

Effect of Multiple Sites and Competition in Adsorption on the Kinetics of Reactions Catalyzed by Metals

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A model is developed that expresses the adsorption rate (R_a) of saturated hydrocarbons in terms of competition for chemisorption on the same "potential sites" on metal surfaces. The "active site for hydrocarbon chemisorption" is defined as a patch of Z first neighbor free "potential sites." The potential sites are likened to the H chemisorption site. The association of these factors enables one to express R_a as proportional to the fraction of free potential sites (θ_s), at a power equal to Z , and thus to relate R_a to the coverages of adsorbed species. The introduction of numerical values for the coverages predicts large variations both of the adsorption rate R_a (several powers of 10), the orders of reaction (from highly negative up to positive values), and the temperature factor (up to several tens of kcal/mole). The shape of the variations is analyzed, on rhodium, using the H_2 experimental adsorption isotherms. Emphasis is on the use of the isotopic exchange rate as a means to measure the adsorption rate, at adsorption-desorption equilibrium. From the results in the literature and those obtained in this laboratory for the CH_4 - D_2 exchange on Rh, in a pressure range extending over more than three powers of 10, a good agreement is obtained between the experimental values of the order α versus the D_2 pressure (varying from 0 to -1.2) and the calculated values using a single Z value of 7. In the same way, the temperature factor is analyzed.

I. INTRODUCTION

In heterogeneous reactions involving hydrogen and saturated hydrocarbons in the presence of metal catalysts (hydrogenolysis, isomerization, exchange with deuterium), the experimental order versus hydrogen pressure is often negative. In the case of hydrogenolysis and isomerization reactions, this negative order is mainly interpreted in terms of dehydrogenation of the hydrocarbon radicals on the surface. Sometimes the inhibitor effect of hydrogen is so important that it implies a complete dehydrogenation of the active chemisorbed hydrocarbon radical (1, 2).

In the particular case of an isotopic ex-

change reaction, the inhibiting factor cannot be interpreted by the dehydrogenation of the adsorbed hydrocarbon radical but is contained in the adsorption step. Every catalytic isotopic exchange reaction must be studied under conditions where adsorption-desorption equilibrium is attained in order to measure the catalytic activity and not a surface reaction between the gas phase and the solid. The exchange rate is determined from the rate of appearance of the deuterated species in the gas phase, that is the hydrocarbon desorption rate. Neglecting any isotopic effect between H and D, the rate of exchange measures the rate of hydrocarbon adsorption. Therefore, the rate of exchange may be used as a trick to determine the rate of the hydro-

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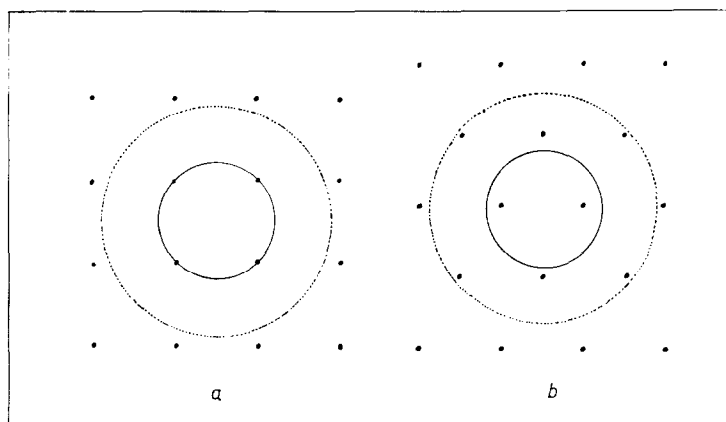


FIG. 1. "Potential sites" lattice: (a) lattice of the (100) Rh face, (b) (111) Rh face. Continuous circle section based on van der Waals covolume of the CH_4 molecule. The space between dotted and continuous circles defines the sites hindered for CH_4 chemisorption.

carbon adsorption, at adsorption-desorption equilibrium. Thus the inhibitor factor for the D_2 pressure appearing in the rate equation of the exchange must also appear in the mathematical expression for the rate of the hydrocarbon adsorption.

In this paper, we develop a model of competitive adsorption between hydrogen and hydrocarbon that may introduce a negative order versus the H_2 pressure on the rate of the adsorption step. The competition has already been proposed by several authors. Kemball (3) considers the competition for the same surface sites and Boudart (4) for two types of surface sites. The resulting inhibiting effect is more important using two types of surface sites. The model we have already proposed (5) is based on the competition for chemisorption on the same surface sites but introduces in the formalism the requirement of the large number of sites involved in the chemisorption of one single hydrocarbon molecule.

Previous measurements of CH_4 chemisorption (6), the smallest of the saturated hydrocarbons, performed on different metal films (Mo, Rh, Re) have shown that the maximum adsorbed quantity $(n_{\text{CH}_4})_{\text{max}}$ is independent of temperature between -80 and $+50^\circ\text{C}$, a temperature range where

CH_4 chemisorption is not accompanied with H_2 evolution. This quantity is very small as compared with the maximum number of H atoms $(n_{\text{H}})_{\text{max}}$ chemisorbed on a clean surface (8). In this temperature range, the ratio $(n_{\text{CH}_4})_{\text{max}}/(n_{\text{H}})_{\text{max}}$ is in the 0.1 range. After saturation by CH_4 , a further amount $(n_{\text{H}})_a$ may be chemisorbed, corresponding to 40% of $(n_{\text{H}})_{\text{max}}$. The number of H chemisorption sites covered by the residues of one chemisorbed CH_4 molecule, calculated by $(n_{\text{H}})_{\text{max}} - (n_{\text{H}})_a / (n_{\text{CH}_4})_{\text{max}}$, is about 7.

The reported experimental facts are in agreement with a steric effect for chemisorption developed previously (7). This effect appears in Fig. 1 where three kinds of sites may be distinguished for the adsorption of a large molecule as compared with the size of the site, whatever the nature of the site:

- adsorption sites, on which a molecule is already adsorbed,
- covered sites by a molecule adsorbed on some neighboring adsorption site, and
- hindered sites, distant from one or several adsorption sites by more than a molecular radius but less than a molecular diameter.

When there remains no more free sites for the adsorption of molecules which are large compared with the size of the adsorption site, the hindered sites for such molecules may still be free for a small molecule like hydrogen.

Introducing in the theoretical analysis of the steric effect (7) the value of seven sites occupied by the chemisorbed CH_4 molecules, one calculates a fraction of sites hindered for CH_4 chemisorption and free for H chemisorption of about 40%, as observed.

The value of seven H sites covered by the radicals resulting from the chemisorption of one CH_4 molecule indicates that the chemisorbed hydrocarbon radical is large compared with the size of the site. Let us remember that the CH_3 or CH_2 radical has a similar size, in the gas phase, to the CH_4 molecule. This suggests that the CH_4 chemisorption step needs a patch of free neighbor sites of the same order of magnitude, even in the high temperature range where CH_4 chemisorption is accompanied by H_2 evolution and isotopic exchange is measurable. Let us notice that this remark applies a fortiori to higher saturated hydrocarbons.

II. MODEL OF COMPETITIVE ADSORPTION

The model presented here considers a uniform surface and does not include all the features related to possible defects present at the surface of practical catalysts. We consider, at the surface of the metal, a two-dimensional lattice of "potential sites," the space distribution of which is set by the crystallographic structure of the metal. It is also assumed that the size of the potential site is of the same order as that of the H chemisorbed atom (8). At zero coverage, all potential sites are assumed to be equivalent among themselves and equivalent for adsorption either of H_2 or of the hydrocarbon. We do not intend to specify here the nature or the location of the site (on

the metal atom, between two or more metal atoms).

When in interaction with a gas phase composed of H_2 and hydrocarbon, the potential surface sites may be divided into three fractions:

- θ_{H} , the one covered by hydrogen chemisorbed atoms,
- θ_{C} , the one covered by all the hydrocarbon chemisorbed radicals, and
- θ_{s} , the one remaining free for chemisorption,

with:

$$\theta_{\text{H}} + \theta_{\text{C}} + \theta_{\text{s}} = 1. \quad (1)$$

Without any assumption on the mechanism, the rate of the hydrocarbon adsorption step (R_{a}) is proportional to the hydrocarbon pressure (p_{HC}) times a term representing the second partner of the reaction, i.e., the free surface.

$$R_{\text{a}} = kp_{\text{HC}}f(\theta_{\text{s}}). \quad (2)$$

In the particular case of H_2 chemisorption, the dissociative chemisorption step implies the presence of two free potential sites first neighbor and the function of the free surface is classically given by θ_{s}^2 in Eq. (2):

$$R_{\text{a}} = kp_{\text{H}_2}\theta_{\text{s}}^2 = kp_{\text{H}_2}(1 - \theta_{\text{H}})^2. \quad (3)$$

The main feature of this model lies in the association of the two factors:

- both gases (here H_2 and the hydrocarbon) may be adsorbed on the same potential sites and there is thus a competition for adsorption, and
- hydrocarbon molecule needs a large number Z of free neighbor potential sites to be adsorbed.

Thus a patch of Z first neighbor potential free sites is an "active site for hydrocarbon chemisorption." In Eq. (2) θ_{s} must appear at a power equal to Z . Through the function θ_{s}^Z , the fraction of available "active site for the chemisorption of the hydro-

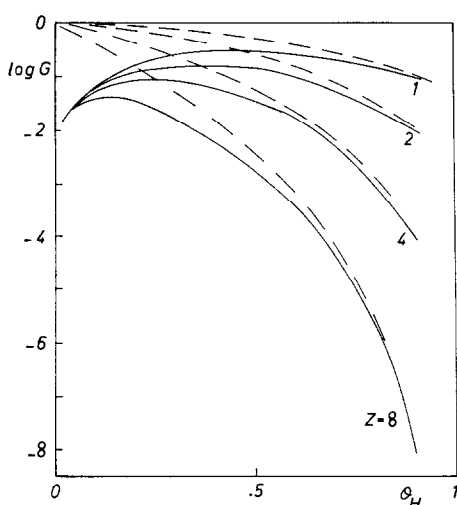
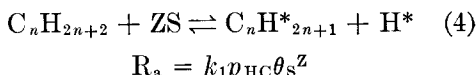


FIG. 2. Variation with the hydrogen coverage (θ_H) of the function G_R (solid line) and G_D (dashed line), for different Z values.

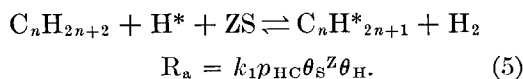
carbon" on a given metal is defined from the coverages in hydrogen (θ_H) and in hydrocarbon (θ_C) [Eq. (1)]. The hydrocarbon rate of adsorption is written:

—according to a dissociative chemisorption mechanism:



where * denotes chemisorbed species, and

—according to a reactive chemisorption mechanism:



Let us recall that from Eq. (1):

$$\theta_S = 1 - \theta_C - \theta_H \quad (6)$$

The introduction of this function in Eq. (4) or (5) shows the relation between the hydrocarbon adsorption rate and the coverages θ_H and θ_C .

It is interesting first to examine quite generally what may be predicted from these equations before introducing numerical values for the parameters θ_C and θ_H .

Let us examine the simplified case, fre-

quently encountered in kinetic studies, where θ_C is negligible. Equations (4) and (5) become:

$$R_a = k_1 p_{HC} (1 - \theta_H)^Z \quad (7)$$

$$R_a = k_1 p_{HC} \theta_H (1 - \theta_H)^Z \quad (8)$$

Let us define:

$$G_D = (1 - \theta_H)^Z \quad (9)$$

$$G_R = \theta_H (1 - \theta_H)^Z \quad (10)$$

Independently of the shape of the H_2 isotherm, the variation with coverage of the logarithm of the functions G_R and G_D are presented in Fig. 2, for different values of Z . The importance of the effect is clearly emphasized in this figure, particularly for the usual working conditions of hydrogen coverage, i.e., higher than 0.5. These functions G_R and G_D express the hydrogen coverage dependence of the hydrocarbon adsorption rate. The dependence versus the hydrogen pressure may be written:

$$G_D = K_D p_{D_2}^{\alpha_D} \quad (11)$$

$$G_R = K_R p_{D_2}^{\alpha_R} \quad (12)$$

where α_D and α_R are the order respectively for a dissociative (D) or a reactive (R) adsorption mechanism, in the frame of the adsorption model presented here.

At small θ_H values, the function G_D approaches unity and the order α_D is nearly zero while G_R collapses to θ_H . For a dissociative chemisorption, $\theta_H = K^{\frac{1}{2}} \cdot p^{\frac{1}{2}}$ and the order α_R approaches 0.5. On the other hand, when θ_H is near unity, $1 - \theta_H = K^{-\frac{1}{2}} \cdot p^{-\frac{1}{2}}$ and both orders α_D and α_R approach $-Z/2$. These extreme values for the variations of the orders are summarized in Table 1. Let us note that the experimental observation of a positive order versus the H_2 pressure for the hydrocarbon adsorption rate makes it possible to differentiate between a dissociative or a reactive chemisorption mechanism, in the case of negligible θ_C .

Another important deduction from this

model of competitive adsorption is the important variations of the order α when the coverage θ_H is varied, either by a pressure variation or by a temperature modification. Important negative values of α are predicted depending upon the Z value. Within the limits fixed in Table 1, the shape of the variation of α with θ_H will depend upon the heterogeneous system and more precisely upon the H_2 adsorption isotherms.

A temperature factor on the hydrocarbon adsorption rate (E_a) may also be deduced according to Eqs. (7) or (8) which is decomposed into:

$$E_a = E_1 + E_G$$

where E_1 characterizes the temperature factor of k_1 and E_G is the temperature factor of the functions G calculated, in a small temperature interval, according to:

$$G = G^\circ \exp - E_G/RT. \quad (13)$$

The values of the temperature factors E_G are calculated in Table 1, for the two limiting cases of θ_H . They are expressed in terms of enthalpy variation (ΔH) for H_2 adsorption, where $(\Delta H)_0$ denotes the enthalpy variation at zero coverage and $(\Delta H)_1$ at coverage near unity. Thus the

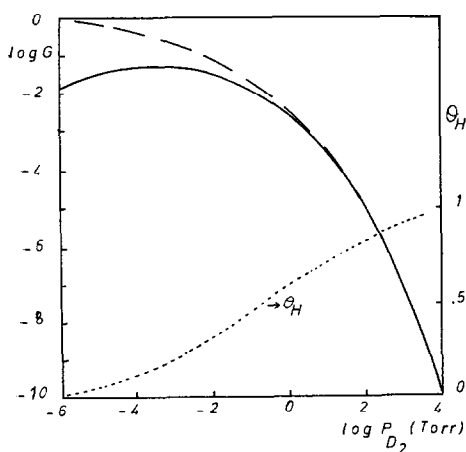


FIG. 3. Calculated values of G_R (solid line) and G_D (dashed line) from the D_2 adsorption isotherms on rhodium film (10) at 400°K, for $Z = 6$. The pressure is expressed in Torr (1 Torr = 133.3 N m⁻²).

TABLE 1

Calculated Values, for θ_H Approaching Zero or Unity, of the Function G_D and G_R [Eq. (9) or (10)], the Orders α_D and α_R [Eq. (11) or (12)], and the Temperature Factors [Eq. (13)]

$\theta_H \rightarrow 0$	$G_D \rightarrow 1$ $G_R \rightarrow K^{\frac{1}{2}} \cdot p^{\frac{1}{2}}$	$\alpha_D \rightarrow 0$ $\alpha_R \rightarrow 0.5$	$(E_G)_D = 0$ $(E_G)_R = \frac{1}{2}(\Delta H)_0$
$\theta_H \rightarrow 1$	G_D G_R	α_D α_R	$E_G = - (Z/2)(\Delta H)_1$

model also predicts large differences of the temperature factors according to the coverage θ_H and in particular of the apparent activation energy characterizing the hydrocarbon adsorption rate.

III. VARIATIONS OF THE ORDER α AND THE TEMPERATURE FACTOR E_G (SMALL θ_c)

We will now develop in more detail the two general effects predicted by the competitive adsorption model presented in this paper, namely, the variations with the coverage θ_H of the order α and of the temperature factor E_G . In order to keep this development as general as possible, we will use different Z values to calculate the hydrocarbon rate of adsorption [Eq. (7) or (8)] using numerical values of θ_H deduced from experimental hydrogen adsorption isotherms.

We have measured the adsorption-desorption isotherms of D_2 on Rh films, in an extended range of temperature and pressure (six powers of 10). The isotherms were found to obey a Roberts isotherm, based on a dissociative mobile adsorption with nearest neighbor repulsion (9). These measurements are presented elsewhere (10).

It has been shown (6) that the fraction of the metal surface not covered by hydrocarbon radicals behaves like a bare surface toward the adsorption equilibrium of H_2 . From these isotherms, we have calculated the functions G_R and G_D , in an extended pressure range, using different Z values. A typical result is shown in Fig. 3. From Figs. 2 and 3, one sees that the differences between the functions G_R and G_D

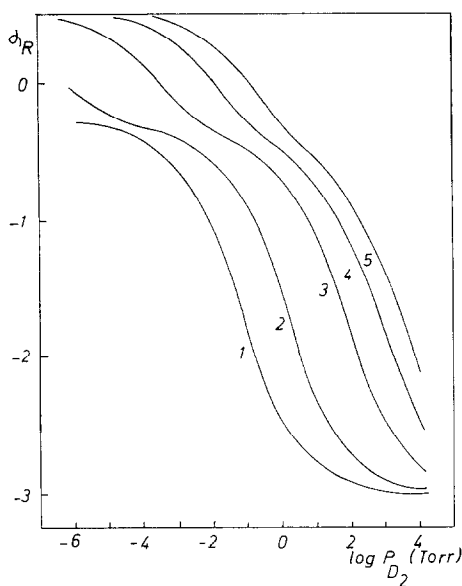


FIG. 4. Calculated values of the order α_R [Eq. (12)], for $Z = 6$, from the D_2 isotherms measured on Rh (10), at different temperatures: (1) 250°K, (2) 300°K, (3) 400°K, (4) 500°K, (5) 600°K.

are small as soon as the inhibiting term becomes important. Only for small θ_H values—where few kinetic results are obtained—are the functions more different from each other. For this reason in the development of the model, we will principally examine the function G_R .

One sees in Fig. 3 that G_R has a continuous curvature. Developing a small part of the curve, one easily verifies that within a small interval of pressure of a factor 2 to 4, as practically used in kinetic studies, the α_R variations are very small and within the accuracy of the experimental determination of the orders. It is thus possible to compare the values of α_R with the experimental order α_a affecting the hydrocarbon adsorption rate (section IV). In a pressure range as large as the one examined in Fig. 3, an important variation of α_R with pressure is calculated. The plot of α_R versus the logarithm of the hydrogen pressure, for $Z = 6$ at different temperatures, allows the important variation of the order α_R with pressure (Fig. 4) to appear clearly.

The extreme values of α_R , calculated in Table 1, are observed in this figure: For high θ_H , this value is obtained at high pressure and low temperature and for negligible θ_H it is obtained at low pressure and high temperature. The extended pressure range examined in Fig. 4 may be covered in practice when working on the same metal used under different forms (single crystal, ribbon, film, powder, or supported metal). The introduction of numerical values of θ_H , deduced from experimental observations, in Eqs. (9) or (10) makes it possible to calculate the dependence of the rate of hydrocarbon adsorption [Eq. (7) or (8)] on the hydrogen pressure corresponding to any particular experimental conditions.

In the same way, the temperature factor E_G [defined by Eq. (13)] affecting the adsorption rate according to $E_a = E_1 + E_G$ is calculated. In a temperature interval of about 50°K generally used in temperature effect measurements, the linear approxima-

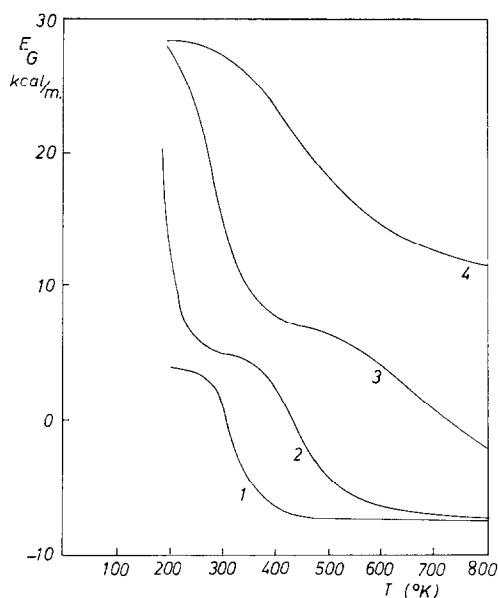


FIG. 5. Variations of E_G with temperature, computed at each temperature, for a small temperature variation of 5°, according to Eq. (13), for $Z = 6$: (1) 10^{-6} Torr, (2) 10^{-3} Torr, (3) 1 Torr, (4) 10^2 Torr.

tion may be assumed for the relationship between $\log G_R$ and $1/T$. In such a temperature range, a value for G_R° and E_G may be defined according to Eq. (13). We have plotted in Fig. 5 the values of E_G , calculated with a particular Z value of 6, for different pressures. Dramatic variations of E_G are recorded. In the pressure and temperature range where most of the kinetic studies on rhodium catalysts are performed (between 1 and 10^3 Torr, 300 to 600°K), the values of E_G range between -7.5 and 25 kcal/mole, depending upon the particular experimental conditions. Let us note that, on rhodium, the enthalpy variation $(\Delta H)_0$ at very low coverage, determined from the D_2 isotherms is -15 kcal/mole (10). Figure 5 predicts a greater E_G value as the pressure is greater, at constant temperature, and also smaller values of E_G as the temperature increases, at constant pressure.

IV. COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES

In order to check the model, we use here the isotopic exchange reaction as a trick to determine experimentally the hydrocarbon adsorption rate (R_a) by the measurement of the rate of exchange (R_e) at chemical equilibrium. The experimental dependence versus the D_2 pressure and temperature of the adsorption rate, measured by the exchange rate, may thus be compared with the calculated dependence according to the model.

For this purpose we have chosen, as an example, the CH_4 - D_2 exchange reaction on rhodium, mainly for four reasons:

- this system has been extensively studied in the literature and results are obtained over a large pressure range (10, 11, 15);
- it has been verified that these measurements are performed at chemical equilibrium (11, 12);
- the hydrocarbon coverage (θ_C) is known (13); and

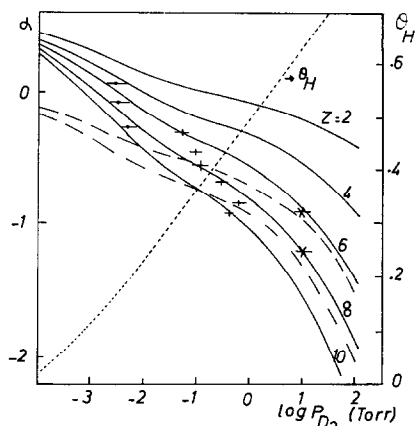


FIG. 6. Comparison, at 450°K, of the experimental values of the order α , measured for the CH_4 - D_2 isotopic exchange on rhodium films: \times , from Kemball (11); $+$, our results (15); \bullet , our results (10), with the calculated values for different Z values according to Eqs. (11) and (12) (α_R , solid lines; α_D , dashed lines).

—the adsorption-desorption isotherms of D_2 have been measured over a large range of temperature and pressure on this metal (10).

Thus for the CH_4 - D_2 isotopic exchange reaction on rhodium, we know the rate of exchange, the order with respect to the partial pressure, and the coverages θ_H and θ_C .

We will express the rate of exchange R_e by the usual kinetic equation in order to relate the order α_e to the inhibiting factor α_R due to the hydrogen coverage in Eq. (8).

$$R_a = R_e = k_e p_{D_2}^{\alpha_e} p_{CH_4}^{\beta_e} \quad (14)$$

where α_e and β_e are the empirical orders versus the deuterium and hydrocarbon pressure, respectively. At low hydrocarbon coverage, it is generally assumed that the order β is equal to unity, as discussed in the following section (V). For an isotopic exchange reaction, we may associate Eqs. (8), (10), (12), and (14) and derive with $K_G = k_e/k_1$:

$$G_R = K_R p_{D_2}^{\alpha_R} = K_G p_{D_2}^{\alpha_e}. \quad (15)$$

TABLE 2
Temperature Factors for CH₄
Chemisorption, on Rhodium

E _a	E _G ^R	E ₁	E _G ^D ^a	E ₁	H ₂ pressure (Torr)	Refer- ence
24	11	13	12	12	10	11
18.6	6.6	12	9.5	9	5.10 ⁻²	6
7.3	—	7.3	—	7.3	<10 ⁻¹⁰	16

^a E_G^R and E_G^D characterize the temperature factor affecting the function G (for Z = 7), respectively, for a reactive or a dissociative mechanism.

The experimental results available in the literature of the order α_e for the CH₄-D₂ exchange on rhodium are plotted in Fig. 6 together with the calculated values of α_R and α_D for different Z values. (The experimentally reported values of α_e range from 0 to -1.2 corresponding to D₂ pressures respectively in the 10⁻³ and 10 Torr ranges.) The experimental values of α_e , in a range of D₂ pressure extending over about four powers of 10 are in agreement with the calculated values of α_R for a single value of Z of about 7 ± 2 .

Temperature factors have been published for the same isotopic exchange reaction. In practice, for kinetic studies, this factor E_e is generally measured for the exchange rate and not for the rate constant. We have seen, in section III, that the temperature factor E_a for the hydrocarbon adsorption rate, which is measured by the exchange rate, is decomposed:

$$E_a = E_e = E_1 + E_G.$$

On rhodium, between 410 and 490°K, Kemball (11) reported 24 kcal/mole for E_e, in the 10 Torr range, while, in the 0.1 Torr range, work performed in this laboratory has given a value of about 18.6 kcal/mole (Table 2). The value of 18.6 kcal/mole, already reported by Frennet and Lienard (6), is slightly different from some values published previously (14, 15). This value is obtained from experiments where the hydrocarbon coverage θ_C is small, as considered in this part of the analysis of

the adsorption model. The other values are the averages of all experiments including those where θ_C is not negligible.

The observed variations of E_a = E_e are in good agreement with the variation of the temperature factor E_G calculated from the function G [Eq. (13)]. From these calculations, a difference of the values of E_G at 10 and 0.1 Torr is of 4.4 kcal/mole according to a reactive mechanism and of 2.5 kcal/mole according to a dissociative mechanism. The observed difference of 5.4 kcal/mole for the values of E_a would suggest that the methane chemisorption proceeds via a reactive mechanism giving a constant value of E₁, independent of temperature and pressure, which is in agreement with the assumption that E₁ is the activation energy of an elementary step.

On the other hand, in recent work performed on a clean rhodium tip by a combination of field emission and molecular beam techniques, Stewart and Ehrlich (16) measured an activation energy of (7.3 ± 1.5) kcal/mole for the adsorption of CH₄. Due to the technique used, these authors do not have to take account of a contribution of E_G and the question arises if the activation energy so determined is not what we called here E₁.

If the apparent activation energy of CH₄ adsorption E_a as measured from exchange reactions may reach values as high as 24 kcal/mole, the activation energy E₁ calculated using the adsorption model is much smaller and is closer to the value of 7.3 kcal/mole determined by Stewart and Ehrlich (16). Anyway, the experimental procedure used by these authors (non-isothermal system) to determine E₁ was so different from the one used here that the comparison between these values is not simple.

In the frame of a reactive mechanism, the adsorption model accounts for the observed differences both of the order α and of the temperature factors, obtained in different pressure ranges.

V. NONNEGLECTIBLE COVERAGES IN HYDROCARBON RADICALS

In the case where θ_C is not very small compared with unity, the factor θ_S^Z is dependent on the coverages θ_H and θ_C and is thus more complicated than the function G_R . For this reason, we will examine only the orders α_R and β and their variations versus respectively the hydrogen and the hydrocarbon pressure. It is necessary to develop completely Eq. (6) expressing the factor θ_S . Let us use the simplifying assumption used previously (13), namely, that the fraction of the metal surface not covered by radicals behaves like a bare surface toward the adsorption equilibrium of H_2 .

If θ_H^0 characterizes the H_2 coverage, in the absence of chemisorbed hydrocarbon radicals, the hydrogen coverage θ_H in the presence of chemisorbed hydrocarbon radicals is defined by:

$$\theta_H = \theta_H^0(1 - \theta_C). \quad (16)$$

Introducing this equation into Eq. (6):

$$\theta_S = (1 - \theta_H^0) \cdot (1 - \theta_C). \quad (17)$$

It is necessary to introduce in this equation numerical values for θ_C which are dependent on the metal and the hydrocarbon. We have chosen here the same system: CH_4 - D_2 on rhodium, for the reason examined in the preceding section. We have previously reported (13, 14) that for this system θ_C is given by:

$$\theta_C = \frac{K_1 \theta_H^0 p_{CH_4} / p_{D_2}^2}{1 + K_1 \theta_H^0 p_{CH_4} / p_{D_2}^2}. \quad (18)$$

This relation has been verified in a range of pressure ($3 \cdot 10^{-3}$ to 0.2 Torr) and temperature (150–225°C) corresponding to a range of θ_C , extending from a few percent to more than 0.9, that has been largely extrapolated in this paper. Even if Eq. (18) is not fully satisfied in the extrapolated upper range, it will be useful to obtain the numerical values in order to calculate θ_S .

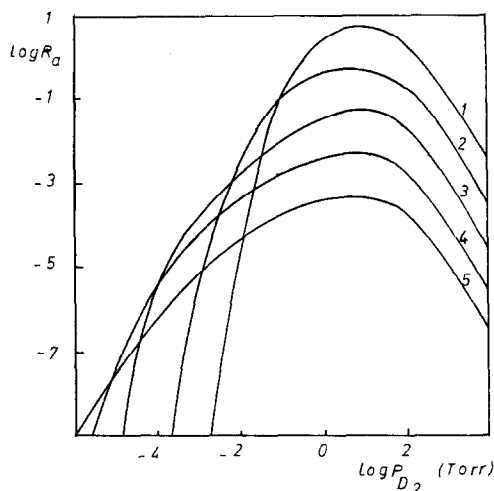


FIG. 7. Influence of the hydrogen pressure on the hydrocarbon rate of adsorption R_a , according to Eq. (19) ($Z = 6$) at constant ratios of CH_4/D_2 pressures: (1) 10^2 , (2) 10, (3) 1, (4) 10^{-1} , (5) 10^{-2} . The numerical values of θ_H^0 and θ_C are obtained on rhodium, at 400°K, for the CH_4 - D_2 system.

The rate of adsorption, according to a reactive chemisorption mechanism, is written, following Eq. (5):

$$R_a = k_1 \cdot p_{HC} \cdot \theta_H^0 (1 - \theta_H^0)^Z \cdot (1 - \theta_C)^{Z+1}. \quad (19)$$

The inhibiting effect on the rate is due to both factors $(1 - \theta_H^0)$ and $(1 - \theta_C)$, where θ_H is dependent only on the H_2 pressure whereas θ_C depends on both H_2 and hydrocarbon pressure [Eq. (18)]. Because of the large value of Z , large effects are to be expected for rather small values and small variations of θ_H^0 and θ_C . We have plotted the calculated values of the adsorption rate, according to Eq. (19), for different p_{CH_4}/p_{D_2} ratios (Fig. 7). One sees, in this figure, that at a constant temperature and a given value of D_2 pressure, the rates are very different according to the values of the pressure ratios.

At each pressure ratio there is a volcano-shaped curve with a flat maximum extending over a range of D_2 pressure of a few powers of 10. Corresponding to the avail-

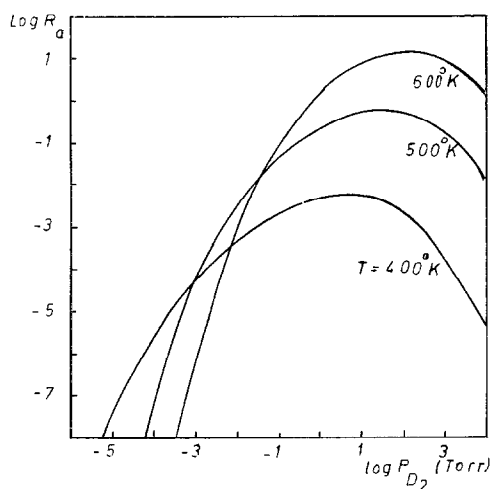


FIG. 8. Variation of the hydrocarbon adsorption rate [Eq. (19)] with the hydrogen pressure, plotted in logarithmic coordinates. The values are computed, for a constant pressure ratio of CH_4/D_2 of 0.1, at different temperatures, with the numerical values adopted in Fig. 7 ($Z = 6$).

able range of measurable rates allowed by the technique, useful experimental conditions may be found only in a restricted range of D_2 pressure and partial pressure ratio. Out of these limits, the rate rapidly becomes nonmeasurable.

The dramatic variation of the catalytic activity for the exchange, following the choice of experimental conditions, is clearly emphasized in Fig. 8 for a constant value of the ratio of hydrocarbon and D_2 pressures. In each curve, calculated at a constant temperature, two parts may be distinguished. On the right hand side of the figure, θ_C is negligible and the inhibiting effect is entirely due to the factor $(1 - \theta_H)^Z$. On the left hand side, the inhibiting effect is caused by the increase of the hydrocarbon coverage which is much more pronounced at elevated temperature.

In the same manner as we have previously calculated the order α_R versus the H_2 pressure, in the case of negligible θ_C , the orders α and β may be computed from Eqs. (14) and (19). Figure 9 represents the variations of the orders α_R and β with D_2

pressure for a constant pressure ratio. In the same figure, the calculated values of θ_H and θ_C have been plotted in order to define the surface conditions of coverages corresponding to the experimental parameters. The dashed line represents the value of α_R one should have for the same D_2 pressure, in the absence of hydrocarbon (see Fig. 4). Two parts may be distinguished in this figure from the point where the α curve deviates from the dashed line (pressure around 10^{-1} Torr in this case). At the right hand side of the figure, in the particular experimental conditions chosen here, where the methane-hydrogen pressure ratio is equal to unity and the temperature 400°K , θ_C remains very low. The approximation of θ_C being negligible, used in the first part of this paper, applies in this case. The order β versus the hydrocarbon pressure is always positive and equal to unity. Thus the only inhibiting factor is expressed by the negative value of α_R . The left hand side of Fig. 9 corresponds to the influence of θ_C on the different parameters and gives rise to an inhibiting factor due to $(1 - \theta_C)^{Z+1}$ in Eq. (19). Due to Eq. (18):

$$1 - \theta_C = \frac{1}{1 + K_1 \theta_H^0 p_{\text{CH}_4} / p_{\text{D}_2}^2}. \quad (20)$$

When θ_C approaches unity, this factor collapses to:

$$1 - \theta_C = \frac{p_{\text{D}_2}^2}{K_1 \theta_H^0 p_{\text{CH}_4}}. \quad (21)$$

This factor appears with the exponent $Z + 1$ in Eq. (19). Thus, a negative order β is to be expected and its most negative value would approach $-Z$ if Eq. (18) still applies for such an extrapolation. On the other hand, the order versus the H_2 pressure, contained in this factor $(1 - \theta_C)$, would rise to positive values, up to 2 ($Z + 1$). This contribution to the order α may be much more important than the one contained in the inhibiting factor

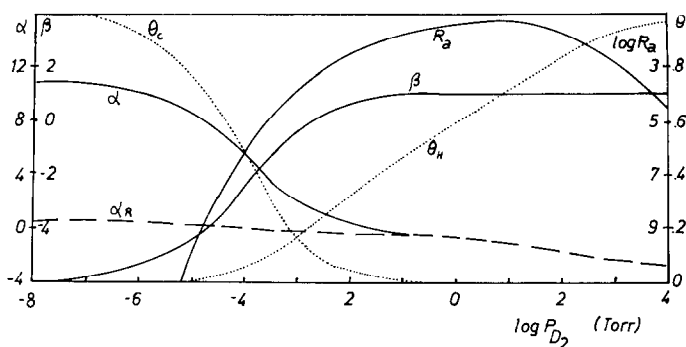


FIG. 9. Effect on the adsorption rate R_a and on the orders α and β of the coverages θ_H and θ_C according to Eq. (19). Temperature: 400°K, $Z = 6$, $p_{CH_4}/p_{D_2} = 1$, rhodium film.

$(1 - \theta_H^0)^Z$ and the resulting order α may become positive.

It is still interesting to distinguish two parts in the left hand side of Fig. 9 according to the values of the rate R_a in comparison with its maximum value. The range of measurable reaction rates scarcely exceeds two to three powers of 10, due to experimental limitations. Starting from the maximum value of R_a , this range of rates corresponds to values of θ_C not higher than 20%. The order β is still positive, but lower than unity, but the order α is also positive. Due to the experimental conditions chosen in the example of Fig. 9, this range is obtained for a D_2 pressure between 10^{-3} and 10^{-1} Torr, i.e., only two powers of 10.

When the D_2 pressure is lower than 10^{-3} Torr, the values of the rate R_a drop dramatically as θ_C increases. Therefore the time necessary to obtain the steady conditions between the gas and the adsorbed species becomes very long. This will be exemplified and discussed in another paper dealing with measurements performed on surfaces out of equilibrium with the gas phase. From the point of view of the catalytic activity, the phenomena generally described as a slow and important deactivation of the catalyst may be the evolution toward the equilibrium. These phenomena must not be confused with poisoning by coke. Figure 9 strikingly illustrates the

interrelation of the different parameters, viz. the rate of adsorption R_a , the orders α_R and β , and the surface coverages. The pressure range in which the different parts distinguished in this figure are observable is affected by the pressure ratio (Fig. 7) and the temperature (Fig. 8).

The particular values given in these figures are based on the hydrogen and methane coverages obtained on rhodium. The nature of both the hydrocarbon and the metal will affect these values, in particular by changing the equilibrium constant K_1 in Eq. (18), the dissociative scheme, the adsorption-desorption isotherms of hydrogen, and the value of Z .

VI. DISCUSSION

The Active Site

The adsorption of a molecule on a surface is governed by the product of the reactant pressure and a certain function of the second partner of the reaction, that is, the surface site. This surface site is often represented by an asterisk and is generally considered as identical for the adsorption of different species. Quite generally, in the literature (17, 20, 21), "potential sites" and "active sites for chemisorption" are not differentiated. Furthermore, no difference is introduced between the "active site for chemisorption" and the active site for a heterogeneous reaction. The hydrogen

chemisorption site is mostly used to measure the site density. As Maatman (17) recently pointed out, because it is usually difficult to know the active site density, most authors have by-passed the problem. Some attempts have been made to calculate this site density, mainly by the transition state theory, but direct measurements of the site density are rarely obtained. In some models, the sites are divided into different fractions for the chemisorption of different gases (18). Lih (19) has introduced an "unavailability factor" in order to define the fraction of sites not available for chemisorption of one reactant.

For the definition of the "active site for hydrocarbon chemisorption," the particular requirements that are taken into account, in this paper, are the consequence of the comparison of the size of the "potential sites"—defined by the crystallographic structure of the metal—to the size of the molecule to be adsorbed. Furthermore, let us remember that it is assumed that all potential sites are equivalent a priori for the adsorption of the two reactants, inducing competition for the same potential sites.

We restricted the model to the simplifying assumption of a uniform surface, which is probably not encountered for practical catalysts. Let us note, however, that Ross and Stonehart (22) have concluded that Rh and Pt surfaces behave uniformly towards the H_2 - D_2 equilibrium. It would be interesting to investigate other hypotheses more closely related to practical catalysts where the crystallites are small and exhibit different crystallographic planes. In the frame of the model, one may account for the presence of different crystallographic planes by a balanced sum of θ_s affected by different Z values.

The fraction of "active sites for hydrocarbon chemisorption" may be defined by the function θ_s^Z only if the adsorbed hydrogen atoms cannot be displaced from their adsorption site by collision with the

hydrocarbon molecule or with the corresponding intermediate complex, and also if the residence time on one site of the adsorbed hydrogen atom, if they are mobile, is large as compared with the lifetime of the intermediate complex leading to adsorption of a hydrocarbon molecule. The model shows clearly, by the use of the function θ^{sz} , the effect of a steric factor on the adsorption rate. Nevertheless, this function implicitly contains an energetic factor as appears by the analysis of the function G , because the function G is defined by the θ^{sz} that take the energetics of adsorption into account. In this way the model that is proposed here to define "the active site for chemisorption" may not be considered as purely geometric.

Variation of the Order of Reaction and Temperature Factor

The kinetic treatment presented in this paper relates the order α with respect to the D_2 pressure, for the adsorption rate of a hydrocarbon, measured by the isotopic exchange rate, to the value of the order α_R calculated using the D_2 adsorption isotherms according to Eq. (12) ($\theta_C \ll 1$). Figure 4 clearly emphasizes the importance of the variations of α_R due to θ_H as well as the continuous character of this variation. It is interesting to point out that a sole value of Z accounts for the whole variations of α reported in the literature, in the case developed in Fig. 6.

When the experimental conditions lead to surface coverages high enough to affect both factors $(1 - \theta_H^0)$ and $(1 - \theta_C)$ in Eq. (19), a simultaneous variation of α_R and β is predicted (Fig. 9). As β decreases and may become negative, the order α_R increases at the same time and may become positive. This observation has been reported in the literature, in particular for isotopic exchange reactions. For example, Tetenyi and co-workers (23), when measuring the isotopic exchange between D_2

and C_2H_6 on nickel, observe a simultaneous variation of both orders, from -1.1 to $+0.84$ for α and from $+1.1$ to $+0.6$ for β when varying the temperature.

Although the model proposed in this paper is easily verified with isotopic exchange reactions when the whole system is at chemical equilibrium, the question arises as to what extent it may be applied to other catalytic reactions. Since an adsorption step is always involved as the first step in a catalytic reaction and is thus significant for the overall rate of a reaction, a similar influence of the factor θ_s^Z is to be expected on the reaction rate for reactions other than isotopic exchange reactions.

The competition for adsorption of two different molecules on the same sites has already been proposed to account for the inhibiting factor versus the H_2 pressure. As reported, for example, by Kemball (3) about ethane hydrogenolysis: "The magnitude of the inhibition by H_2 is more than can be explained by competition between hydrogen atoms and the hydrocarbon for the surface of the catalyst." This conclusion is formulated because no difference is established between hydrogen and hydrocarbon chemisorption sites leading to values of Z not higher than 2 that fail to account for the amplitude of the observed effect. On the contrary, the use of a large Z value for the hydrocarbon—which is reasonable in view of the experimental adsorption results—enables us to define continuous variations of the order α and β with large amplitude (Fig. 9). This amplitude applied to the elementary step of adsorption is of the same importance as the one observed, for example, for hydrogenolysis reactions of saturated hydrocarbons (1, 2, 23).

The temperature factor that may be deduced from Fig. 8 clearly shows two different cases according to the range of experimental conditions. At the right hand side of the maximum rate, the temperature factor affecting the reaction rate corresponds to low θ_G values and is analyzed in

Section III. At the left hand side, the temperature factor decreases and may even become negative. Such a decrease has been reported (15) for the CH_4 adsorption rate on rhodium film, as measured by the CH_4 - D_2 exchange rate.

On the other hand, we have shown that the apparent activation energy of the hydrocarbon adsorption rate may be split into two terms $E_1 + E_G$ where E_G , the temperature factor affecting the function G , varies with pressure and temperature (Fig. 5). It seems reasonable to expect such variations of the temperature factor affecting the isotopic exchange reactions to occur according to the range of hydrogen pressure where these measurements are performed. Such variations of the order α and of the apparent energy factor are observed for an adsorption elementary step as measured by the CH_4 - D_2 exchange presented here. Thus such variations do not necessarily imply a modification of reaction mechanism or a change of the rate-determining step. Therefore it seems very improbable to determine a reaction mechanism, for a heterogeneous reaction with $Z > 2$, only by the determination of the orders and of the apparent activation energy and their variations.

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