

# Adsorption assisted desorption in catalytic cycles

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## Abstract

Adsorption assisted desorption is an important phenomenon in catalytic cycles. It takes place when a desorption step is not equilibrated. The surface concentration or fugacity of the desorbing species can be higher than its equilibrium value because of a preceding adsorption step in the catalytic cycle. This results in an increased rate of desorption. Qualitative and quantitative examples of this effect are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction: a reminder of transition state theory

In general, the kinetics of elementary steps with reactants and products in Maxwell–Boltzmann equilibrium can be described by Transition State Theory (TST). For adsorption  $a$  and desorption  $d$ , of a molecule  $M$  to and from a site  $*$ :



the net desorption rate,  $v$ , is:

$$v = v_d - v_a \quad (2)$$

with:

$$v_d = k_d[*M] \text{ and } v_a = k_a[*][M] \quad (3)$$

where brackets denote values of concentration, fugacity, or activity, and the rate constants  $k_d$

and  $k_a$  are obtained by TST. In particular, in the spirit of TST, values of  $k_d$  do not depend on the presence or absence of the reverse step of adsorption. Indeed, the TST value of  $k_d$  is obtained by assuming that  $*M$  reaches its transition state from energy equilibrated reactants without any account of reaction products formed when the reacting system crosses the transition state: from the viewpoint of TST, the systems that cross the transition state just fall in a black hole to join other reaction products.

Before the formulation of transition state theory, the independence of forward and reverse rates was postulated in 1882 by Hertz, who boldly proposed that the rate of evaporation of liquid mercury into a vacuum at temperature  $T$  should be equal to the rate of condensation of mercury vapor in equilibrium with the liquid at the same temperature  $T$ , as calculated by the gas kinetic theory. Forty years later, and after several aborted trials, the Hertz equality was established experimentally by Volmer and Estermann

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over a broad range of temperatures. Details can be found elsewhere [1]: The difficulty in verifying the Hertz assumption was two-fold: surface contamination and surface cooling due to evaporation into a vacuum. The good luck of Hertz was that, as found later, the condensation coefficient of mercury atoms on a liquid or solid surface of mercury is very close to unity in a broad range of temperatures. As remarked by Tulley [2], “it is only when desorption occurs on a time scale faster than energy equilibration times that the presence or absence of the gas phase could be of any appreciable consequence.”

## 2. The concept of adsorption assisted desorption

From the preamble on transition state theory, it seems unlikely that a phenomenon called adsorption assisted desorption (AAD) would have been discovered and recognized. Yet it was, by Tamaru and coworkers [3–5], in careful studies of desorption of CO from polycrystalline surface of palladium and rhodium. The authors used a method first proposed by Tamaru [6] in which a gaseous  $C^{18}O$  molecules in equilibrium with a surface are replaced suddenly by  $C^{16}O$  molecules and the rate of desorption of  $C^{18}O$  molecules is followed with time. This powerful method, named isotopic switch by Tamaru [6], or isotope jump [7], or steady state isotopic transient kinetic analysis [8], is most revealing when the isotope jump is probing a working catalyst running at the steady state. In the work of Tamaru and coworkers [3–5], it was found that the rate of desorption of  $C^{18}O$  in the presence of  $C^{16}O$  in the gas phase was faster than in vacuo, hence the appellation of AAD.

In the case of the Hertz experiment with mercury, the surface coverage is of course independent of the vapor pressure in contact at the surface. But in the case of CO in contact with a metal surface, surface coverage depends on gaseous pressure. Thus, the observations of

Tamaru et al. were interpreted by Zhdanov [9] as well as by Lombardo and Bell [10] as a consequence of the frequently found increase of the rate constant  $k_d$  with increasing surface coverage,  $\theta$ .

In a substantial extension of work by Takagi et al. [11], Lauterbach et al. [12] investigated the rate of desorption of CO from an Ir(111) surface between 390 and 460 K into vacuum and under  $^{13}C^{18}O$  pressure in an isotopic switch from  $^{12}C^{16}O$  to  $^{13}C^{18}O$  with the CO surface coverage determined by FT-IRAS. By presenting their extensive data in two different ways, the authors obtained two sets of curves: those of surface coverage vs. time that look qualitatively like those of Tamaru and coworkers [3–5] and also the curves of the logarithm of surface coverage vs. time. Comparison between these two sets of curves leads Lauterbach et al. to the following conclusion: “Careful evaluation of our data shows that taking into account the coverage-dependent rate coefficients of desorption (...), it is possible to describe the results of desorption under equilibrium conditions very well with data measured for desorption into vacuum.”

With the evidence reviewed above, one strong statement can be made: adsorption assisted desorption exists. Whether all existing measurements of desorption rates in a non-catalytic adsorption–desorption situation can be explained by the effect of surface coverage  $\theta$  on the rate constant for desorption  $k_d$  remains an open question. Perhaps AAD could be explained by ligand exchange, a  $SN_2$ -like mechanism, by which an entering phosphine ligand displaces carbon monoxide bound to molybdenum hexacarbonyl [13]. But, as just discussed, the effect of  $\theta$  on  $k_d$  certainly explains quantitatively recent data on AAD phenomena. In view of the importance of desorption in any catalytic cycle, AAD must be important in catalysis. This is enough motivation to explore further the role of AAD in catalytic cycles, as will be done in this paper. Before starting, a reminder of general aspects of catalytic cycles will be presented first.

### 3. Adsorption assisted desorption in catalytic cycles

For any elementary step that conforms to TST, for instance the desorption step of Eq. (1), we can write a relation:

$$v_d/v_a = \exp(A/RT) \quad (4)$$

where  $A = -\Delta G$  is the Affinity of that step. This relation was first written by De Donder [14], and used later by myself in explaining kinetic coupling in catalytic cycles [15]. The De Donder relation says that the *kinetic* irreversibility of the step is equal to the exponential of its *thermodynamic* driving force. It tells us that an elementary step is always a two-way step, i.e., reversible thermodynamically (symbol  $\rightleftharpoons$ ); but it can be kinetically a *one-way step* (symbol  $\rightarrow$ ) if, for instance,  $v_d \gg v_a$ , or an equilibrated step if  $v_a = v_d$  (symbol  $\rightleftharpoons$ ) when  $A = 0$ . In a catalytic cycle at the kinetic steady state, the net rate, or turnover frequency of the cycle,  $v$ , is equal to the net rate  $v_{+i} - v_{-i}$  of each step, when  $v$  is multiplied by the stoichiometric number  $\sigma_i$  of the step, i.e., the number of times the step must occur for one cycle of the catalytic reaction to occur:

$$\sigma_i v = v_{+i} - v_{-i} \quad (5)$$

Because of the kinetic coupling between steps in the catalytic cycle, these steps may be one-way, two-way, or equilibrated, at the kinetic steady state. In particular, a desorption step may not be equilibrated in a catalytic cycle, as postulated in the classical Langmuir–Hinshelwood mechanism where both adsorption and desorption are assumed to be equilibrated, while a surface reaction step is rate determining.

Let us explore how a desorption step can operate in excess of equilibrium, when  $v_d > v_a$ . Clearly, one way to increase  $v_d$  at constant product pressure and constant temperature is to increase the concentration or fugacity of the adsorbed species above its equilibrium value. This can be done through a kinetically coupled preceding adsorption step in the catalytic cycle.

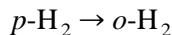
With the fugacity of the adsorbed species higher than that corresponding to equilibrium with the desorbed species, the latter is not an inhibitor of the desorption step if  $v_d \gg v_a$ . The lack of inhibition of the rate of a catalytic cycle by a desorption product is therefore an indication that adsorption assisted desorption has taken place.

In fact, kinetic coupling between steps in a catalytic cycle works in both ways through the Le Chatelier principle. A thermodynamically unfavorable step is helped either by removal of a product through a subsequent step faster than the rate at which the product can return to reactant; or by accumulation of a reactant through a preceding step. The latter case is that of AAD in a catalytic cycle.

In fact, soon after Yamashita et al. [16] published their work on AAD, they found that a similar phenomenon was observed in the decomposition of methanol on  $\text{Cr}_2\text{O}_3$ . In that case, adsorbed formate ions formed by adsorption of methanol decompose to reaction products much faster under ambient pressure of methanol than in its absence. This is the first reported case of AAD in a catalytic cycle, although other examples were reported previously, but not recognized as cases of AAD. Let us describe briefly four such cases as well as a carefully documented case of AAD in the sense of the Tamaru school.

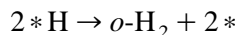
### 4. The para-hydrogen conversion of tungsten

This is a historical, if not dramatic story of a 20-year quarrel that was settled by the recognition that the chemical conversion of  $p\text{-H}_2$  to  $o\text{-H}_2$  on tungsten at liquid nitrogen temperature was a case of what I call AAD in this paper. The fact is that the catalyzed reaction:

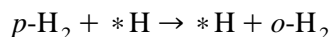


takes place at 90 K on metals, a rather extraor-

dinary observation. A mechanism was proposed by Bonhoeffer and Farkas [17] in 1931:



But in 1935, Roberts [18] showed that the heat of adsorption of  $\text{H}_2$  on a W filament started at  $45 \text{ kcal mol}^{-1}$  on a bare surface and decreased to  $15 \text{ kcal mol}^{-1}$  at what was believed to be a complete monolayer of H on W at 273 K and  $10^{-4}$  Torr of  $\text{H}_2$ . It is impossible for  $*H$  to desorb at any measurable rate at 90 K with the lowest heat of adsorption measured by Roberts. Hence, Rideal [19], in whose Cambridge laboratory Roberts had performed the adsorption work, proposed instead the mechanism:



This mechanism became known as the Eley–Rideal mechanism [20] mentioned in most books on heterogeneous catalysis.

But in 1950, at a Discussion of the Faraday Society on Heterogeneous Catalysis, Rideal and Trapnell reported a set of adsorption isotherms at pressures of about  $10^2$  Torr. They found that  $\text{H}_2$  is atomically chemisorbed on W evaporated films with a heat of adsorption of about  $1.8 \text{ kcal mol}^{-1}$  corresponding to an almost complete monolayer at 90 K. This is very different from the results of Roberts at lower pressures and higher temperatures. Very fairly, Rideal and Trapnell concluded that “these results make it probable that the conversion proceeds by the Bonhoeffer–Farkas mechanism.” There is no need for an Eley–Rideal mechanism: the observations at 90 K, of the high surface coverage by hydrogen at that temperature with the corresponding low value of the heat of adsorption of dihydrogen, can be understood as a striking example of adsorption assisted desorption.

### 5. Dehydrogenation of methylcyclohexane (M) to toluene (T) on platinum

The kinetic study of that reaction by the group of Sinfelt et al. [21] provides a qualitative

but clear example of AAD. The reaction was taking place sufficiently far away from equilibrium, so that the absence of inhibition of the rate by toluene was an indication of a situation where the fugacity of adsorbed toluene was in excess of its equilibrium value. Moreover, the rate of reaction was not depressed by substantial addition of benzene to the reactant so that benzene did not have access to the surface since the latter was largely covered with adsorbed toluene coming from previous adsorption steps in the catalytic cycle. Another way to look at the lack of inhibition by toluene or benzene is that the enhanced surface coverage by toluene corresponds to a pressure or fugacity of toluene in the gas phase, frequently called virtual fugacity. This virtual fugacity is higher than the actual one. In other words, benzene has no chance to compete with toluene at the surface because of AAD and gas phase toluene itself does not inhibit the rate of the overall reaction. The phenomenon of AAD is due to kinetic coupling between steps in the catalytic cycles. Its effect is enhanced by the fact that, in general, the heat of adsorption of a species decreases with increasing surface coverage, as already noted in the case of hydrogen on tungsten, as well as the suggested explanation of AAD in adsorption–desorption phenomena.

### 6. The decomposition of germane $\text{GeH}_4$ on germanium films

A series of publications describe work carried out by Kenzi Tamaru in the 1950s in Princeton in the laboratory of Sir Hugh Taylor, with my occasional participation. They are summarized in Tamaru’s book [22] with appropriate references. Here is a summary. The rate of decomposition of  $\text{GeH}_4$  on Ge is zero order. This suggests that the Ge surface is completely covered with adsorbed hydrogen, as verified by stopping the reaction by quenching it and measuring the amount of chemisorbed hydrogen. By

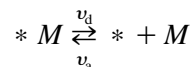
contrast, the surface coverage by hydrogen during the  $H_2$ – $D_2$  exchange was way below a monolayer, under partial pressure of  $H_2$  or  $D_2$  comparable to those present during the decomposition of  $GeH_4$ . Correspondingly, the rate of  $H_2$ – $D_2$  exchange was less than that of decomposition of  $GeH_4$ , suggesting AAD of hydrogen during the decomposition of  $GeH_4$ . Finally, during the decomposition of  $GeH_4$  in the presence of  $D_2$ , no HD appeared among the products. On the contrary, during the decomposition of mixtures of  $GeH_4$  and  $GeD_4$ , the three isotopic species  $H_2$ , HD, and  $D_2$  were observed. Note again that the rate of decomposition of  $GeH_4$  is not inhibited by gas phase hydrogen since the fugacity of surface hydrogen is so much higher than that in the gas phase.

Thus, during decomposition of  $GeH_4$  on Ge, AAD of product is observed, and  $D_2$  separately introduced species during the decomposition of  $GeH_4$  has no access to the surface. The lessons learned from these studies exerted a profound influence on further work by Kenzi Tamaru and myself. In particular, they were responsible over the years for the continuing emphasis by Tamaru of the necessity of studying catalysis, surface species, and kinetics during the catalytic process itself, under dynamic conditions, for instance by the isotope jump technique [22]. As to the case of  $GeH_4$ , it is perhaps the first clear example of AAD in a catalytic cycle, since the desorption of adsorbed H from a practically complete monolayer on Ge is assisted by the adsorption of H in preceding steps. Thus, these preceding steps create a virtual pressure of  $H_2$ , far above that of  $H_2$  at the steady state of the decomposition of  $GeH_4$ . A similar case is that of the decomposition of  $NH_3$  as described in the next section.

## 7. The decomposition of ammonia far from equilibrium

This is a case where AAD can be quantified. Let us return to a desorption step and ask how

far from equilibrium it takes place in a catalytic cycle, irrespectively of its detailed mechanism. All we want to know is how we can measure the affinity  $A$  that drives desorption, as in Eq. (1):



At the steady state of the catalytic reaction, the affinity  $A$  for desorption is by definition:

$$A = \mu_{M^*} - \mu_M - \mu^* \quad (6)$$

where the  $\mu$ s are the chemical potentials of the species  $M^*$ ,  $M$  and  $*$  at the *steady-state*. Let us define a virtual fugacity of  $M$ , denoted by  $M,v$  that corresponds to *equilibrium* between  $M$  on the one hand, and  $M^*$  and  $*$  on the other hand, at their steady-state value of fugacity. Since this corresponds to equilibrium, the affinity is zero and Eq. (6) becomes:

$$0 = \mu_{M^*} - \mu_{M,v} - \mu^* \quad (7)$$

Subtraction of Eqs. (6) and (7) side by side yields:

$$A = \mu_{M,v} - \mu_M \quad (8)$$

But, with the superscript  $\theta$  standing for standard state, we have:

$$\mu_M = \mu^\theta + RT \ln[M] \quad (9)$$

$$\mu_{M,v} = \mu^\theta + \ln RT[M,v] \quad (10)$$

where the quantities between brackets are values of fugacity. Substitution of Eqs. (9) and (10) into Eq. (8) gives finally, with the help of the De Donder relation (4):

$$[M,v]/[M] = \exp(A/RT) = v_d/v_a \quad (11)$$

Thus, if values of virtual and real fugacity in the gas phase can be measured at the same value of surface coverage, the affinity of the desorption step can be obtained, and with it a measure of the one-way behavior of the adsorption step. In particular, with a large value of  $A$ , the desorbed product will not appear as an inhibitor of the turnover frequency of the catalytic cycle, since  $v_d \gg v_a$ .

The decomposition of ammonia was studied at low pressures and high temperatures on foils of W [23] and Mo [24] in the laboratory of Tamaru. Because of the low pressure, the surface coverage by adsorbed N could be determined by AES during the reaction and in a series of equilibrium adsorption isotherms of nitrogen. From the latter, the heat of adsorption was obtained: it decreases with increasing surface coverage. As an example of AAD for Mo, the value of  $A$  for desorption of  $N_2$  at 1000 K and a number of  $N_2$  molecules per  $cm^3$  equal to  $8.2 \times 10^8$ , was found to be equal to  $41 \text{ kJ mol}^{-1}$  by using Eq. (11) with values of  $[M, v]$  and  $[M]$  determined at the same value of surface coverage during reaction and from the equilibrium isotherms. This corresponds to  $v_d/v_a = 142$ . Thus, desorption is assisted appreciably by the high coverage of the surface by nitrogen as a result of steps preceding desorption. The kinetic assistance is enhanced by the decrease in the heats of adsorption of  $N_2$  with coverage.

## 8. Decomposition of ethanol to acetaldehyde and hydrogen on a niobium molecular heterogeneous catalyst supported on silica gel

In any study of solid catalysts, the main obstacle to quantitative understanding is the non-uniformity of the surface as well as interactions between adsorbed intermediates. In other words, there are too few examples today of what are called heterogeneous molecular catalysts [25], or also single site catalysts. In the case of AAD studies, the work of Iwasawa and coworkers [26–30] on a niobium molecular supported catalyst must be singled out not only because of its quantitative content but also for the originality of its observations.

In brief, the facts are as follows. *First*, the authors prepared a complex of niobium attached on a silica surface; they determined its structure and, in particular, showed by EXAFS that there were no Nb–Nb bonds observable so that the

complexes are indeed molecular. *Second*, they found that this catalyst dehydrogenated ethanol readily and selectively to acetaldehyde and dihydrogen through OH and  $OC_2H_5$  intermediates co-ordinated to Nb. *Third*, they discovered that the reaction stopped when ethanol was pumped out at the temperature of the reaction; in the pumped-out conditions, the bound intermediates decomposed to ethene and diethylether as the temperature was raised. *Fourth*, the normal reaction, once stopped, could be restarted by introducing *t*-butanol or six other nucleophiles: the initial rates of acetaldehyde production could be correlated with the donor number of these adducts, defined as the logarithm of the equilibrium constant between these molecules and  $SbCl_5$ . *Fifth*, kinetic isotope effects observed by reacting  $C_2H_5OH$ ,  $C_2H_5OD$ ,  $C_2H_5-OD$ , or  $C_2D_5OD$  imply that the rate determining step is the C–H bond scission in the ethyl group. *Sixth*, after the reaction is started with  $C_2H_5OH$  and is switched to  $C_2D_5OD$ , products  $H_2$ , HD, and  $D_2$  appear successively in that order by ligand exchange between the seven ligands in the coordination sphere of Nb before the last step of desorption to products; the appearance of  $H_2$ , HD, and  $D_2$  could be described by a simple kinetic model. *Seventh*, the mechanism based on a first reversible stronger addition of  $C_2H_5OH$  to the Nb complex, followed by a second reversible weaker addition, could be modeled with only four adjustable parameters.

The authors' interpretation of this 'self-assisted' dehydrogenation is simple: the second  $C_2H_5OH$  molecule appearing in the co-ordination sphere of Nb interacts with the metal in such a way that it promotes the  $\beta$ -C–H bond scission of the first appearing ligand, the mechanism of this promotion being as described in the literature. In my own words, and in the language of heterogeneous catalysis, the reaction is bimolecular: it is a reaction limited by desorption and the second co-ordinated molecule, as it is adsorbed, assists the desorption of the first one.

## 9. Postscript

The concept of adsorption assisted desorption (AAD) has come of age. It was latent in the Princeton work of the 1950s, dealing with the catalytic decomposition of germane. The concept of AAD attracted considerable attention as it was first proposed by the Tamaru group, first in an adsorption–desorption elementary step, then as a means of assistance at the end of a catalytic cycle. This latest development was further developed by the Tamaru school currently led by Professor Iwasawa, a former student of Professor Tamaru. I like to think that AAD is particularly important as an illustration of kinetic coupling in catalytic cycles. The latter is at the root of the doctrine of Kenzi Tamaru as illustrated by many of his investigations: what matters is to study the dynamics of catalytic reactions while they proceed, at the steady state, through kinetic and spectroscopic probes, that peer into the ‘black box’ surrounding the reactor space.

## References

- [1] M. Boudart, *Kinetics of Chemical Processes*, Butterworth-Heinemann, Boston, 1991, pp. 38–40.
- [2] J.C. Tulley, in: C.B. Duke (Ed.), *Surface Science: The First Forty Years*, North-Holland, Amsterdam, 1994, p. 674.
- [3] T. Yamada, T. Onishi, K. Tamaru, *Surf. Sci.* 133 (1983) 533.
- [4] T. Yamada, K. Tamaru, *Surf. Sci.* 138 (1984) L155.
- [5] T. Yamada, K. Tamaru, *Surf. Sci.* 146 (1984) 341.
- [6] K. Tamaru, *Adv. Catal. Rel. Subj.* 15 (1964) 1964.
- [7] M. Boudart, R.L. Burwell, Jr., in: E.S. Lewis (Ed.), *Investigation of Rates and Mechanisms of Reactions*, Chap. 12, Wiley, New York, 1974.
- [8] J.G. Goodwin Jr., J.U. Nwalor, *Topics Catal.* 1 (1994) 285.
- [9] V.P. Zhdanov, *Surf. Sci.* 157 (1985) L384.
- [10] S.J. Lombardo, A.T. Bell, *Surf. Sci.* 245 (1991) 213.
- [11] N. Takagi, J. Yoshinobu, M. Kawai, *Phys. Rev. Lett.* 73 (1994) 292.
- [12] J. Lauterbach, M. Sushchikh, W. Henry Weinberg, *Z. Phys. Chem.* 198 (1997) 1997.
- [13] J.R. Graham, R.J. Angeliu, *Inorg. Chem.* 6 (1967) 2082.
- [14] T. De Donder, *L’Affinité*, Gauthier-Villars, Paris, 1927.
- [15] M. Boudart, *J. Phys. Chem.* 87 (1983) 2786.
- [16] K. Yamashita, S. Naito, K. Tamaru, *J. Catal.* 94 (1985) 353.
- [17] W. Bonhoeffer, A. Farkas, *Z. Phys. Chem. B* 12 (1931) 231.
- [18] M.K. Roberts, *Proc. R. Soc. A* 152 (1935) 445.
- [19] E.K. Rideal, *Proc. Cambridge Philos. Soc.* 35 (1939) 130.
- [20] D. Eley, E.K. Rideal, *Proc. R. Soc. A* 178 (1941) 429.
- [21] J.H. Sinfelt, H. Hurwitz, R.A. Shulman, *J. Phys. Chem.* 64 (1960) 1559.
- [22] K. Tamaru, *Dynamic Heterogeneous Catalysis*, Academic Press, London, 1978.
- [23] H. Shindo, C. Egawa, T. Onishi, K. Tamaru, *J. Chem. Soc. Faraday I* 76 (1980) 280.
- [24] M. Boudart, C. Egawa, S.T. Oyama, K. Tamaru, *J. Chim. Phys.* 78 (1981) 987.
- [25] M. Boudart, *J. Mol. Catal. A* 120 (1997) 271.
- [26] M. Nishimura, K. Asakura, Y. Iwasawa, *J. Chem. Soc., Chem. Commun.*, 1986, p. 1660.
- [27] M. Nishimura, K. Asakura, Y. Iwasawa, *Chem. Lett.*, 1987, p. 573.
- [28] M. Nishimura, K. Asakura, Y. Iwasawa, in: M.J. Phillips, M. Ternan (Eds.), *Proc. 9th Intern. Cong. Catal.*, Vol. 4, Calgary, Chemical Inst. Canada, Ottawa, 1988, p. 1842.
- [29] Y. Iwasawa, in: J.W. Hightower, W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), *Proc. 11th ICC, Baltimore, Studies in Surf. Sci. and Catal.*, Vol. 101, Elsevier, Amsterdam, 1996, pp. 23–25.
- [30] Y. Iwasawa, *Acc. Chem. Res.* 30 (1997) 103.