from figure 1a that the line of compensation has a slope = 0.803 mol kcal^{-1} that corresponds, according to eq. (3), to an isokinetic temperature, $T_{iso} = 627$ K. Before discussing the implications of this value, it might be appropriate to check the result using the recommendations of Linert [6] and Exner [7], i.e., to search for the intersection of the Arrhenius lines of the original experimental data. Such a common point of intersection should pertain (at $T = T_{iso}$) if the special form of the Arrhenius relation, eq. (4), holds:

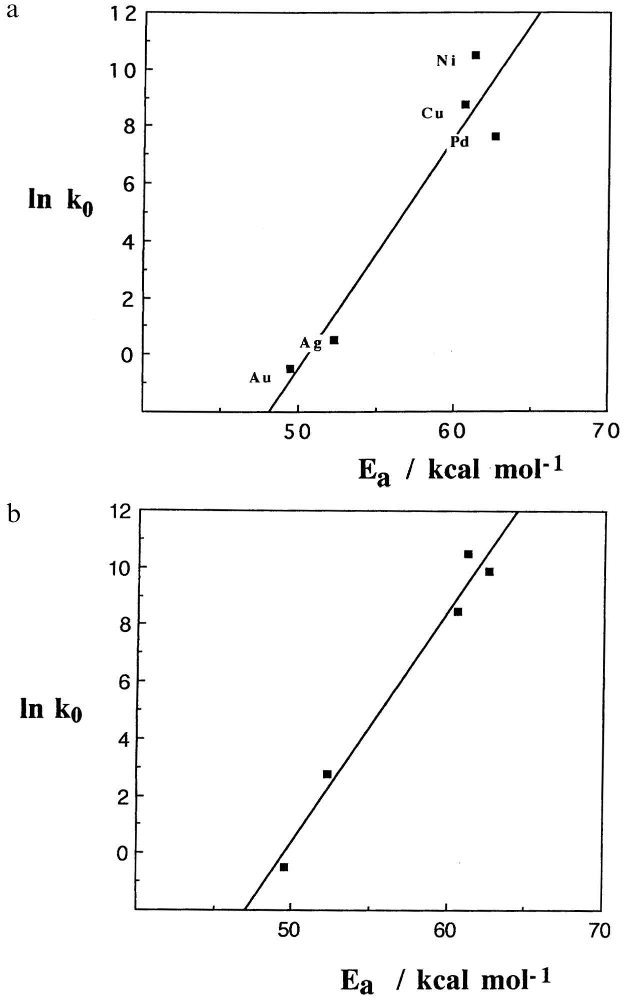

Figure 1. (a) A conventional compensation effect plot of $\ln k_0$ versus E_a from table 1. The slope of the line, 0.803 mol kcal^{-1}, gives $T_{iso} = 627$ K. (b) A similar graph as in (a) but with the $\ln k_0$ for Pd and Ag increased by $2.303 \times 0.96 = 2.21$ to make them on level with the other data. The slope is now 0.8091 mol kcal^{-1}, giving $T_{iso} = 622$ K.

$$\ln k = \ln Z - E_a/R(1/T - 1/T_{iso}) . \qquad (4)$$

In figure 2 we have re-drawn the figure 5 of Grabke's paper [1] and we have extended the lines to search for such an intersection. It is observed that the lines intersect at $1/T_{iso} \approx 1.6 \times 10^{-3}$ K^{-1}. Actually, there is not a single point of intersection but the lines for Cu and Au intersect at a slightly different ordinate value than do the lines for Ag and Pd. The abscissa is, however, more or less the same,viz. 1.6×10^{-3} K^{-1}. It follows that $T_{iso} \approx 1000/1.6 = 625$ K. The slight difference in ordinate – 0.96 units – corresponds to a difference in the value of $\ln Z$ in eq. (4), perhaps caused by a variation in the number of surface sites. Such slight differences are often found in studies on the compensation effect [8] and result in parallel lines of eq. (2). Using this difference, $\Delta \log Z = 0.96$, we have raised the data for Ag and Pd in figure 1a by adding the term $\Delta \ln Z = 2.303 \times 0.96$. The resulting compensation line (figure 1b) has a slope of 0.8091 mol kcal^{-1}, giving $T_{iso} = 622$ K (compared to 0.8025 mol kcal^{-1} and $T_{iso} = 627$ K in the previous treatment), with $R^2 = 0.975$ to be compared to $R^2 = 0.910$ in the previous case (R = correlation coefficient). Thus a treatment following Bond [8] gives a better statistical fit to the compensation line. The present treatment gives $1/T_{iso} = 1/622 = 1.608 \times 10^{-3}$ K^{-1} in very good agreement with the abscissa value of the intersections of figure 2.

We have also performed a statistical analysis following the ideas of Linert and Exner [6,7] under the assumption that all five sets of data converge to one and the same point. This point of best statistical significance was found to have an abscissa value of 1.55×10^{-3} K^{-1}, indicating a $T_{iso} = 645$ K. As the analysis described above so clearly shows (figures 1a and 1b) that the assumption of one single point of intersection does not describe the data, we are confined to note that this statistical analysis gives a T_{iso} not far from the one arrived at in figure 2.

The important coclusion is, therefore, that the system is characterized by an isokinetic temperature of 625 ± 5 K.

3. Discussion

It has been suggested by one of us [4] that a model of selective energy transfer may be used to deduce quantitatively the isokinetic temperature. The parameters used are the vibration frequency ν of that vibration mode of the reacting molecule that most closely corresponds to

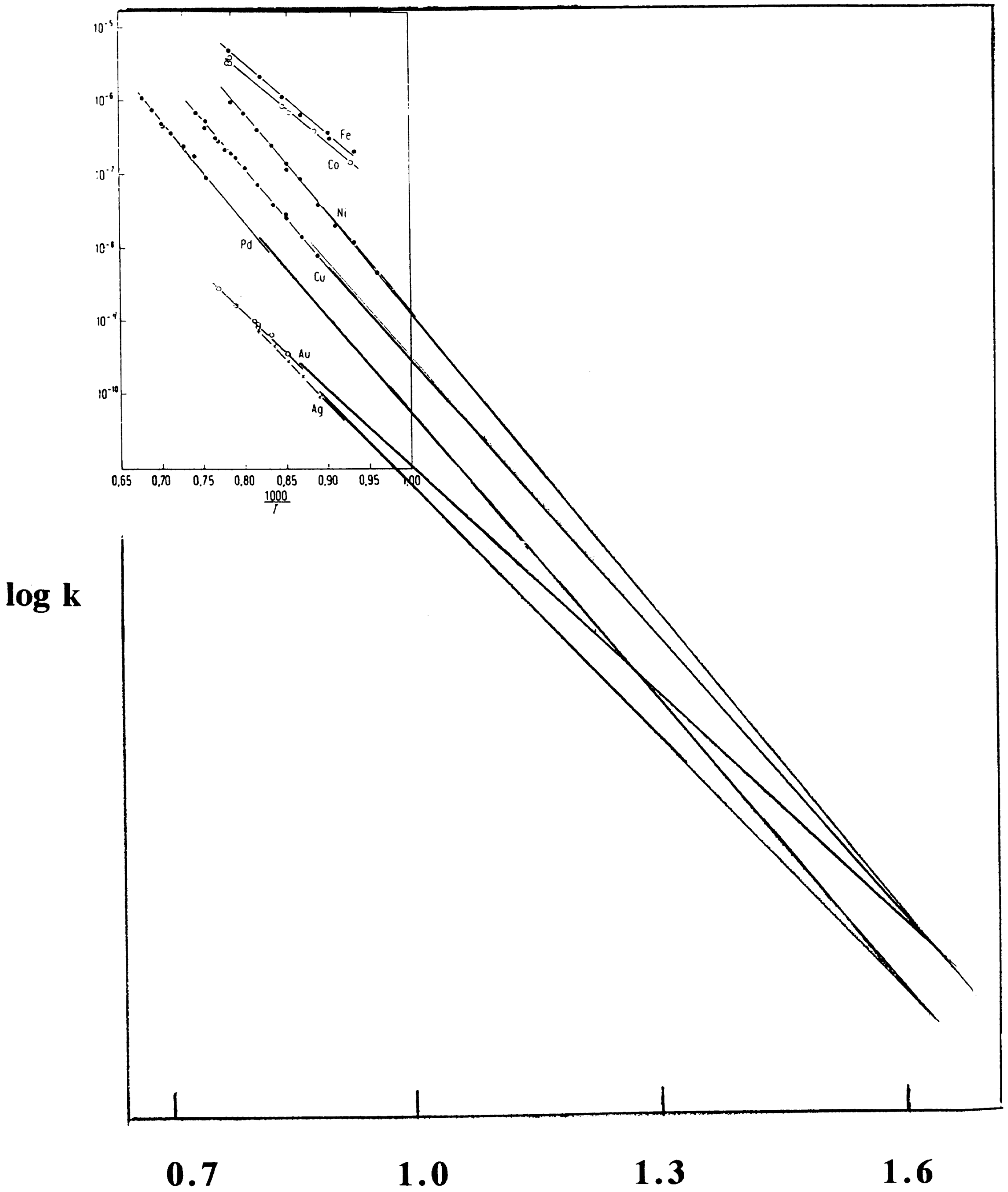

Figure 2. The Arrhenius relation of the experimental data of Grabke [1] re-drawn and extended from figure 5 of ref. [1]. k has the dimension of mol s^{-1} cm^{-2} atm^{-1}.

the movements of atoms towards the structure of the activated state and the frequency ω of that vibration mode of the "heat bath" that supplies the energy.

If conditions for a complete resonance are present, i.e. $\nu = \omega$, then it holds [4] that

$$T_{\text{iso}} = Nhc\nu/2R = 0.715\nu\,, \tag{5}$$

where N, c, h, R are the constants of nature with ν expressed in cm^{-1}. Assuming for the moment that such a condition prevails in the experiments of Grabke et al. [1], we obtain $\nu = 625/0.715 = 875$ cm^{-1}. That wave number should thus correspond to the vibration mode of the CO_2 molecule undergoing reaction. Can such a vibration be found?

Searching for such a vibration wave number, it is important to note that coordinated CO_2 ligands retain the characteristics of the O–C–O bending mode (ν_2) of the free molecule (667 cm^{-1} [9]) to a certain degree. Most investigators place these vibrations in the range 600–830 cm^{-1} [5]. For side-on complexes, with known structures characterized by X-ray diffraction, the wave numbers are around 740 cm^{-1}. The exact value depends on the detailed structure of the coordinated CO_2 [10], which in its turn can be assigned by measuring the isotope shifts of the stretching (ν_1 and ν_3) vibrations [10]. As the above-mentioned value of 875 cm^{-1} is outside these limits one can conclude that – as far as CO_2 is concerned – the assumption of complete resonance is not correct.

In the absence of full resonance one must use the full relation between ν and ω as deduced [4]:

$$T_{\mathrm{iso}} = NhcR - 1(\nu^2 - \omega^2)\omega^{-1} \times \{\pm\pi/2 - \mathrm{arctg}(0.5\nu\omega(\nu^2 - \omega^2)^{-1}\}^{-1} . \quad (6)$$

To solve this equation for the experimentally found isokinetic temperature, $T_{\mathrm{iso}} = 625$ K, we can construct the curves describing the dependence of T_{iso} on the heat bath frequency ω for any value of ν. We select four arbitrary values, viz. $\nu = 740, 760, 790$ and 830 cm^{-1}. The results are shown in figure 3. By cutting the curves by the line $T_{\mathrm{iso}} = 625$ K one gets four data points (ω, ν). These points are plotted in a diagram, figure 4, and an interpolation line is drawn to join them. From this relation of figure 4 one would be able to estimate the value of ν in the reacting molecule, had we only known the nature of the source of energy.

As there are no phonons of the appropriate wave number common for all the five metals investigated by Grabke [1], i.e., Au, Ag, Pd, Cu, Ni, this source of energy must be traced somewhere else. Let us suggest that the source of energy lies in the vibrations of the free, gaseous CO_2 molecules that must be present in excited states at the high temperatures [1] of the experiment. The most likely vibration mode is δ(OCO), that emits radiation at 667 cm^{-1} [9]. By interpolation (figure 4) one can estimate $\nu = 780$ cm^{-1} as the most probable vibration frequency for the reacting molecule. Such a value, 780 cm^{-1}, falls well within the limits of δ(OCO) of coordinated CO_2 species [5,10]. As coordination and adsorption are strongly related, one might assume that also species adsorbed on a metal surface would have vibrations in this region and that therefore the reacting species is an adsorbed, bent CO_2 molecule. The rate-determining step is therefore, as suggested by Grabke [1], $CO_{2(\mathrm{ads})} \rightarrow CO_{(\mathrm{ads})} + O_{(\mathrm{ads})}$.

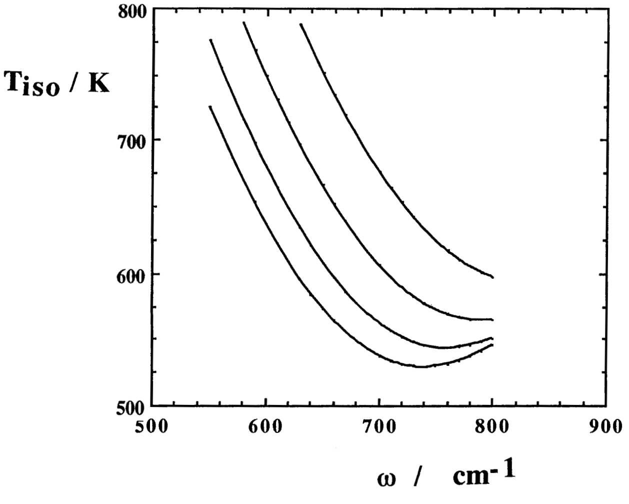

Figure 3. The isokinetic temperature calculated from eq. (6) for four arbitrary values of ν, the critical vibration of the molecule. From left to right $\nu = 740, 760, 790$ and 830 cm^{-1}.

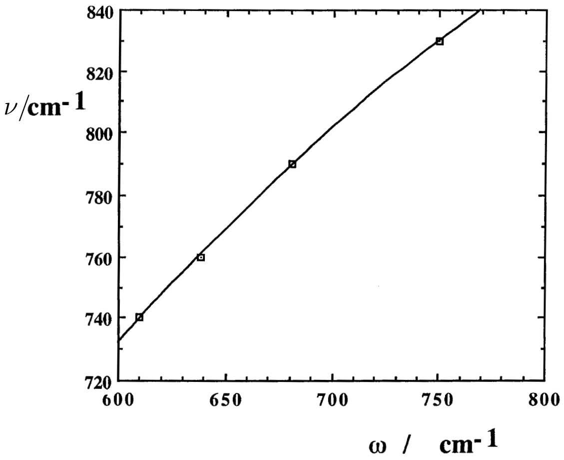

Figure 4. Interpolation graph indicating that the isokinetic temperature $T_{\mathrm{iso}} = 625$ K will occur for the heat bath frequency $\omega = 667$ cm^{-1} if the vibration mode of the reacting molecule occurs at $\nu = 780$ cm^{-1}.

At the prevailing high temperatures at least gold [11] is characterized by a high mobility of the atoms at the surface. Thus the similiarity between isolated atoms at low temperatures and the conditions of surface adsorption sites at high temperatures is enhanced. Agreeing with this, the adsorption must be quite weak as the same value is assumed to hold for all the five metals in question, Au, Ag, Pd, Cu and Ni.

4. Conclusion

These results are in accord with accepted paradigms, i.e., the reacting species must be adsorbed before it can react. As we have no information about the stretching vibrations of the molecule, nor of the shifts from isotopic substitution, we cannot say anything about the coordination type of the adsorbed species in this special case [10]. Whatever the details of the structure, however, one might conclude that the bending mode of the CO_2 molecule is of importance for the reaction.

As implied in the discussion above, there is a strong similarity between the reaction discussed here and described by Grabke [1] and the reactions of CO_2 coordinated on individual metal atoms as recorded by Mascetti et al. [12]. One should, however, note that the species of the latter type, formed at 15 K, react almost completely to form CO and M–O already when heated to 110 K, whereas the experiments of Grabke [1] were performed at about 1300 K.

If the reacting species adsorbed at the surface at this temperature were comparable to the CO_2 complexes formed at low temperatures, the enthalpy of adsorption should be positive or zero. This statement is in agreement with the proposal just made that the adsorption is weak and not very metal-specific. Furthermore, the weak adsorption is a requirement also for the equal – or nearly equal – value of $\ln Z$ from eq. (4) as is observed in figure 2, without which there should be no isokinetic effect. If the reacting species were strongly adsorbed, one should expect a pronounced sensitivity to the specific metal used.

The above-made conclusion is also in good agreement with the findings of Grabke [1]: The species that react are adsorbed, the adsorbed species are, however, very "mobile".

It should also be remarked here, in the context of testing the proposed model [4], that in a general case, a well defined isokinetic effect would result from formula (6) only in two cases: *either* at "complete resonance" with a more or less broad distribution of ω at the shallow minimum of the curve resulting from (6), cf. figure 3 here, *or* under not so well developed conditions of resonance (i.e. $\nu \neq \omega$) but with a very sharp frequency distribution of the ω band. As gaseous CO_2 with its narrow IR bands is supposed to supply the energy, the present analysis gives a good example of this latter case.

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