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Hydrogenation of Ethylene on Metallic Catalysts

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The National Standard Reference Data System is a Government-wide effort to provide for the technical community of the United States effective access to the quantitative data of physical science, critically evaluated and compiled for convenience, and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology.

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The NSRDS-NBS series of publications is intended primarily to include evaluated reference data and critical reviews of long-term interest to the scientific and technical community.

A. V. Astin, Director.
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Hydrogenation of Ethylene on Metallic Catalysts
Juro Horiuti and Koshiro Miyahara

Reaction rate data for the catalyzed hydrogenation of ethylene, primarily in the presence of unsupported metallic catalysts, are critically reviewed. Reaction mechanisms are discussed in detail, and a statistical mechanical treatment of the reaction is given, according to the generalized theory of reaction starting from the well-known procedure of Glasstone, Laidler, and Eyring. Data for single-element catalysts and alloys are included and interpreted, as are data illustrating differences due to the physical form of the catalyst (film, foil, wire, powder, and some supported systems). Problems are discussed concerning reproducibility of experimental results over repeated runs, and as a function of catalyst pretreatment. The data is analyzed in 29 graphs and 29 tables, some of which are very extensive. The bibliography includes 141 references.

Key Words: Critical data, ethylene, hydrogenation, metallic catalysts, reaction mechanisms, reaction rates.

1. Introduction

The catalyzed hydrogenation of ethylene in the presence of metallic catalysts, especially nickel, has been a subject of intensive investigations, as a prototype of catalyzed hydrogenations of the sort, since its discovery by Sabatier and Senderens [1].1 The catalyzed hydrogenation was found to be associated with parahydrogen conversion [2], which turned out to be a useful profile of the reaction. In 1932 deuterium appeared as a powerful tool for revealing further profiles of the reaction. These profiles were traced in the early days by following the parahydrogen content as well as deuterium content in hydrogen by means of the thermal conductivity method developed by Farkas, Eley, and others [3, 4]; the deuterium content was at that time also determined by measuring the density of water to which the hydrogen of samples in question was converted [5]. The research work has been substantially facilitated since 1950 when the infrared and mass spectrometers came into daily use for investigations of adsorbed states and for the determination of deuterium content as well as the relative amounts of different deuterocompounds.

Notwithstanding this progress in experimental techniques, there remained a serious, unresolved difficulty in exploring the catalyzed hydrogenation of ethylene. Rates of the catalyzed hydrogenation as well as of the associated reactions decline markedly and apparently uncontrollably on repetition of the runs over the same sample of catalyst. Few data are thus available, as they stand, for analysis of the catalyzed hydrogenation. It has been found, so far, that the decline in rate is caused, not only by impurities in the reactants, e.g., mercury vapor, or in catalysts which have escaped their pure preparation, but also by products of a side reaction of ethylene, i.e., its polymerization or dehydrogenated adsorption on the catalyst.

The character of catalyzed hydrogenation depends further on the form and condition of the catalyst, i.e., differs for evaporated films, powders, wires, and plates or catalyst supported on some dispersed medium, e.g., alumina or silica gel. For instance, ethylene is polymerized over nickel catalyst supported on kieselguhr but not over unsupported nickel powder. Moreover, some alloy catalysts are considerably more active than either of their components.

Films of various metals evaporated on glass walls were introduced by Beeck [6] in 1945 for the investigation of catalyzed hydrogenation. The evaporated film had been accepted at that time as the cleanest possible surface, and this piece of work hence raised lively hopes of correlating the catalytic activity and the characteristics of catalyst metals in view of the associated difficulty mentioned above. For this reason, more emphasis should be laid on unsupported catalysts than on supported catalysts, which might be associated with additional complications.

We deal in this monograph mainly with the catalyzed hydrogenation in the presence of unsupported catalysts, especially of evaporated films of pure metals, and shall refer to supported catalysts just for reference. Experimental data on the decline of catalytic activity are first reviewed, describing relevant methods of the experimental investigation. Summaries are then given of the observed kinetics of the catalyzed hydrogenation and of the different phases of profiles of the reaction. Attempts to formulate a mechanism of the phenomena in question are next reviewed, and finally the experimental results are accounted for systematically on the basis of the associative mechanism [7-11].

References are often made to the optimum, i.e., the point of maximum rate of the catalyzed hydrogenation with respect to temperature at given partial pressures of ethylene and hydrogen. For the sake of clear and concise presentation, protium and deuterium atoms are denoted by H and D when they are discriminated. When they are not, either of
2. Reproducibility of Observations

The catalytic activity declines, as mentioned in the introduction, when a run of catalyzed hydrogenation of ethylene is repeated with the same sample of metallic catalyst. This effect is especially pronounced in case of unsupported catalysts. It is prerequisite for a reasonable study of the catalyzed hydrogenation to elucidate the nature of this decline. The present knowledge about it is reviewed in the following, in terms of experimental results and comments upon or inference from them; except that the second figure of the mark is replaced by a Roman capital letter, e.g., as 2.A, 2.D.1, etc., and comments or inferences are denoted similarly except that the second figure of the mark is replace d by a Roman capital letter, e.g., as 2.A, 2.D.1, etc.

2.1. Beeck [6] used metal films evaporated on a glass wall kept at $-183^\circ$ C and showed that, when the films were contacted preliminarily with ethylene, the rate of the catalyzed hydrogenation at 0 $^\circ$C decreased, on the metals indicated in parentheses, to 10 percent (Ta), 20 percent (W), 40 percent (Ni), or 95 percent (Pt, Rh) of the rates without the preliminary contact in the respective cases.

2.2. The rate of the catalyzed hydrogenation depends on the sequence in which reactant gases are introduced over the catalyst. Toyama [12] observed the rates of three consecutive runs conducted over a sample of nickel powder reduced from its oxide (termed reduced nickel in what follows), introducing in the first run hydrogen and ethylene simultaneously, in the second hydrogen in advance and in the third ethylene in advance; each run was conducted after evacuating the product of foregoing run. In the second and third runs, the catalyst was left overnight at room temperature in contact with the reactant gas introduced in advance before the other was admitted. The second run gave a rate higher than the first, while the third run gave a rate lower than both the first and second.

2.3.1. The following qualitatively coincident results were obtained when admitting repeatedly small doses of ethylene over films of Ni [6, 13, 14], Pd [15], W [16], or Ir [17] evaporated on a glass wall of a vessel kept at room temperature [18]. No gas whatever was detected inside the vessel until the total sum, $Q$, of the number of molecules of ethylene admitted exceeded a certain value $A$, when ethane alone began to appear with further increase of $Q$. When $Q$ exceeded a certain other value $B (A)$, ethylene began to appear in the gas phase. Now, both the number of ethane molecules and the number, $Q'$, of adsorbed ethylene molecules ($Q$ minus the total number of ethylene and ethane molecules in the gas) increased until $Q$ exceeded a certain third value, $C (> B)$, beyond which both $Q'$ and the number of ethane molecules remained, respectively, constant.

Number $A$ corresponded to 30 percent coverage of the surfaces at room temperature provided that the number of hydrogen atoms adsorbed at $-183^\circ$ C [13] equaled the number of their adsorption sites and each ethylene molecule occupied two such sites. The number of ethane molecules formed at $Q = B$ approximately equaled $Q'$ at that point. The above results are shown in figure 1 [18], where the respective values, of $Q$, $A$, $B$, and $C$, are indicated with vertical broken lines.

2.3.2. Mckee [19] found by the use of reduced nickel of 1.41 m$^2$ BET area that the number $A$ in 2.3.1 increased with fall of temperature from
2 × 10⁻¹⁷ C₂H₄ molecules at −22 °C to 13 × 10⁻¹⁷ C₂H₄ molecules at −78 °C, which corresponded to the increase of coverage from ca. 3 to 20 percent of the surface.

2.4. Ethylene in contact with a metal film left on it compouds of a composition which varied with the temperature during contact, the extent of evacuation after contact and the sort of metal. The composition of the compounds was C₂H₆,₈ at 25 °C [14] and C at 170 °C [13] on nickel film and C₂H₅,₃,₈ at 100 °C on Ir [17]. This process is called dehydrogenated adsorption and the compound termed adsorbed complex in what follows.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temp. °C</th>
<th>Reaction time, min</th>
<th>% Removed</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>23</td>
<td>1</td>
<td>60</td>
<td>Beeck [14]</td>
</tr>
<tr>
<td>Rh</td>
<td>23</td>
<td>long</td>
<td>100</td>
<td>Beeck [14]</td>
</tr>
<tr>
<td>Pd</td>
<td>0</td>
<td>5</td>
<td>50 - 60</td>
<td>Stephens [15]</td>
</tr>
</tbody>
</table>

The product of the treatment in case of Rh was almost exclusively ethane, while in case of Ni 90 percent of the product were saturated hydrocarbons of carbon number 4 to 8.

2.5. The adsorbed complex can be removed from the surfaces by hydrogen treatment around room temperature as shown in table 1. The adsorbed complex is not so readily removed from nickel as it is from iridium. The removal from nickel is, on the other hand, appreciably slower than the catalyzed hydrogenation on the same metal, by a factor of several hundreds [13]. This aspect contrasts with that of preadsorbed acetylene which cannot by hydrogenated off nickel at 23 °C, whereas 40 percent of it can be hydrogenated off rhodium at the same temperature in 1 hr [14].

2.6. Thomson and Wishlade [20] saturated an evaporated nickel film with radioactive ¹⁴C₂H₄ at 20 °C, evacuated it subsequently a little while and followed its removal by different treatments with radioactivity measurements. 2 percent of the radioactivity were thus lost by contacting the saturated film with nonradioactive ethylene, another 10 percent were lost by allowing this film to catalyze the hydrogenation of 10 cm Hg nonradioactive ethylene with equimolar hydrogen, and the radioactivity still remaining was further diminished by 30 percent by a hydrogen treatment. The 58 percent radioactivity thus left could not be reduced further when allowing the film once again to catalyze the hydrogenation of nonradioactive ethylene of partial pressure around 9 cm Hg with equimolar hydrogen.

These results contrast with those obtained by Cormack, Thomson, and Webb [21] for alumina-supported catalysts of Ni, Rh, Pd, Ir, and Pt saturated with ¹⁴C₂H₄ which lost, respectively, 36.5 percent (Pd), 76 percent (Ni), 77.5 percent (Rh), 84 percent (Ir), and 93.5 percent (Pt) of the radioactivity as they catalyzed the hydrogenation of nonradioactive ethylene.

2.7. A rapid exchange between ethylene-d₄ and light ethylene was observed by Miyahara [22] on a freshly evaporated nickel film even at −23 °C, contrary to a negative result reported by Conn and Twigg [23]. Flanagan and Rabinovitch [24], tracing the experiment of Conn and Twigg [23], were able to observe an exchange reaction at 60 °C by using much more nickel wire than Conn and Twigg.

2.8. Results given next show that the dehydrogenated adsorption of ethylene occurs even in the pres-
ence of hydrogen, i.e., under the normal condition of the catalyzed hydrogenation.

2.8.1. Jenkins and Rideal [13] observed the catalyzed hydrogenation of 20 mm Hg ethylene with equimolar hydrogen at 20 °C over evaporated nickel film for 10 min, evacuated the product and repeated the experiment consecutively. The rates of total pressure decrease found were 3.50 mm Hg/min in the first run, 1.90 mm Hg/min in the second run and 1.30 mm Hg/min steadily in the third and several subsequent runs. When they contacted the evaporated film preliminarily with ethylene, the steady value (1.30 ~ 1.60 mm Hg/min) was obtained throughout from the first run on.

2.8.2. The catalytic activity of metal films is appreciably reduced by impurities, especially mercury [25] and oxygen [22, 27]; the former also diminishes the adsorption of hydrogen on metal films. Mercury is liable to be introduced into a reaction vessel along with reactant gases [26] and in consequence accumulates on the metal film. A trace of oxygen amplifies the decline of catalytic activity when the run of catalyzed hydrogenation is repeated [22], creating, besides, an induction period as seen in figure 2(a) [22]. Figure 2(b) [22] shows that a nearly reproducible rate of hydrogenation is secured by removing the impurities.

2.8.3. Miyahara [26] determined, under the pure conditions attained in 2.8.2, the quantities, \( Q_E \) and \( Q_H \), of ethylene and hydrogen adsorbed, respec-

![Figure 2(a)](image)

**Figure 2(a).** The courses of repeated hydrogenations of ethylene with ca. equimolar hydrogen contaminated with oxygen at 50 °C over evaporated nickel film [22]; mercury excluded.

**Table 2.** Number of moles of ethylene (\( Q_E \)) and hydrogen (\( Q_H \)) adsorbed on evaporated nickel films in course of hydrogenation of ethylene by equimolar hydrogen [26].

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Surface of evaporated Ni film</th>
<th>( Q_E \times 10^8 )</th>
<th>( Q_H \times 10^8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>F</td>
<td>17.1</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>16.8</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>15.4</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>17.6</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>13.1</td>
<td>1.7</td>
</tr>
<tr>
<td>101</td>
<td>F</td>
<td>15.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>16.0</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>S*</td>
<td>9.8</td>
<td>-8.8</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>11.6</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>9.5</td>
<td>0.5</td>
</tr>
<tr>
<td>145</td>
<td>F</td>
<td>9.6</td>
<td>-9.6</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>11.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>10.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

A given run of catalyzed hydrogenation were conducted over nickel films evaporated on the wall, kept at 200 °C, of a reaction vessel of 120 cm³ capacity, by admitting the reactant gas mixture into the reaction vessel. Such a run was followed in some cases by another on evacuation of the product of the foregoing run. The films thus used were kept at 500 °C in H₂ of few mm Hg for an hour, evacuated at the same temperature to \( 10^{-7} \) mm Hg and then coated with new evaporation of nickel, and one or two runs were similarly conducted over the newly coated films. The sur-
face of a film either freshly evaporated or freshly coated is signified by F, and that used once as above by S; C refers to a surface used several times consecutively at 200 °C, each such run was preceded by an evacuation at the same temperature, until the rate decreased from that over F by a factor of several tens. 

Q_E and Q_H were determined, as the excess of the number of moles of ethylene and hydrogen initially introduced into the reaction vessel over that of ethylene and hydrogen remaining in gas plus that combined in ethane, on the basis of the experimental result [61] that the adsorption of ethane is inhibited by ethylene. Gas mixtures were sampled for Q_E and Q_H determinations immediately after the measurement of the initial rate of total pressure decrease, which lasted a few seconds just after the introduction of the reactant gas mixture, except in a run marked with asterisk; gas mixture was sampled in the latter case toward the end of the run, when the total pressure decreased no longer perceptibly.

8.2. The dehydrogenated adsorption of ethylene in 10 min. a freshly evaporated film to ethylene at 200 °C for bidened surface” [13] which was obtained by exposing those once used for a run of hydrogenation, and C refers to surfaces used several times consecutively at 200 °C, until the end of the run, when the total pressure decreased no longer perceptibly.

2.9. The following further data on the dehydrogenated adsorption of ethylene are available.

2.9.1. Miyahara [26] observed the distribution of deuterium in ethylene and hydrogen in the initial stage of catalyzed deuteration of light ethylene as shown in table 3 under the pure conditions established in 2.8.2. The optimum temperature for an equimolar mixture of ethylene and deuterium of 0.1 mm Hg initial total pressure was found 50 °C in this case. \(^{1}H_2\) was evolved in case of F but not of S at temperatures below the optimum (−45 and −23 °C), whereas \(^{1}H_2\) was evolved above the optimum in both the cases.

2.9.2. Formation of ethane from ethylene caused by its dehydrogenated adsorption on reduced nickel was almost suppressed, according to Hirota and Teratani [28], by a preliminary adsorption of CO, which covered 30 percent of the BET area of the reduced nickel, whereas the same preliminary adsorption on the same catalyst was almost ineffective with respect to catalyzed hydrogenation.

<table>
<thead>
<tr>
<th>React. temp. °C</th>
<th>State of film surface</th>
<th>Deuterated % C(_2)H(_4)</th>
<th>Deuterated % C(_2)H(_4) min(^{-1})</th>
<th>Relative amounts</th>
<th>Deuterium atom fraction in</th>
<th>C(_2)H(_4)</th>
<th>H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>F</td>
<td>35</td>
<td>74.3</td>
<td>44</td>
<td>36</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>20</td>
<td>56.9</td>
<td>64</td>
<td>30</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>F</td>
<td>40</td>
<td>110.3</td>
<td>45</td>
<td>38</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>43</td>
<td>98.0</td>
<td>66</td>
<td>28</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>32</td>
<td>F</td>
<td>45</td>
<td>129.7</td>
<td>49</td>
<td>34</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>41</td>
<td>107.1</td>
<td>40</td>
<td>36</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>75</td>
<td>F</td>
<td>40</td>
<td>102.1</td>
<td>21</td>
<td>35</td>
<td>28</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>38</td>
<td>97.0</td>
<td>29</td>
<td>38</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>110</td>
<td>F</td>
<td>18</td>
<td>54.0</td>
<td>16</td>
<td>32</td>
<td>32</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>21</td>
<td>50.2</td>
<td>21</td>
<td>29</td>
<td>37</td>
<td>10</td>
</tr>
</tbody>
</table>

"Deuterated percent C\(_2\)H\(_4\)," in the third column represents the percentage decrease of the sum of the numbers of moles of C\(_2\)H\(_4\) = \(\sum E_n\) from the sum at the beginning of the catalyzed hydrogenation, when C\(_2\)H\(_4\) is practically exclusively C\(_4\)H\(_4\). F denotes the surface of freshly evaporated film and S that used once for a run; cf. legend of table 2.
2.E.1. The dehydrogenated adsorption will lead to an evolution of \(^1\text{H}_2\) as in 2.9.1, if it consists simply of a release of hydrogen molecules into the gas. If it supplies, on the other hand, hydrogen in an intermediate state of the catalyzed hydrogenation, e.g., \(\text{H}(a)\) directly, then \(^1\text{H}_2\) will also appear in the gas as a product of conversion of this intermediate, unless steps consuming it are rapid enough to suppress the conversion, e.g., to inhibit the recombination of the \(\text{H}(a)\)'s by lowering their activity. It follows now from the observed absence of \(^1\text{H}_2\) evolution over \(S\) surfaces below the optimum that dehydrogenated adsorption occurs neither under immediate release of hydrogen molecules nor to evolve them through the intermediate state. Under the latter conditions the dehydrogenated adsorption, if any, may be traced by a deviation from the stoichiometry of normal hydrogenation; the total pressure would not then decrease, in case of catalyzed hydrogenation of ethylene with excess hydrogen in a constant volume, as far as corresponding stoichiometrically to the exhaustion of the ethylene. On account of absence of such a deviation (cf. 4.1), the dehydrogenated adsorption is concluded to be practically suppressed on \(S\) surface.

The validity of the above arguments rests upon the postulate that the hydrogenation and the dehydrogenation of ethylene are exclusively reactions occurring on metallic catalysts. This is assumed throughout in what follows.

2.E.2. It follows from the preferential inhibition of dehydrogenated adsorption observed in 2.9.1 that the two reactions do not occur on the same site, insofar as both reactions on their respective sites are admitted to be blocked solely by the product, adsorbed complex, of dehydrogenated adsorption. It is induced from this conclusion and 2.9.2 that the nickel catalyst's surface consists of two parts, (d) and (h), which catalyze the dehydrogenated adsorption and hydrogenation, respectively; the former remains poisoned by adsorbed complex if it is on an \(S\) surface below the optimum (2.9.1) and also by \(\text{CO}_2\) (2.9.2) [28].

2.10. Experimental results are reviewed next from which diverse theories are derived on the state of catalyst's surface.

2.10.1. Crawford, Roberts, and Kemball [29] annealed nickel films, evaporated on glass walls kept at \(-195\,^\circ\text{C}\), at different temperatures from 0 to 400 \(^\circ\text{C}\) and observed their activity in catalyzing both the hydrogenation with \(^1\text{H}_2\) and the deuteration of light ethylene. The rate of hydrogenation with \(^1\text{H}_2\) decreased when the runs were repeated on the same surface but their rates per unit BET area remained constant for a definite annealing temperature and decreased only with rise of the annealing temperature. Both the activation heat of hydrogenation with \(^1\text{H}_2\) and the deuterium distribution in the ethane formed by the deuteration remained unchanged throughout [29].

2.10.2. The BET area referred to in 2.10.1 decreased by a little over 40 percent when contacting the film with ethylene as shown in table 4, irrespective of the annealing temperature.

<p>| Table 4. Change of BET area of evaporated nickel film by adsorption of (\text{C}_2\text{H}_4) at (-80,^\circ\text{C}) [29] |
|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Annealing temp. (^\circ\text{C})</th>
<th>Volume of (\text{C}_2\text{H}_4) adsorbed (\text{cm}^3) (S.T.P.) (\times 10^3)</th>
<th>BET area (\text{cm}^2 \times 10^{-2})</th>
<th>(\overline{\mathcal{A}}_1)</th>
<th>(\overline{\mathcal{A}}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>23.2</td>
<td>12.8</td>
<td>0.55</td>
</tr>
<tr>
<td>25</td>
<td>12</td>
<td>19.6</td>
<td>11.0</td>
<td>0.56</td>
</tr>
<tr>
<td>100</td>
<td>8</td>
<td>13.4</td>
<td>7.8</td>
<td>0.58</td>
</tr>
</tbody>
</table>

2.10.3. Campbell and Duthie [30] found that the BET area of nickel film decreased to the same extent when allowing the film preliminarily to adsorb \(\text{N}_2\) or \(\text{O}_2\), or \(\text{Hg}\).

2.10.4. Jenkins and Rideal [13] found that nickel surface covered by acetylenic complex and preliminarily evacuated, evolved hydrogen, amounting to be equimolar with the acetylenic complex, as temperature was raised gradually from 20 \(^\circ\text{C}\) up to 170 \(^\circ\text{C}\) in a closed space. On cooling it down to room temperature the evolved hydrogen was absorbed, but not completely.

2.10.5. Foss and Eyring [27] found the rates of consecutive runs of hydrogenation to be reproducible on a carbided nickel surface\(^3\) when this was treated with 5 cm Hg hydrogen at 250 \(^\circ\text{C}\) for 30 min before every run. The reproducible rate thus established was about one half that on a freshly evaporated film but was several tens of times larger than that on a carbided surface (see footnote 3) not treated with hydrogen.

2.10.6. A preliminary contact of the catalyst in 2.10.5 with ethylene retarded the hydrogenation in the beginning of its course, but did no longer so several minutes later [27].

2.F. Kemball et al. [29], attributed the decrease of BET area in 2.10.1 and 2.10.2 to a sintering of the catalyst's surface caused by the heat of hydrogenation or adsorption but did not take into account the effect of adsorbed complex. Campbell and Duthie [30] referred the effect, on the basis of 2.10.3, to the adsorbed complex, which was suggested to decrease the quantity of krypton adsorbed in BET measurements, thus simulating a reduction in BET area, although their reason why it should decrease the adsorption of krypton does not appear clear.

Result 2.9.1 speaks definitely against sintering as responsible for the rate decrease. The decrement

---

\(^1\)The two parts may be attributed to different lattice planes exposed on the catalyst surface; cf. 2.11.1.

\(^2\)Cf. 2.8.3.
of the rate between F and S in 2.9.1 becomes monotonously smaller with rise in temperature; it falls from 64 percent at \(-45^\circ\)C to 8 percent at 110 \(^\circ\)C, as seen in table 3. If sintering was responsible for the decline in rate, its extent and in consequence the rate decrement ought to be the greater, the higher the reaction temperature and the greater the rate of heat evolution, i.e., the reaction rate times reaction heat per mole. The reaction rate increases from \(-45\) to 32 \(^\circ\)C monotonously by a factor of more than ten, as seen in the same table, and the reaction heat per mole, though slight, increases as well. The decrement of rate should hence increase monotonously with rise of temperature. This is quite contrary to the experimental result, and the sintering can, therefore, not be responsible for the decrease in rate.

It appears, however, necessary to regard 2.10.1, 2.10.2, and 2.10.3 with caution, in view of 2.8.2, because of a possible intrusion of mercury, which has been positively evidenced under similar experimental conditions [31].

Jenkins and Rideal [13] attributed the result of 2.10.4 to the migration of carbon atoms from the surface into the bulk of metal so that a clean metallic surface, available for adsorption of hydrogen, was regained. However, results 2.10.5 and 2.10.6, backed by 2.5 and 2.6, indicate the substantial effect of hydrogen in recovering a catalytically active metallic surface from the carbided surface. These results lead to the view, amplifying upon 2.E.2, that the treatment before every run in 2.10.5 released part (h) from the poisoning due to the foregoing run, leaving part (d) steadily poisoned so as to secure the reproducibility of the results.

2.11. The following results might provide further informations relative to the dual catalyst surface advanced.

2.11.1. Cunningham and Gwathmey [32] observed the activity of individual lattice planes of nickel single crystal in catalyzing the hydrogenation of ethylene from 50 to 200 \(^\circ\)C, preliminarily treating the lattice planes with hydrogen at 500 \(^\circ\)C. They found that \((321) > (111) \text{ and } (110) > (100)\) as shown in figure 3, where the Miller indices represent the relevant activities. They also observed that lattice planes other than (111) and (100) lost their metallic luster by contact with ethylene at 450 \(^\circ\)C, which they termed carbon deposition.

2.11.2. Farnsworth and Woodcock [33] observed effects of heating in high vacuum, bombardment with \(\text{Ar}^+\) ions etc., on the activity of nickel and platinum plates in catalyzing the hydrogenation of ethylene with equimolar hydrogen at 0.1 to 1.0 mm Hg total pressure. The results are shown in table 5, where the catalytic activity is given in terms of the first order rate with respect to hydrogen partial pressure. The table shows the enhanced activity due to heating in high vacuum and bombardment in treatments (1) and (3), which is all but lost again by annealing at 550 \(^\circ\)C as seen in treatments (2), (4), and (5).

### Table 5. Rates of hydrogenation of ethylene over catalysts of diverse pretreatments [33].

<table>
<thead>
<tr>
<th>Pretreatments</th>
<th>Activity (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni catalyst</td>
<td>Pt catalyst</td>
</tr>
<tr>
<td>(1) Heat-treated and quenched........</td>
<td>45 ± 5</td>
</tr>
<tr>
<td>(2) Heat-treated, quenched, and annealed...</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>(3) Bombarded with positive argon...</td>
<td>700 ± 100</td>
</tr>
<tr>
<td>(4) Bombarded, and annealed..........</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>(5) Bombarded, heat-treated, quenched, and annealed...</td>
<td>7 ± 2</td>
</tr>
</tbody>
</table>

Approximate temperature of: heat-treatment of nickel, 850; annealing nickel, 500 to 550 \(^\circ\)C; heat-treatment of platinum, 1050 to 1350; annealing platinum, 700. Quenching was always preceded by an induction heat-treatment of at least one-half hour to insure uniformity in surface structure of the catalyst preceding the quenching. The quenching was accomplished by suddenly stopping the induction heating current and allowing the catalyst to cool in vacuum to room temperature.

Farnsworth and Woodcock attributed the enhanced activity to lattice defects created by the treatments (1) and (3) in table 5 [33].

2.G. The following are general conclusions regarding the reproducibility of observations on the catalyzed hydrogenation.

The decline of catalytic activity, though considerably reduced by purification of reactants, persists, even in the case where purest reactants are used, which is attributed to a poison produced by dehydrogenated adsorption of ethylene, i.e., adsorbed complex, termed acetylenic complex [6], carbide [13], coke [34], or polymer [34]. It is induced from experimental results that the catalyst surface consists of two parts: one part (d) causes the dehydrogenated adsorption of ethylene, is readily poisoned by adsorbed complex and is not readily recoverable; the other part (h) catalyzes the hydrogenation, is but slowly poisoned and readily recoverable.

The carbided surface [13] shows no decline of catalytic activity at all, which might hence appear pertinent to the investigation of the catalyzed hydrogenation. The carbided surface might, however, be substantially degenerated from the genuine metallic surface, on account of the considerable differences in their properties as discussed in section 8. To the best of our present knowledge it appears that catalyzed hydrogenation on a genuine metallic surface is observed with an S surface below the optimum, provided that the reactant gases are rigorously freed from impurities, especially mercury and oxygen. Above the optimum, where hydrogenation and dehydrogenated adsorption are simultaneously going on, it would be necessary for the elucidation of the catalyzed hydrogenation to find a reasonable way to analyze the observed overall reaction with respect to the two individual reactions.
Much more work will be necessary before hydrogenation which is associated with dehydrogenated adsorption can be reasonably discussed on the level of lattice planes and lattice defects of catalysts.

3. Catalytic Activity of Various Pure Metals and Alloys

The rate of catalyzed hydrogenation of ethylene is very sensitive to the preliminary treatment of the catalyst metal, apart from the working conditions as reviewed in 2, and this treatment must be precisely specified, should the informations gained be of any significance. Informations on catalytic activities which are more or less significant in this sense are reviewed next, if not immediately assignable to intrinsic properties of the catalyst material.

3.1. Beeck observed the activity of evaporated films of various metals in catalyzing the hydrogenation of ethylene comparatively at 0 °C [6, 14]. The rates

FIGURE 3. Activities of crystal planes of Ni in catalyzing the hydrogenation of ethylene [32].
were strictly proportional to hydrogen pressure and independent of ethylene pressure, according to Beeck, although no data are given [6, 14] of their absolute magnitude. The results are shown in figure 4 and table 6 in terms of activity $\lambda$, percent $d$-character of metallic bonds and adsorption heat of reactants on the metals. The quantity $\lambda$ is the ratio between the first order rate with respect to hydrogen per unit BET area on a given metal and that on rhodium. Figure 4(a) shows that the activity increases generally with the percent $d$-character of metals and that the activity of a Ni film with the preferred orientation of the (110) lattice plane parallel to the glass base, marked with (110), is ca. four times as large as that of a Ni film with random orientation of crystallites. Figure 4(b) shows that Rh is the metal at the maxima of both the activity and percent $d$-character and at the minima of the adsorption heats of both ethylene and hydrogen.

The results obtained by Beeck [6, 14] have been commented upon from a variety of aspects as below.

3.1.1. Phenomenologically, a linear relation was advanced by Schuit [35] between $\log_{10} \lambda$ observed by Beeck [6, 14] and the product of percent $d$-character and the valency of metals according to Pauling [36], as shown in figure 5.

3.1.2. The closest distance between two Rh atoms is 2.69 Å in its f.c.c. crystal of lattice constant 3.80 Å indicated in figure 4(b). This closest distance is nearly coincident with the ideal metal-metal distance, 2.73 Å, for the associative adsorption of ethylene without strain as calculated by Twigg and Rideal [37] assuming the carbon-metal distance to be that in nickel carbonyl, 1.82 Å. Notwithstanding this nice agreement, our present theoretical equipment appears not replete enough to afford a consistent explanation of the maximum activity at rhodium in this way.

3.1.3. Beeck [14] suggested that the rate of catalyzed hydrogenation was controlled by the process of hydrogenated desorption, e.g., the reversal of dehydrogenated adsorption, of the adsorbed complex which makes room for adsorption of hydrogen. This can hardly be the case, however, since the catalyzed hydrogenation is progressively poisoned by adsorbed complex in its course as elucidated in section 2., and moreover, the hydrogenated desorption is far slower than the catalyzed hydrogenation [13] as mentioned in 2.5.

3.1.4. Ethylene is subject to the dehydrogenated adsorption as concluded in 2.4 and 2.B and, as seen from tables 1 and 6, the less active catalyst is that which is not easily rid by hydrogenated desorption of the adsorbed complex thus formed and associated with a high initial heat of adsorption [14].

3.1.5. The activation heat of the catalyzed hydrogenation over different metals amounts uniformly to 10.7 kcal, except in the case of tungsten where it is 2.4 kcal/mole [6]. It follows that the catalytic activity is proportional to the preexponential factor for all these metals except tungsten [6, 14].

3.1.6. An exception similar to that in 3.1.5 is found in case of tungsten by a statistical-mechanical analysis of kinetic data [38]. We obtain $10^{15}$ cm$^{-2}$ as an order of magnitude for the number of sites of the critical complex per unit area of the catalyst's surface from an analysis of kinetic data of the reaction involving no hydrocarbon over tungsten, which is in the line with the number derived from almost all available data for more than 60 cases of reactions over other metallic catalysts; but the number was found exceptionally low, around $10^{9}$ cm$^{-2}$, in case of the exchange reaction between methane and deuterium over tungsten.

3.1.7. The above results, 3.1.4, 3.1.5, and 3.1.6, are accounted for on the basis of the following theoretical results. Toya [39] has shown by first principles of quantum mechanics that hydrogen adatoms exist in $r$- and $s$-states and that the hydrogen adsorbed first on nickel exists predominantly in the $r$-state, adatoms in the $s$-state increasing with further increase of the adsorbed amount. The $r$-state is that of adatoms in the usual sense, whereas

<table>
<thead>
<tr>
<th>Rh</th>
<th>Pd</th>
<th>Pt</th>
<th>Ni</th>
<th>Fe</th>
<th>W</th>
<th>Cr</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log_{10} \lambda$</td>
<td>0</td>
<td>-0.8</td>
<td>-1.65</td>
<td>-2.6</td>
<td>-3.0</td>
<td>-4.0</td>
<td>-4.2</td>
</tr>
<tr>
<td>$-\Delta H_f$ kcal/mole</td>
<td>50</td>
<td>58</td>
<td>68</td>
<td>102</td>
<td>102</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>$-\Delta H_r$ kcal/mole</td>
<td>26</td>
<td>29 – 32</td>
<td>32 – 36</td>
<td>45 – 52</td>
<td>45</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>% $d$-character</td>
<td>50</td>
<td>46</td>
<td>44</td>
<td>40</td>
<td>39.7</td>
<td>43</td>
<td>39</td>
</tr>
</tbody>
</table>

The critical complex is the system of a step, i.e., the set of particles involved in the step, as a particular configuration with its representative point on the critical surface. The critical surface partitions the configuration space appropriate to the initial system of the step from that to the final system and is situated so as to minimize the rate of transit of representative points of the relevant canonical ensemble in either direction; the initial or final system is the same set of particles at the state before or after the occurrence of the step, respectively. The critical complex includes as its special case the activated complex as defined by Eyring et al. [H. Eyring, J. Chem. Phys. 3, 107 (1935); W. F. K. Wynne-Jones and H. Eyring, ibid. 3, 492 (1935); M. C. Evans and M. Polanyi, Trans. Faraday Soc. 31, 875 (1935); 32, 446 (1937); M. Polanyi, J. Chem. Soc. 629 (1937)] with special reference to the saddle point of the potential energy of the system of the step. In cases where there exist interactions between systems of the step and other particles, the appropriate configuration space and the relevant canonical ensemble should be those of the assembly comprising all the interacting species [cf. J. Horiuti and T. Nakamura, Advances in Catalysis 17 (1966), section II.A.).

4 Ethylene is assumed [37] to be held by two adjacent metal atoms breaking its $\pi$-bond and forming two carbon-metal bonds, and all bonds of the carbon atoms are tetrahedrally disposed like those of ethane.
the $s$-state is that of H atoms dissolved in the metal but retained between the electronic surface of metal and a plane through the centers of the metal atoms in the first layer. Observed variations of electric resistance [40] and work function [41, 42] with amount of hydrogen adsorbed have been adequately explained on this basis, and it was inferred that [43] the $r$-state on tungsten is of an extremely low energy so that the $s$-state does not practically exist on tungsten, that hydrogen is irrevocably adsorbed [44], and that hydrocarbons are stripped of hydrogen atoms to leave carbon deposit on tungsten. Methane will thus diminish the number of sites of the critical complex as in 3.1.6.

It would be of some interest to decide whether adatoms of $r$- or $s$-state partake in the hydrogenation reaction. Takeuchi and Asano [45] allowed nickel oxide reduced at 200 °C to adsorb one after the other small quantities of tritium and protium. Then, ethylene was admitted over the catalyst. The ethane thus formed was found less radioactive when protium was admitted first; hence, that decided which the initially adsorbed hydrogen was active in hydro- 

genation. It would follow from this experimental result, with reference to Toya’s theory, that only hydrogens in the $r$-state were catalytically active. Since nickel might not, however, be sufficiently reduced and evacuated at 200 °C, it is desirable to confirm the result with nickel reduced and evacuated at higher temperature or with a clean surface of evaporated nickel film.

3.2. The close correlation of the catalytic activity with properties, of metals as seen in figures 4(a) and 4(b) would suggest an investigation of alloys whose properties vary continuously with composition. The theory of catalysis of Dowden [46] predicts, in particular, that Ni alloyed with more than 60 percent Cu has its $d$-holes filled by electrons from Cu and is deprived of its catalytic activity. A lively interest has been aroused by this state of affairs in the catalytic activity of alloys for ethylene hydrogenation which has, however, been earlier explored by Rienäcker and his co-workers [47–51].

3.2.1. Rienäcker’s work provides the following information.
3.2.1.1. Alloys of transition elements with Cu, i.e., Ni-Cu [47], Pd-Cu [48], and Pt-Cu [48, 50], were prepared in the form of thin plates, which by means of x-ray analysis were confirmed to be disordered when flashed or flashed and quenched but ordered with a superlattice when alloys of the appropriate atomic ratio were annealed. In their experiments runs were conducted by allowing an equimolar mixture of ethylene and hydrogen of 1 atm total pressure to flow through a catalyst bed and by analyzing the effluent gas for the ethane-yield; the absence of methane in the effluent gas was therewith confirmed. The results are shown in figure 6 in comparison with the extent of parahydrogen conversion effected by the same catalysts. The following comments are remarked [50, 51, 48].

The activity of these alloys in catalyzing the hydrogenation increases, as seen from figure 6 with their activity in catalyzing parahydrogen conversion increases, as seen from figure 6 with their activity in catalyzing parahydrogen conversion [51].

Alloys with superlattice have lower activation heats, although their activity is much the same as that of disordered alloys [47, 48, 49].

3.2.1.2. The catalytic activity of Cu-Ag alloy was observed by Rienäcker and Bommer [49] at 550 and 700 °C, but its dependence on composition was found imperceptible.

3.2.2. Further data are provided on the dependence of the activity of alloys on their composition.

3.2.2.1. Kowaka [52] observed at 100 °C a pronounced activity of Ag-Pd alloys of Pd content above 40 atom percent in hydrogenation of ethylene but practically none below 40 atom percent.

3.2.2.2. Best and Russell [53] have observed the activity of Cu-Ni alloys in catalyzing the hydrogenation of ethylene from −70 to above 100 °C; the results indicate that the activity of the alloys outweigh that of any pure component, in contrast with the results at 500 °C shown in figure 6.

3.2.2.3. Farnsworth et al. [54, 55], observed the hydrogenation of ethylene over Cu-Ni alloy plates subjected to bombardment with Ar+. Figure 7 shows the results obtained at 40 °C in terms of the first order rate with respect to hydrogen pressure. The activity of these alloys attained a maximum at a certain value of bombarding current, whereas such is not the case with pure nickel. The figure shows the maximum exaltation of activity at 60.5 percent Cu content. Figure 8 shows the relative activity at 40 °C of catalyst plates bombarded and then annealed at different temperatures. The activity of pure nickel decreases gradually with increase of annealing temperature, whereas the activity of alloys keeps constant until the annealing temperature attains 400 °C, beyond which it decreases steeply. Farnsworth et al. [54, 55], attributed the latter, steep decrease to the migration of copper atoms from inside the alloy to the part of surface, which originally is rich in nickel and lattice defects created by the bombardment.

![Figure 6: Activity of alloys in catalyzing the hydrogenation of ethylene in comparison with that in catalyzing parahydrogen conversion [51].](image)

An equimolar mixture of C2H4 and H2 was allowed to flow with a rate of 20 cm³/min and 50 cm length at 1 atm total pressure. The catalyst was conditioned at 650 to 800 °C in a flow of hydrogen for several dozens of hours before every run. The content of ethane in the effluent gas was determined, hence the percentage conversion. Para-hydrogen conversion was observed with the same catalysts statically at 255 mm Hg hydrogen pressure by means of the thermal conductivity method.

![Figure 7: Catalytic activity at 40 °C of Cu-Ni alloys bombarded with Ar+ ion versus bombarding current [54].](image)

Catalytic activity is given in terms of first order rate with respect to hydrogen pressure. Alloy plates were preliminarily evacuated to 10⁻⁴ mm Hg at 900 °C.
3.3. Important contributions have recently been made by application of the microcatalytic method [56] developed by Emmett’s school to the studies of promotion and poisoning effects of preadsorbed hydrogen on the hydrogenation of ethylene, para-hydrogen conversion and $^4$H–$^2$D equilibration over Cu-Ni alloy catalysts. In the microcatalytic method, helium is allowed to flow, as a carrier, through a differential reactor packed with 5 cm$^3$ catalyst which is directly connected with a gas chromatograph. A slug of reactant gas mixture, 60 percent H$_2$ + 40 percent C$_2$H$_6$, was passed over the catalyst and then directly through the chromatographic column.

3.3.1. Hall et al. [57, 58, 59], observed the above mentioned reaction at 200 °C with the catalysts pretreated in two ways, i.e., “H$_2$-treated” and “He-treated,” with a view to find the expected effect of preadsorbed hydrogen diminished in case of “He-treated,” as compared with that of “H$_2$-treated.” The catalysts were reduced in a flow of hydrogen overnight at 350 °C and, in case of “H$_2$-treated,” cooled in the same flow down to the reaction temperature, or, in case of “He-treated,” kept in a flow of helium at 350 °C for 30 to 45 min and then cooled in the same helium flow down to the reaction temperature. The catalytic activity is given in terms of percent hydrogenation at 200 °C per m$^2$ BET area as observed by passing a 6 cm$^3$ NTP slug of 60 percent H$_2$ + 40 percent C$_2$H$_6$ in the helium carrier of 50 cm$^3$/min flow rate.

The conversion over “He-treated” nickel was reduced to 82 percent by passing slugs of the same composition 16 times consecutively. In case of Cu-Ni alloys, Hall and Emmett [58] found that the conversion over “H$_2$-treated” (cf. legend of fig. 10) catalyst was unchanged by passing slugs repeatedly, whereas that over the “He-treated” one (cf. legend of fig. 10) thus gradually increased.
4. Reaction Kinetics of Catalyzed Hydrogenation

The reaction kinetics of the catalyzed hydrogenation was extensively investigated over a variety of simple metals as catalyst, whereas work on alloys was limited so far to studies on the dependence of kinetic parameters, e.g., rate and activation heat, upon the composition of alloys under suitably selected conditions as reviewed in section 3. A detailed account of the reaction kinetics is hence given next, with special reference to catalysts of simple metals for hydrogenation of ethylene.

4.1. The rate \( v_\text{h} \) of the hydrogenation is determined on the basis of the material balance in accordance with the stoichiometric equation

\[ C_2H_4 + H_2 = C_2H_6. \quad (4.1) \]

The applicability of the material balance has been verified by Rienäcker and Bommer [47] at 596 °C by a flow method. Miyahara, Teratani, and Tsunou [51] has shown mass-spectrometrically that the equimolar gas mixture of reactants of 0.1 mm initial total pressure over evaporated nickel film was converted exclusively to a mixture of ethylene, hydrogen, and ethane. Miyahara [22] observed that

They hence concluded [58] that the poisoning by absorbed complex referred to by Beeck [6, 14] and Jenkins and Rideal [13] is a relatively minor as compared with that of preadsorbed hydrogen.

Hall and Emmett [58] found that the activity of “He-treated” alloys in terms of log (% conversion at 200 °K per m²) increased monotonously with the mean valency of metal atoms in the alloy according to the valence bond theory of Pauling [36] as well as with percent \( d \)-character over the region of its composition, where the catalytic activity varied linearly with atom percent of nickel as seen from the curve “He-treated” in figure 9.

The activation heat of catalyzed hydrogenation at temperatures around 200 °K was found [58], irrespective whether “He-treated” or “H₂-treated,” to be 8 kcal for pure Cu, ca. 5 kcal for a Cu-7.8 percent Ni alloy and 4 kcal for Cu-alloys of Ni contents of 14.7 percent and above, including pure nickel.

3.3.3. Hall, Lutinski, and Hassel [59] have investigated comparatively the effects of an alternative set of pretreatments, i.e., “outgassed” and “H₂-cooled,” on the catalytic activity in hydrogenation of ethylene, parahydrogen conversion and \( ^1 \text{H}_2 - D_2 \) equilibration at 200 °K with Cu-Ni alloys. The catalysts were reduced at 350 °C for 2 hr, at 500 °C for 2 hr and then again at 350 °C for 12 hr. In the pretreatment “outgassed,” the reduction at 350 °C overnight was followed by evacuation at the same temperature and then by cooling down to the reaction temperature. The pretreatment “H₂-cooled” is the “H₂-treated” one followed by an evacuation at the reaction temperature for 30 min. The amount of preadsorbed hydrogen is expected to be diminished in case of “outgassed” relative to that of “H₂-cooled.” It was thus found that the activity of “H₂-cooled” Cu-Ni alloys was two to three times that of “outgassed” alloys uniformly for all three reactions, while the reverse was again the case with pure nickel.

It is remarkable that parahydrogen conversion as well as \( ^1 \text{H}_2 - D_2 \) equilibration over a Cu-Ni alloy of 72.4 atom percent Ni is accelerated severalfold by the preliminary passage of a slug of ethylene in both cases of pretreatment, although the reactions are retarded by coexistent ethylene. The activation heat of parahydrogen conversion was found 4.2 kcal in either case of pretreatment, whereas the preliminary passage of an ethylene slug reduced it to 3.9 kcal for the “outgassed” and 3.0 kcal for the “H₂-cooled” catalyst, respectively. The activation heat of \( ^1 \text{H}_2 - D_2 \) equilibration was 5 kcal in either case of pretreatment.

3.4. Ru-Pt binary catalysts of 20–40 percent Ru content being not specified whether being alloyed or not, are known to exhibit an activity 2 ~ 6 times larger than that of pure platinum [60] in catalyzing the hydrogenation of such polar compounds as nitrobenzene, cyclohexanone, maleic acid, and methyl butynol, whereas no contribution appears to have been made toward the study of its catalytic activity in hydrogenation of ethylene.
the total pressure of a 0.93:1 mixture of ethylene and hydrogen decreased from its initial value of 30.0 mm Hg ultimately down to 15.6 mm Hg in a constant volume over evaporated nickel film coincidently at 91, 114, and 129 °C, which verified the conclusion from the material balance of eq (4.1) that the final total pressure should be 30.0 mm Hg × 1/(1 + 0.93) = 15.6 mm Hg. We have seen, on the other hand, that a small amount of ethylene is subjected to dehydrogenated adsorption, which may cause a deviation from the above material balance (cf. 2.E.1); it is inferred from these results that the disturbing effects of the dehydrogenated adsorption are negligible for sufficient amounts of reactant gases.

4.2. Table 7 shows the kinetic parameters of the catalyzed hydrogenation in the presence of metallic catalysts. The first row shows the kinetic parameters of the uncatalyzed homogeneous hydrogenation in gas as observed by Pease [62] for reference, which ought to be excepted from the following illustration of columns referring to the catalyzed heterogeneous hydrogenation. Every blank indicates the lack of relevant description in the original paper, whereas “none” means that an appropriate process is not applied according to the original paper.

The column I gives the isotopic specification of the hydrogenation of ethylene, protium, deuterium and their mixture which are denoted by \( ^1\text{H}, \text{D}, \text{H} \), respectively, in accordance with the symbolism noted in section 1.\(^6\)

The column II indicates the species of metal used as catalyst and the column III the form (and/or condition) of the catalyst, i.e., powder, foil, plate, wire, thimble, evaporated film or supported; when supported, the description is given, e.g., as 1 percent on SiO\(_2\), indicating the weight percent of the catalyst metal and the material of supporter.

The column IV gives the procedures of prepartion of the catalyst in order of their application. The column V presents, in distinction from the “preparation” in column IV, the pretreatment of the catalyst for conditioning the catalyst in order to secure reproducibility. “None” means that no such treatment is applied except the evacuation of the product of the foregoing run, in cases where the reaction is followed in a closed space as commented upon below.

The column VI gives temperature and column VII shows the initial values, \( P_{\text{E,0}} \) and \( P_{\text{H,0}} \), of partial pressures of \( \text{C}_2\text{H}_4 \) and \( \text{H}_2 \), \( P_{\text{E}} \) and \( P_{\text{H}} \), respectively.

The column VIII gives three points of specification of the “modes of measurement.” The first point specifies whether the “static,” “stir,” “circulation,” “thermal siphon,” “flow” or “flow-circulation” method of following the reaction was used.

In the “static” or “stir” method, the reactant gas mixture is kept statically or stirred by means of a stirrer in a closed vessel over the catalyst, while in “circulation” the reactant gas mixture is driven by a circulation pump through a closed circuit over the catalyst. In the “thermal siphon” method, the circulation is effected by thermal siphon instead by means of a circulation pump. In the “flow” method, the reactant gas mixture is allowed to pass through a catalyst bed toward an open space. In the “flow-circulation” method, the gas mixture is rapidly circulated over the catalyst through a circuit, which is fed slowly with reactant gas mixture at one spot while the circulating gas is led out from the opposite spot of the circuit. The second point specifies that “hydrogen” or “ethylene” is brought into contact first with the catalyst, and the other reactant subsequently, or else that a homogeneous “mixture” of reactants is admitted over the catalyst. The third point specifies the modes of following the rate law. In case of “static,” “stir,” “circulation,” or “thermal siphon,” where the whole gas mixture is kept in a closed space, the rate law is determined either by measuring the “initial” rate, i.e., the rate of reaction at the moment of contact of reactant gas mixture with the catalyst at different partial pressures of reactant gases, or by following the “course” of the reaction by decrease of reactants or increase of products or both. In the former case, enough accuracy of measurements and reproducible experimental conditions have to be secured, whereas in the latter case it should be guaranteed that the course is not associated with such an advance of poisoning that distorts the coherence of data. The coincidence of the rate laws deduced by these alternative methods is a necessary condition for them being reality. The “initial” rate and the “course” method with the whole gas mixture kept in a closed space correspond, respectively, to the differential rate measurement by means of differential reactor [111] and the analysis of integral-conversion data [112] in case of the flow method, which are denoted in the Table by “differential” and “integral,” respectively. In the “flow-circulation” method the conditions of differential reactor is secured by the rapid circulation.

The column IX shows the rate law, \( v_h \propto P^n P_{\text{E}} P_{\text{H}} \) of the catalyzed hydrogenation in terms of \( m = \partial \ln v_h/\partial \ln P_{\text{E}} \) and \( n = \partial \ln v_h/\partial \ln P_{\text{H}} \), where \( v_h \) is the rate. Attached figures, if any, indicate the range of application of the rate law. The column X gives the optimum temperature referred to in section 1, if observed at all.

In case of the “static,” “stir,” “circulation,” or “thermal siphon” methods, where the whole gas mixture is confined in a constant volume over the catalyst, the reaction is followed in a closed space as commented upon below.

---

\(^6\) Hydrogen atoms of approximately 99 percent D content is denoted by D, light hydrogen with natural D content by \( ^1\text{H} \), respectively, but hydrogen gas of intermediate D content is denoted by H in this table.
Table 7. Reaction Kinetics of Catalytic Hydrogenation of Ethylene - Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Metal</th>
<th>Form</th>
<th>Preparation</th>
<th>Reaction</th>
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<th>Preparation</th>
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</table>

**Rate Law**

$$ Rate = k \ [A]^n \ [B]^m $$

Where:
- **Rate** is the reaction rate.
- **k** is the rate constant.
- **[A]** and **[B]** are the concentrations of reactants A and B, respectively.
- **n** and **m** are the reaction orders with respect to [A] and [B], respectively.

**Activation Heat**

$$ \Delta H_{act} = \frac{1}{2} \sum (\Delta H_{rxn}) $$

Where:
- **ΔH_{act}** is the activation heat.
- **ΔH_{rxn}** is the reaction heat for each reaction step.

**Activation Energy**

$$ E_{act} = \frac{1}{2} \sum (E_{rxn}) $$

Where:
- **E_{act}** is the activation energy.
- **E_{rxn}** is the reaction energy for each reaction step.

**Optimum Pressure**

$$ P_{opt} = \frac{1}{2} \sum (P_{rxn}) $$

Where:
- **P_{opt}** is the optimum pressure.
- **P_{rxn}** is the pressure for each reaction step.

**Optimum Temperature**

$$ T_{opt} = \frac{1}{2} \sum (T_{rxn}) $$

Where:
- **T_{opt}** is the optimum temperature.
- **T_{rxn}** is the temperature for each reaction step.

**Liberation of Metal**

$$ M_{lib} = \frac{1}{2} \sum (M_{rxn}) $$

Where:
- **M_{lib}** is the liberation of metal.
- **M_{rxn}** is the metal for each reaction step.

**Homogeneous Reaction**

$$ R_{hom} = \frac{1}{2} \sum (R_{rxn}) $$

Where:
- **R_{hom}** is the homogeneous reaction.
- **R_{rxn}** is the reaction for each reaction step.
<table>
<thead>
<tr>
<th>Reaction kinetics</th>
<th>Flow, differential</th>
<th>Flow, differential</th>
<th>Initial</th>
<th>Initial</th>
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<td>Static mixture, initial</td>
<td>0.0</td>
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<td>1</td>
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<td>Initial, mixture initial</td>
<td>0</td>
<td>1</td>
<td>(P_1 = 150, P_2 = 300)</td>
<td>(P_1 = 100, P_2 = 200)</td>
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<tr>
<td>Initial, mixture initial</td>
<td>1</td>
<td>0</td>
<td>(P_1 = 150, P_2 = 300)</td>
<td>(P_1 = 100, P_2 = 200)</td>
</tr>
</tbody>
</table>

**Table 2:** Reaction kinetics of catalyzed hydrogenation of olefins — Continued

- **Rate law:**
  - \( \frac{d[P_1]}{dt} = \frac{1}{1 + 1} \left( \frac{P_1}{P_2} \right) \) (Gutierrez, 1977)
  - \( \frac{d[P_1]}{dt} = \frac{1}{1 + 1} \left( \frac{P_1}{P_2} \right) \) (Gay, 1974)

- **Optimum conditions:**
  - Activation energy back-calc.: 150 kJ/mol
  - Activation energy back-calc.: 150 kJ/mol

**References:**
- [12, 74]
- [73]
- [72]
- [6]
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<td>Reaction</td>
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<td>Preparation</td>
<td>250 – 300 °C</td>
<td>in H₂ 40 min, evac. at reaction temp.</td>
<td>Pretreatment</td>
<td>Reaction temp. °C</td>
<td>Initial pressures of ethylene (P₀) and hydrogen (Pₐ₀) mm Hg</td>
<td>Modes of measurement</td>
<td>Rate law</td>
<td>Optimum temp. 0 °C/(= Tₓ – 273)</td>
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<td><strong>Reaction</strong></td>
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<td><strong>Form</strong></td>
<td><strong>Preparation</strong></td>
<td><strong>Pretreatment</strong></td>
<td><strong>Reaction temp. °C</strong></td>
<td><strong>Initial presence of ethylene (P_\text{E}, \text{Pa})</strong> and <strong>hydrogen (P_H, \text{Pa})</strong> mm Hg</td>
<td><strong>Modes of measurement</strong></td>
<td><strong>Rate law</strong></td>
<td><strong>Optimum temp. tx °C(=T_K -273)</strong></td>
<td><strong>Activation heat kcal mol</strong> -1</td>
<td><strong>Authors</strong></td>
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<tr>
<td>C/H\textsubscript{2} + H\textsubscript{2}</td>
<td>Pt</td>
<td>Supported on Al\textsubscript{2}O\textsubscript{3}</td>
<td>H\textsubscript{2}PCl reduced in vac. at 200 °C and reduced in H\textsubscript{2} at 200 °C 12 hr</td>
<td>Reduction for shorter time than in &quot;preparation,&quot; as activity decayed</td>
<td>18–52</td>
<td>P_{E,Pa} = 50–200 \ P_{H,Pa} = 20–200</td>
<td>Static, ethylene, initial</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = -0.5 ) at 50 °C</td>
<td>9.9 ± 0.5 (0–50 °C)</td>
<td>[88]</td>
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<tr>
<td>C/H\textsubscript{2}</td>
<td>Pt</td>
<td>do</td>
<td>do</td>
<td>do</td>
<td>18–52</td>
<td>P_{E,Pa} = 50–200 \ P_{H,Pa} = 20–200</td>
<td>Static, ethylene, initial</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = -0.5 ) at 50 °C</td>
<td>10.9 ± 0.5 (0–50 °C)</td>
<td>[88]</td>
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<tr>
<td>C/H\textsubscript{2} + D\textsubscript{2}</td>
<td>Pt</td>
<td>Supported on Al\textsubscript{2}O\textsubscript{3}</td>
<td>H\textsubscript{2}PCl reduced in H\textsubscript{2} at 300 °C, exposed to air at room temp., 200 °C in H\textsubscript{2} 0.5 hr</td>
<td>Reduction for shorter time than in &quot;preparation,&quot; as activity decayed</td>
<td>-20–50</td>
<td>P_{E,Pa} = 100–250 \ P_{H,Pa} = 50–100</td>
<td>Static, ethylene, initial</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = -0.3 ± 0.1 ) at 50 °C</td>
<td>15 ± 2 (0–40 °C)</td>
<td>(P_E = P_H = 100)</td>
<td>[88]</td>
</tr>
<tr>
<td>Supported 1% on SiO\textsubscript{2}</td>
<td>“Division” gel impregnated with H\textsubscript{2}PCl</td>
<td>10 min in H\textsubscript{2}flow at reaction temp.</td>
<td>45–90</td>
<td>P_{E,Pa} = 5.3–302 \ P_{H,Pa} = 11.4–760</td>
<td>Flow, differential</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = 0 ) at 50 °C</td>
<td>16</td>
<td>8.4 ± 0.4</td>
<td>[81]</td>
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<td>Supported 0.05% on SiO\textsubscript{2}</td>
<td>H\textsubscript{2}PCl calcined at 338 °C in air 1 hr, reduced in H\textsubscript{2} at 500 °C 3 hr</td>
<td>Reduction for shorter time than in &quot;preparation,&quot; as activity decayed</td>
<td>0–78</td>
<td>P_{E,Pa} = 50–290 \ P_{H,Pa} = 50–160</td>
<td>Static, ethylene, initial</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = -0.5 ) at 50 °C</td>
<td>16</td>
<td>(P_E = 22.8, P_H = 153)</td>
<td>[90]</td>
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<tr>
<td>Supported 1% on SiO\textsubscript{2}</td>
<td>H\textsubscript{2}PCl reduced in H\textsubscript{2} at 300 °C, exposed to air at room temp., 200 °C in H\textsubscript{2} 0.5 hr</td>
<td>Reduction for shorter time than in &quot;preparation,&quot; as activity decayed</td>
<td>0–78</td>
<td>P_{E,Pa} = 50–290 \ P_{H,Pa} = 50–160</td>
<td>Static, ethylene, initial</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = -0.5 ) at 50 °C</td>
<td>16</td>
<td>(P_E = 22.8, P_H = 153)</td>
<td>[90]</td>
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<td>Supported 1% on pumice</td>
<td>H\textsubscript{2}PCl reduced in H\textsubscript{2} at 300 °C, exposed to air at room temp., 200 °C in H\textsubscript{2} 0.5 hr</td>
<td>Reduction for shorter time than in &quot;preparation,&quot; as activity decayed</td>
<td>0–78</td>
<td>P_{E,Pa} = 50–290 \ P_{H,Pa} = 50–160</td>
<td>Static, ethylene, initial</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = -0.5 ) at 50 °C</td>
<td>16</td>
<td>(P_E = 22.8, P_H = 153)</td>
<td>[90]</td>
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<td>Plate</td>
<td>Pd</td>
<td>10 min in H\textsubscript{2}flow at reaction temp.</td>
<td>0–100</td>
<td>P_{E,Pa} = 100–500 \ P_{H,Pa} = 100–500</td>
<td>Flow-circulation</td>
<td>( \Delta \ln \frac{\text{P_E}}{\text{P_H}} = 0 ) at 50 °C</td>
<td>10.6 (0–42 °C) \ 1.2 (102–209 °C)</td>
<td>[91]</td>
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<td>Foil</td>
<td>Pd</td>
<td>100–300 °C in H\textsubscript{2} 30 min</td>
<td>0–200</td>
<td>P_{E,Pa} = 20–80 \ P_{H,Pa} = 20–100</td>
<td>Circulating, hydrogen, initial</td>
<td>( \frac{\text{P_E}}{\text{P_H}} = \frac{\text{P_E}}{\text{P_H}} ) at 50 °C</td>
<td>230</td>
<td>(P_E = 2.6, P_H = 117)</td>
<td>[87]</td>
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**TABLE 7. Reaction kinetics of catalyzed hydrogenation of ethylene.**
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<td>Reaction</td>
<td>Metal</td>
<td>Form</td>
<td>Preparation</td>
<td>Pretreatment</td>
<td>Reaction temp. °C</td>
<td>Initial pressures of ethylene ( P_{\text{E},0} ) and hydrogen ( P_{\text{H},0} ) (mm Hg)</td>
<td>Modes of measurement</td>
<td>Rate law</td>
<td>Optimum temp. ( T_{\text{opt}} ) ( ^\circ \text{C} ) (( T_{\text{opt}} - 273 ))</td>
<td>Activation heat kcal · mole (^{-1} )</td>
<td>Authors</td>
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<tr>
<td>( \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>Pd</td>
<td>Foil</td>
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<td>650 °C in ( \text{H}_2 ) 12 hr</td>
<td>70 – 130 ( P_{\text{E},0} + P_{\text{H},0} = 380 )</td>
<td>Flow, differential</td>
<td>( \frac{\Delta \ln \text{D}}{\Delta \ln P_{\text{E}}} = a )</td>
<td>10 – 14</td>
<td>5.3 – 5.8</td>
<td>[48]</td>
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<td>Thin limb</td>
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<td>Annointed at 800 °C 2 hrs in ( \text{H}_2 ) 1 min</td>
<td>0 – 180 ( P_{\text{E},0} + P_{\text{H},0} = 100 )</td>
<td>Static, mixture, course</td>
<td>1</td>
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<tr>
<td>( \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>Pd</td>
<td>Powder</td>
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<td>Evac. 1 hr at 550 °C</td>
<td>0 – 90 ( P_{\text{E},0} + P_{\text{H},0} = 100 )</td>
<td>Stir, hydrogen, course</td>
<td>0</td>
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<td>Supported ( \text{PdCl}_2 ) reduced with KOH and ( \text{H}_2\text{O}_2 )</td>
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<td>200 °C in ( \text{O}_2 ) 200 °C in ( \text{H}_2 )</td>
<td>70 – 120 ( P_{\text{E},0} = 1.7 ) to ( 11.0 ) ( P_{\text{H},0} = 0.9 ) to ( 6.4 )</td>
<td>Static, hydrogen, initial</td>
<td>1</td>
<td>1</td>
<td>–2.9</td>
<td>[93]</td>
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<td>...do...</td>
<td>75 – 105 ( P_{\text{E},0} = 199 ) to ( 560 )</td>
<td>...do... ( r_\text{H} = \frac{P_{\text{H}}}{P_{\text{E}} ^ {0.5} } ) ( 11.4 )</td>
<td></td>
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<td>[93]</td>
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<tr>
<td>Supported ( \text{on SiO}_2 )</td>
<td>“Davison” gel impregnated with ( \text{PdCl}_2 )</td>
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<td>Circul., mixture, initial</td>
<td>( -0.03 \pm 0.07 )</td>
<td>8.4 ± 0.4</td>
<td>[81]</td>
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<tr>
<td>Supported ( \text{on Al}_2\text{O}_3 )</td>
<td>Reduced from a convenient salt in ( \text{H}_2 ) at 400 °C, exposed to air at room temp., 200 °C in ( \text{H}_2 ) 0.5 hr</td>
<td>–36 – 77 ( P_{\text{E},0} = 25 ) to ( 300 ) ( P_{\text{H},0} = 25 ) to ( 350 )</td>
<td>Static, ethylene, initial</td>
<td>0</td>
<td>1</td>
<td>(18 °C)</td>
<td>11.4 ± 1.0 (50 – 77 °C) ( (P_{\text{E}} - P_{\text{H}} = 100) )</td>
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<td>[64]</td>
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<td>( \text{C}_2\text{H}_4 + \text{D}_2 )</td>
<td>Rh</td>
<td>Evaporated film</td>
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<td>None</td>
<td>–120 - –100 ( P_{\text{E},0} = 2.7 ) ( P_{\text{H},0} = 8.1 )</td>
<td>Static, initial</td>
<td>–0.74 ± 0.18</td>
<td>0.85 ± 0.11</td>
<td>(76 °C)</td>
<td>7</td>
<td>[76]</td>
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<tr>
<td>( \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>Rh</td>
<td>Supported ( \text{on SiO}_2 )</td>
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<td>“Davison” gel impregnated with ( \text{RhCl}_3, 3\text{H}_2\text{O} )</td>
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<td>Circul., mixture, initial</td>
<td>–0.74 ± 0.18</td>
<td>0.85 ± 0.11</td>
<td>(76 °C)</td>
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<tr>
<td>( \text{C}_2\text{H}_4 + \text{D}_2 )</td>
<td>Rh</td>
<td>Supported ( \text{on Al}_2\text{O}_3 )</td>
<td></td>
<td>Reduced from a convenient salt in ( \text{H}_2 ) at 400 °C, exposed to air at room temp., 200 °C in ( \text{H}_2 ) 0.5 hr</td>
<td>–18 – 110 ( P_{\text{E},0} = 50 ) to ( 100 ) ( P_{\text{H},0} = 26 ) to ( 250 )</td>
<td>Static, ethylene, initial</td>
<td>0</td>
<td>1</td>
<td>(79 °C)</td>
<td>12 ± 2 (73 – 110 °C) ( (P_{\text{E}} - P_{\text{H}} = 100) )</td>
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<tr>
<td>( \text{C}_2\text{H}_4 + \text{D}_2 )</td>
<td>Ru</td>
<td>Supported ( \text{5% on Al}_2\text{O}_3 )</td>
<td></td>
<td>RuCl(_3, 3\text{H}_2\text{O} ) reduced in ( \text{H}_2 ) at 200 °C 5 hr</td>
<td>0 – 80 ( P_{\text{E},0} = 28 ) to ( 100 ) ( P_{\text{H},0} = 54 ) to ( 165 )</td>
<td></td>
<td>–0.2</td>
<td>1</td>
<td>(54 °C)</td>
<td>8.7 ± 0.5 (32 – 80 °C) ( (P_{\text{E}} - 75, P_{\text{H}} = 36) )</td>
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TABLE 7. Reaction kinetics of catalyzed hydrogenation of ethylene. — Continued

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<tr>
<td>Reaction</td>
<td>Metal Form</td>
<td>Preparation</td>
<td>Pretreatment</td>
<td>Reaction temp. °C</td>
<td>Initial pressures of ethylene (P&lt;sub&gt;E&lt;/sub&gt;,&lt;sub&gt;0&lt;/sub&gt;) and hydrogen (P&lt;sub&gt;H&lt;/sub&gt;,&lt;sub&gt;0&lt;/sub&gt;) mm Hg</td>
<td>Modes of measurement</td>
<td>Rate law</td>
<td>Optimum temp. t&lt;sub&gt;0&lt;/sub&gt; °C (= T&lt;sub&gt;0&lt;/sub&gt;/K&lt;sub&gt;0&lt;/sub&gt; = 273)</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ru</td>
<td>Supported on SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>“Davison” gel impregnated with RuCl&lt;sub&gt;3&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>700 °C in H&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>700 °C in H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>550-700</td>
<td>150-275</td>
<td>T&lt;sub&gt;E&lt;/sub&gt;+T&lt;sub&gt;H&lt;/sub&gt; = 760</td>
<td>1</td>
<td>0, 0.2</td>
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<td>[47]</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; + D&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Os</td>
<td>Supported on A1&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ammonium chloroosmate reduced in H&lt;sub&gt;2&lt;/sub&gt; at 400 °C, exposed to air, 200 °C in H&lt;sub&gt;2&lt;/sub&gt; 0.5 hr</td>
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<td>150-250 °C; if in H&lt;sub&gt;2&lt;/sub&gt;, 40 min, evac. at reaction temp.</td>
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<td>Reaction</td>
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<td>Form</td>
<td>Preparation</td>
<td>Pretreatment</td>
<td>Reaction temp. °C</td>
<td>Initial pressures of ethylene (PE₀) and hydrogen (PH₀) mm Hg</td>
<td>Modes of measurement</td>
<td>Rate law</td>
<td>Optimum temp. t_k K (°C)</td>
<td>Activation heat kcal mol⁻¹</td>
<td>Authors</td>
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<tr>
<td>C₂H₄ + H₂</td>
<td>Cu</td>
<td>Supported on brick</td>
<td>Cu(NO₄)₂ decomposed at 200 °C in H₂, annealed at 300 °C 8 hr</td>
<td>0 — 100</td>
<td>PEₐ = 95 — 570 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 570} ) Static, mixture, initial</td>
<td>0</td>
<td>1</td>
<td>( 15.4 ) (not annealed 0 — 60 °C) 13.2 (annealed 60 — 100 °C) ( Pₐ = Pₐ - 380 )</td>
<td>[100]</td>
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<td>Supported on glass beads</td>
<td>Cuprous hydroxides reduced</td>
<td>194 — 220</td>
<td>PEₐ = 55 — 100 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 100} ) Static, mixture, initial</td>
<td>1</td>
<td>1</td>
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<td>6 ( Pₐ = Pₐ - 380 )</td>
<td>[100]</td>
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<td>Supported on Sepiolite</td>
<td>Sepiolite silica gel impregnated with Cu(NO₄)₂</td>
<td>275 °C in H₂</td>
<td>PEₐ = 152 — 532 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 532} ) Circul., mixture, initial</td>
<td>0.06 ± 0.12</td>
<td>0.69 ± 0.09</td>
<td>0.4 ± 0.4</td>
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<td>[11]</td>
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<td>Supported on kieselguhr</td>
<td>Cu(NO₄)₂ reduced at 300 °C in H₂</td>
<td>109 — 258</td>
<td>PEₐ = 133 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 133} ) Circul., mixture, course</td>
<td>1 ( (T &lt; T_k) ) 0.5</td>
<td>( \frac{Pₐ}{1 + 4Pₐ^{1/2}} ) &gt; 14.1</td>
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<td>[101]</td>
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<tr>
<td>C₂H₄ + H₂</td>
<td>Cu</td>
<td>Powder mixed with Mg(OH)₂</td>
<td>CuO in H₂, reduced at 300 °C</td>
<td>20 — 40</td>
<td>PEₐ = 50 — 100 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 100} ) Static, mixture, course</td>
<td>1 ( (T &lt; T_k) ) 0</td>
<td>( \frac{Pₐ}{1 + 4Pₐ^{1/2}} ) &gt; 11.8 ( (C_2H_2) ) 11.5 ( (C_2D_2) ) ( (Pₐ = Pₐ - 50) )</td>
<td>[103]</td>
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<tr>
<td>C₂H₄ + D₂</td>
<td>Fe</td>
<td>Exaporated film</td>
<td>None</td>
<td>120 — 100</td>
<td>PEₐ = 2.1 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 2.1} ) Static, initial</td>
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<td>7.3 ( Pₐ = 55, Pₐ = 52 )</td>
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<tr>
<td>C₂H₄ + H₂</td>
<td>Fe</td>
<td>Exaporated film</td>
<td>52 °C 1 hr</td>
<td>32 °C 15 min</td>
<td>PEₐ = 10 — 300 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 300} ) Static, ethylene</td>
<td>initial ( -0.6 ) 0.87</td>
<td>( 14.1 ) ( (C_2H_2) ) ( (C_2D_2) ) ( (Pₐ = Pₐ - 50) )</td>
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<td>[77]</td>
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<td></td>
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<td>Powder</td>
<td>Fertil oxalate reduced, smothered in vac.</td>
<td>Evac. at 360 °C 2 hr</td>
<td>0 — 175</td>
<td>Static</td>
<td>Decrease from 0.0 to 0.19 as ( Pₐ ) increases 0.84</td>
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<td>[104]</td>
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<td>C₂H₄ + D₂</td>
<td>Fe</td>
<td>Powder</td>
<td>... do ( \ldots ) do ( \ldots ) do ( \ldots )</td>
<td>... do ( \ldots ) do ( \ldots ) do ( \ldots )</td>
<td>Static, hydrogen, course</td>
<td>0.94</td>
<td>( 14.1 ) ( (C_2H_2) ) ( (C_2D_2) )</td>
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<tr>
<td>C₂H₄ + H₂</td>
<td>Fe</td>
<td>Powder</td>
<td>0.15% MgO as impurity</td>
<td>425 — 450 °C in H₂ 8 hr</td>
<td>450 °C in H₂</td>
<td>8 hr</td>
<td>32 °C 2 hr</td>
<td>89 — 40</td>
<td>PEₐ = 50 — 385 ( \frac{1}{2} \ln \frac{Pₐ}{Pₐ - 385} ) Static, mixture, course</td>
<td>0 ( (T &lt; T_k) ) 1 — 0.5</td>
<td>( 12.0 ) ( (C_2H_2) ) ( (C_2D_2) ) ( (Pₐ = Pₐ - 240) )</td>
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TABLE 7. Reaction kinetics of catalyzed hydrogenation of ethylene. — Continued
<p>| Table 7. Reaction kinetics of catalyzed hydrogenation of ethylene. — Continued |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
| Reaction | Metal | Form | Preparation | Pretreatment | Reaction temp. °C | Initial pressures of ethylene (P_E, atm) and hydrogen (P_H, atm) mm Hg | Modes of measurement | Rate law | Optimum temp. (T_x°C(=T_x-K-273)) | Activation heat kcal mole (^{-1}) | Authors |
| C(<em>2)H(<em>4) + H(<em>2) | Fe | Powder, 1.59% K, 1.3% Al, (\text{Al}<em>2\text{O}<em>3) | 450 – 500 °C in H(<em>2) for (60 \text{ hr}) | 450 °C in H(<em>2) 1 hr evac. 2 hr | (-89 \text{ to } -40) | (P</em>{E,x}+P</em>{H,x}=450) | Static, mixture, course | (\alpha \ln \frac{P</em>{E,x}}{P</em>{E,x}+P</em>{H,0}}=\frac{\alpha}{\ln P</em>{E,x}}) | (-35 °C) | 5.3 ((-50 \text{ to } -40 °C)) | [105] |
| | Fe | Powder, 0.15% Al, (\text{Al}<em>2\text{O}<em>3) as impurity | Fe oxide reduced at 400 – 440 °C, 59 hr and 515 – 532 °C 8 hr in H(<em>2) | 400 °C in H(<em>2) 1 hr | (-50 \text{ to } -20) | (P</em>{E,x}=100–400) | Circum., initial | (\alpha \ln \frac{P</em>{E,x}}{P</em>{E,x}+P</em>{H,0}}=\frac{\alpha}{\ln P</em>{E,x}}) | (-35 °C) | 4.2 ((P_x=P_{H}=200)) | [106] |
| | Fe | Supported on brick | Fe nitrate calcined at 300 – 400 °C, reduced in H(<em>2) at 450°C, sintered at 500 °C | 0 – 20 | (P</em>{E,x}=253–507) | Static, mixture, initial | (\alpha \ln \frac{P_{E,x}}{P_{E,x}+P_{H,0}}=\frac{\alpha}{\ln P_{E,x}}) | (-0.04 \pm 0.13) | (-0.91 \pm 0.11) | 8.4 (\pm 0.4) | [81] |
| | Co | Supported on SiO(<em>2) | &quot;Sorpsil&quot; impregnated with Fe(NO(<em>3)) | Circum., mixture, initial | 0.04 (-0.10) | 0.55 (\pm 0.66) | (-60 °C) | (-0.19 \pm 0.10) | (-0.91 \pm 0.11) | 8.4 (\pm 0.4) | [81] |
| C(<em>2)H(<em>4) + D(<em>2) | W | Exposed film | None | (-120 \text{ to } -100) | (P</em>{E,x}=2.7) | Static, initial | (\alpha \ln \frac{P</em>{E,x}}{P</em>{E,x}+P</em>{H,0}}=\frac{\alpha}{\ln P</em>{E,x}}) | 5 – 6 | 5.6 | [76] |
| | Ag | Foil | 700 °C in H(<em>2) 24 hr | 550 – 700 | (P</em>{E,x}+P_{H,x}=760) | Flow, differential | (\alpha \ln \frac{P_{E,x}}{P_{E,x}+P_{H,0}}=\frac{\alpha}{\ln P_{E,x}}) | 27.1 | 9.8 ((P_x=P_{H}=300)) | [107] |
| | Ag | Supported on brick | AgNO(<em>3) calcined at 350 – 400 °C, 130 – 250 °C in H(<em>2) | 50 – 100 | (P</em>{E,x}=253–507) | Static, mixture, initial | (\alpha \ln \frac{P</em>{E,x}}{P_{E,x}+P_{H,0}}=\frac{\alpha}{\ln P_{E,x}}) | 0 | 1 | (-100 °C) | [49] |
| C(<em>2)H(<em>4) + H(<em>2) | Cu-Ni alloy | Foil | 700 °C in H(<em>2) 24 hr | 400 – 600 | (P</em>{E,x}+P</em>{H,x}=760) | Flow, differential | (\alpha \ln \frac{P</em>{E,x}}{P</em>{E,x}+P_{H,0}}=\frac{\alpha}{\ln P_{E,x}}) | 2.5 ((\text{max. at ca. } 30 \text{ atom } % \text{Ni})) | 11 | [65] |
| | | Evaporated film | Outgassed in ultra high vacuum at 900 °C | 35 – 85 | (P_{E,x}+P_{H,x}=760) | Flow, differential | (\alpha \ln \frac{P_{E,x}}{P_{E,x}+P_{H,0}}=\frac{\alpha}{\ln P_{E,x}}) | 0.4 | (74.2 \text{ % Ni}) | 6 (-8) | [78] |
| | | Exposed film | Evaporated from Cu and Ni wires, annealed in H(<em>2) at 300 °C overnight | (-15 \text{ to } -15) | (P</em>{E,x}+P_{H,x}=1) | Static, mixture, initial | (\alpha \ln \frac{P_{E,x}}{P_{E,x}+P_{H,0}}=\frac{\alpha}{\ln P_{E,x}}) | 0 | 0 | ((-60 °C)) | (-0.3 \text{ to } -0.9) | [79] |</p>
<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
<th>XII</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Reaction temp. °C</td>
<td>Reaction kinetics</td>
<td>Modes of measurement</td>
<td>Rate law</td>
<td>Optimum temp. (t_x) °C (= (T_x) °K – 273)</td>
<td>Activation heat kcal · mole⁻¹</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\ln \left( \frac{v_x}{v_x^0} \right) = m \ln \left( \frac{P_x}{P_x^0} \right))</td>
<td>Given by the authors</td>
<td></td>
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</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\frac{\partial \ln v_x}{\partial \ln P_x} = m)</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td>(\frac{\partial \ln v_x}{\partial \ln P_x^0} = n)</td>
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<td></td>
<td></td>
<td>(K_x = \frac{v_x}{P_x P_x^0})</td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal Form</th>
<th>Preparation</th>
<th>Pretreatment</th>
<th>Initial pressures of ethylene ((P_n, s)) and hydrogen ((P_h, s)) mm Hg</th>
<th>Flow, differential</th>
<th>Static, mixture, initial</th>
<th>2.2 (20~50 % Ag)</th>
<th>17</th>
<th>[108]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Fe alloy Evaporated film</td>
<td>Evaporated from alloy pellet of 10.8 atom % Fe</td>
<td>350 °C in H₂</td>
<td>(P_n = 10 \times 300) (P_h = 10 \times 300)</td>
<td>0.3</td>
<td>0.0</td>
<td>8.9</td>
<td>[79]</td>
<td></td>
</tr>
<tr>
<td>Ni-Pd alloy Evaporated film</td>
<td>Evaporated from alloy pellet of 5.5 atom % Pd</td>
<td>...</td>
<td>...</td>
<td>-0.2</td>
<td>(-28.5 °C)</td>
<td>0.6</td>
<td>7</td>
<td>[79]</td>
</tr>
<tr>
<td>Cu-Ni alloy Powder</td>
<td>Carbonates decomposed, red. in H₂ at 550 °C overnight</td>
<td>250 °C in H₂</td>
<td>(P_n = P_{n, s} = 1.5) (P_h = P_{h, s} = 760)</td>
<td>Flow, differential</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Fe alloy Wire</td>
<td>Nitrites decomposed at 400 °C in H₂ at 500 °C 10 hr.</td>
<td>100 °C in H₂ 1 hr</td>
<td>(P_n = P_{n, s} = 1.2) (P_h = P_{h, s} = 760)</td>
<td>Flow, differential</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Pt alloy Foil</td>
<td>Evaporated from alloy pellet of 50 atom % Pt</td>
<td>650 °C in H₂ 12 hr</td>
<td>(P_n = P_{n, s} = 1) (P_h = P_{h, s} = 760)</td>
<td>Flow, differential</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Pd alloy Foil</td>
<td>Evaporated from alloy pellet of 50 atom % Pd</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-Ag alloy Foil</td>
<td>Annealed at 800 °C 2 hr in vac.</td>
<td>400 °C in H₂ 1 min</td>
<td>(P_n = 100) (P_h = 100)</td>
<td>Static, mixture, course</td>
<td>5.2 (20~50 % Ag)</td>
<td>8</td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>NaH Lump</td>
<td>Evac. at 200 °C 2 hr</td>
<td>100 (P_n = P_{n, s} = 300)</td>
<td>Static, mixture</td>
<td>8</td>
<td>[108]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiH Lump</td>
<td>Evac. at 200 °C 2 hr</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T₄ hydride Powder</td>
<td>Evac. at 800 °C</td>
<td>200 (P_n = 50<del>500) (P_h = 50</del>500)</td>
<td>Static, hydrogen, initial</td>
<td>1</td>
<td>From positive to negative as (P_n) increases 300 °C</td>
<td>&lt; 0 ((P_n &lt; 80, 250~300 °C))</td>
<td>1.4 (0~150 °C) ((P_h = 41.6, P_{h, s} = 41.7))</td>
<td>[109]</td>
</tr>
<tr>
<td>CaH₂ Powder</td>
<td>Evac. at 450 °C 1 hr</td>
<td>...</td>
<td>(P_n = 50<del>500) (P_{n, s} = 50</del>500)</td>
<td>Static, mixture, initial</td>
<td>1</td>
<td>0</td>
<td></td>
<td>200 ((P_h = 41.6, P_{h, s} = 41.7))</td>
</tr>
</tbody>
</table>
The catalyzed hydrogenation is throughout approximately first order with respect to hydrogen partial pressure, as seen from table 7, irrespective of the catalyst metal, preparation and pretreatment, whereas the dependence of its rate upon ethylene partial pressure varies considerably with catalyst metal, etc. The linear relation between ln $\nu_h$ and ln $P_E$ is rather poor in many cases, hence the values of $m = \partial \ln \nu_h / \partial \ln P_E$ in the table are just as much inaccurate.

4.3. Detailed comments will be made below upon the representative case of nickel.

4.3.1. Zur Strassen [64] has introduced hydrogen over nickel wire enrothed preliminarily by ethylene under its own vapor pressure (0.03 mm Hg) at liquid air temperature, and observed the decrease of total pressure, which was identified with rate $\nu_h$ of reaction (4.1). He thus found that the reaction was first order with respect to hydrogen throughout. The quotient $\nu_h/P_H$ was found to vary with partial pressure $P_E$ of ethylene as [64]

$$\nu_h/P_H \propto P_E/(1 + k'P_E), \quad (4.2)$$

where $k'$ is a constant at constant temperature, decreasing rapidly with increase of temperature, $k'P_E$ passing unity around the optimum temperature, so that $m = \partial \ln \nu_h / \partial \ln P_E$ is zero or unity sufficiently below or above the optimum temperature, respectively.

4.3.2. In the above experiment of zur Strassen [64], the catalyst was initially contacted with ethylene as denoted by "ethylene" in column VIII of table 7. Masuda [70] recently observed the hydrogenation rate in the presence of nickel wire over approximately the same ranges of partial pressures, introducing a homogeneous mixture of reactant gases over the catalyst. The reproducibility of catalytic activity was secured within 15 percent by a pre-treatment at 300 °C in hydrogen of 15 to 20 mm Hg pressure for 1 hr followed by evacuation to $10^{-6}$ mm Hg. The initial rate was thus found proportional to $P_E P_H^{-m}$ from $-45$ to $0$ °C. Figure 11(a) shows the dependence of the initial rate on $P_H$. It follows that $P_H^{-m}$ decreases linearly with time, provided the above rate law holds throughout the course of catalyzed hydrogenation, which is verified as shown in figure 11(b), fulfilling the necessary condition, referred to in 4.2., of the real rate law.

4.3.3. We see from table 7 that $m = 0$ and $n = 1$ at temperatures below the optimum, while $m = n = 1$ above the optimum in most cases, in accordance with eq (4.2). However, $\nu_h$ depends perceptibly upon $P_E$ even at temperatures appreciably below the optimum in those cases where the total pressure of the catalyzed hydrogenation is higher than 1 atm [82], where the catalyst is preliminarily treated with ethylene of much higher pressure [82, 101] than in the case of the experiment of zur Strassen [64], and where the reaction vessel is preliminarily only incompletely evacuated. Even a negative value of $m$ is reported [71, 74] with nickel powder, as shown in table 7. According to Schwab [113], however, this negative value of $m$ disappears when the catalyst and the reactant gases are purified.

4.3.4. Tucholski and Rideal [67] as well as Farkas, Farkas and Rideal [2] reported that the catalyzed hydrogenation in the presence of nickel was zeroth order with respect to total pressure, whereas their experimental results could be fitted adequately to the rate law with $m=0$ and $n=1$, the first order rate $(1/t) \ln (P_{H,0}/P_H)$ remaining fairly constant as shown in table 8, where $P_{H,0}$ is the initial value of $P_H$. 

---

**Figure 11a.** Dependence of the initial rate, $\nu_{H,0}$, of hydrogenation over Ni wire upon $P_{H,0}$ [70]. $\nu_{H,0}$ is the initial value of $\nu_h$ given in hydrogenated percent C,H min$^{-1}$ at $P_E = 0.049$ mm Hg.

**Figure 11b.** Partial pressure of hydrogen, $P_H$ (in mm Hg), in course of a run of catalyzed hydrogenation in the presence of Ni wire [70].

- O: 0 °C.
- O: 25 °C.
- o: 40 °C.
4.3.5. The observations on activation heats are no less divergent than the rate laws. Tuul and Farnsworth [65] have observed the catalyzed hydrogenation of ethylene in the presence of a 2.5 cm² nickel plate subjected preliminarily to different pretreatments. The results are, as shown in figure 12, that the activation heat varies between 3.6 kcal and 12 kcal, revealing the so-called compensation effect. The activation heat was derived from rate constants \( k_h \) at 35, 55, and 85 °C as deduced from experimental results assuming the rate law, \( m = 0, n = 1 \). The linearity of \( \ln k_h \) to \( 1/T \) is, however, rather poor, hence the activation heat is just as much inaccurate. The cleanest surface is, according to them [65], that bombarded by Ar⁺ ion, which reveals the highest activation heat, 12 kcal.

This high value activation heat coincides, however, with that on the carbided nickel surface [13, 82, 114]. Moreover, Tuul and Farnsworth’s observation of the optimum temperature, \( T \), in conjunction with partial pressure of ethylene, \( P_E \), falls into the characteristic correlation between \( T \) and \( P_E \), referred to below, of the carbided surface. It is possible that adsorbed complex on the nickel plate, which was used for every experiment as mentioned above, is decomposed by the bombardment to form the carbided surface. On the basis of the arguments in section 2, the most adequate value of the activation heat below the optimum is 5 to 6 kcal as obtained by Miyahara and others [22, 26, 61, 64, 70, 80] with equimolar mixtures of the reactant gases over evaporated nickel film.

4.4. An optimum temperature is observed, as seen from table 7, not only for nickel catalyst but also for platinum, palladium, iron, and copper catalysts. Tuul and Farnsworth [65] advanced and empirical relation, in case of nickel, between the optimum temperature \( T(°C) \) and \( P_E \) (in mm Hg) as \( T = 30 \log_{10} P_E + 105 \). Sato and Miyahara [80] found linear relations between \( \log_{10} P_E \) and the reciprocal of the absolute temperature of the optimum, \( T \), to hold for reduced nickel wire, freshly evaporated surfaces or carbided surfaces of nickel film, respectively as shown in figure 13; the latter two surfaces have been denoted by F and C, respectively, in 2.8.3. The linear relation over surface F is analytically [80] \( P_E \) in mm Hg

\[
1/T = (1/5300)(14.5 - \log_{10} P_E). 
\]

The optima observed by Tuul and Farnsworth [65] fall on the linear relation over surface C observed by Sato and Miyahara [80] as mentioned above. 4.5. Reference is made to the interesting work of Apelbaum and Temkin [91] on the catalyzed hydrogenation on palladium membrane. The apparatus used was separated into a hydrogen chamber, A, and a reaction chamber, B, by a 0.3 mm thick palladium membrane, as shown in figure 14. The membrane had an area of 15.7 cm² on the side of the reaction chamber. A mixture of hydrogen and ethylene was circulated through the reaction chamber by means of a circulation pump, C, at a rate of 2 liter/min through a circuit which was steadily fed with reactant gas mixture at a rate of 25 cm³/min, while a corresponding amount of circulating gas was led out simultaneously. The reaction was followed by measuring the amount of ethane in the gas led out. Apelbaum and Temkin have thus investigated the kinetics of the catalyzed hydrogenation, simultaneously following the fugacity of adsorbed hydrogen on the side of reaction chamber, which was identified with the hydrogen pressure \( P_A \) in the hydrogen chamber adjusted.
FIGURE 13. Dependence of optimum temperature, $T_x$, on ethylene partial pressure, $P_E$, in catalyzed hydrogenation of ethylene in the presence of nickel [80].


Annexed figures refer to respective authors as
1: Jenkins and Rideal [13], 2: Rideal [63], 3: Tucholski and Rideal [67], 4: Miyahara and Narumi [114], 5: Tsu and Farnsworth [65], 6: zur Strassen [64], 7: Miyahara [80], 8: Sato and Miyahara [80].

TABLE 9. Catalyzed hydrogenation of ethylene over palladium, with fugacity of adsorbed hydrogen followed simultaneously [91]

<table>
<thead>
<tr>
<th>Tem. °C</th>
<th>No. of experiment</th>
<th>Partial pressure, mm Hg in reaction chamber</th>
<th>Fugacity of adsorbed hydrogen, $P_A$, mm Hg</th>
<th>$v_{h,z=0}$, cm$^3$ NTP/hr</th>
<th>$n$, $x=0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$C_2H_4$</td>
<td>$C_2H_6$</td>
<td>$H_2$</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>15</td>
<td>231</td>
<td>84.5</td>
<td>424</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>239.5</td>
<td>77.5</td>
<td>439</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>254.5</td>
<td>59.0</td>
<td>456</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>263.5</td>
<td>35.5</td>
<td>453</td>
<td>64</td>
</tr>
<tr>
<td>176</td>
<td>1</td>
<td>15</td>
<td>242</td>
<td>496</td>
<td>492</td>
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<tr>
<td></td>
<td>2</td>
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<td>345</td>
<td>227</td>
<td>224</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>26</td>
<td>231</td>
<td>504</td>
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<td>7</td>
<td>85</td>
<td>332</td>
<td>336</td>
<td>327</td>
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<td></td>
<td>8</td>
<td>111</td>
<td>290.5</td>
<td>357.5</td>
<td>353</td>
</tr>
</tbody>
</table>

FIGURE 14. Apparatus for simultaneous observation of the catalyzed hydrogenation of ethylene over Pd and of the fugacity of adsorbed hydrogen [91].

A: H-chamber, B: reaction chamber, C: circulation pump, T: cold trap at $-78$ °C, M: Hg-manometer.

We see from table 9 that $P_H = P_A$ at 176 °C but $P_H > P_A$ at 22 °C, which shows that adsorbed hydrogen is in equilibrium with hydrogen in gas or adsorption and desorption are so much rapid at 176 °C but not at 22 °C.

Apel'baum and Temkin observed further the rate $v_h$ of hydrogenation in conjunction with the rate $x$ of diffusion of hydrogen through the membrane to find the increment in number of ethane molecules per diffused hydrogen atom, i.e.,

$$n = \frac{v_h - v_{h,z=0}}{x}$$

The result, $n \approx 0.01$ at 176 °C and $n \approx 0.5$ at 22 °C, indicates that the hydrogen used in the catalyzed hydrogenation originates almost all from gaseous hydrogen in the reaction chamber at 176 °C but from diffused hydrogen at 22 °C in conformity with the above conclusion on the adsorption.

5. Reactions Associated With the Catalyzed Hydrogenation

Farkas, Farkas, and Rideal [2] discovered that the catalyzed hydrogenation of ethylene is accompanied by parahydrogen conversion and exchange of hydrogen atoms when they followed the parahydrogen content and deuterium content in hydrogen by means of the thermal conductivity method. Since 1950, relative amounts of different deuterioethylenes and deuteroethanes in the deuteration product of ethylene have become traceable by means of mass spectrometry. Infrared spectrometry has
also become popular in the analysis of deuterocompounds. The profiles thus disclosed of the catalyzed hydrogenation impressed an unexpected complexity of the problem on the one hand but promised to be powerful tools of solving it on the other hand.

### 5.1. Experimental Methods

Such profiles of the reaction which are traceable by means of the thermal conductivity gage alone are dealt with in 5.1, and those extended by means of mass and infrared spectrometry in 5.2.

5.1.1. Farkas, Farkas, and Rideal [2] followed the para-hydrogen conversion or the deuterium atom fraction in hydrogen in course of the hydrogenation of ethylene at 20 °C in the presence of nickel wire preliminarily oxidized at 600 °C and reduced by hydrogen at 300 °C, grew distinctly rapid as soon as ethylene was exhausted by hydrogenation, as seen in figure 15, (1) its rate being approximately equal to that in the absence of ethylene [2]; (2) that the rate of parahydrogen conversion at 20 °C of 25 mm Hg parahydrogen was unchanged by admixture of 17 mm Hg ethane, (3) that the partial pressure of ethylene due to catalyzed hydrogenation decreased linearly with time at 20 °C for the first 30 min as seen in figure 15, and (4) that the deuterium content of hydrogen decreased linearly with time at 20 °C of 25 mm Hg parahydrogen was unchanged by admixture of 17 mm Hg ethane.

\[
\frac{\partial\%\text{PARAHYDROGEN}}{\partial \text{TIME, min}} = 35.4 \text{ min}^{-1}
\]

![Figure 15. Parahydrogen conversion associated with catalyzed hydrogenation of ethylene [2].](image)

\[P_{0}, s = 19 \text{ mm Hg}, \quad P_{u}, s = 23 \text{ mm Hg}, 20 \text{ °C}.
\]

5.1.2. Twigg and Rideal [68] observed the catalyzed deuteration of light ethylene with equimolar pure deuterium in the presence of the same nickel catalyst as used by Farkas, Farkas, and Rideal [2] with special reference to the deuterium content of hydrogen. Successive measurements of hydrogenation and exchange rate conducted without pretreatments were corrected for an appreciable decay of catalytic activity by measuring the hydrogenation rate at a fixed temperature and the partial pressures of reactants just before every run; then, the hydrogenation rates and exchange rates measured were multiplied by the correction factor \(r_{1}/r_{n}\), where \(r_{1}\) and \(r_{n}\) are the hydrogenation rates observed at the fixed conditions just before the first and the nth run, respectively. Twigg and Rideal [68] observed, on the one hand, the initial rate of hydrogenation and the initial rate of hydrogen exchange \(v_{ex,H} = -dx_{H}/dt\), at 156 °C at different partial pressures of reactants, finding that both reactions were first and zeroth order with respect to hydrogen and ethylene pressure, respectively. They followed, on the other hand, the course of deuterization by determining the deuterium atom fraction, \(x_{D}\), in hydrogen and the nonequilibrium fraction, \(1 - u\), of hydrogen, where \(u = [\text{HD}]/[\text{HD}_{eq}]\) is the ratio between the actual concentration, [\text{HD}], of \text{HD} and the concentration [\text{HD}_{eq}] which would result, were the existent hydrogen equilibrated, i.e., brought to equilibrium with respect to the reaction, \(\text{H}_{2} + \text{D}_{2} = 2\text{HD}\). The nonequilibrium fraction \(1 - u\) is plotted against \(x_{H}\) in figure 16.

The activation heat of hydrogen exchange \(RT\delta ln v_{ex,H}/\partial T\) was found to be 18.6 kcal over the range of temperatures from 84 to 100 °C, and to decrease gradually with increase of temperature down to 4 kcal at 207 °C. It was in excess of the activation heat of hydrogenation, \(RT\delta ln v_{H}/\partial T\), by 4 ~ 5 kcal throughout. Twigg and Rideal [68] remarked that the equilibration was much faster in the absence of ethylene than in its presence and, with reference to the result of figure 16, that the plots of \(1 - u\) against \(x_{H}\) at 156 °C and below accumulated around one straight line (indicated by a broken line in fig. 16) which passed a point \(x_{H} = 0.33\) on the axis of abscissa; other straight lines were obtained at higher temperatures, and these intersect the first line on the axis of abscissa. Horiuti [8, 9] has accounted for these experimental results by theoretical calculations on the basis of the associative mechanism and predicted, as
FIGURE 16. Nonequilibrium fraction $1 - u$ versus deuterium fraction $x_H$ of hydrogen in course of catalyzed deuteration of light ethylene over Ni-wire [68].

\[ u = \frac{[\text{HD}]}{[\text{HD}]_{eq}} \]

where $[\text{HD}]_{eq}$ concentration of HD. $[\text{HD}]_{eq}$ concentration of HD which would result if existing hydrogen were brought to equilibrium with respect to the reaction $\text{H}_2 + D_2 \rightarrow 2\text{HD}$.

elucidated in 14.4, that the slope of curves such as those indicated by broken lines in figure 16 against $x_H$ axis increase considerably when the temperature is lowered below those in the experiments of Twigg and Rideal [68], so that curves run down almost vertically along a perpendicular at $x_H = 1$. Matsuzaki [115] confirmed the results of Twigg and Rideal's experiments by tracing them, on the one hand, and observed relations between $1 - u$ and $x_H$ at temperatures as low as 0 or $-25^\circ C$ as shown in figure 17.

on the other hand, in semiquantitative agreement with the theoretical prediction of Horiuti [8, 9] as described in 14.4.

5.1.3. Farkas and Farkas [85] experimented with platinized platinum foil on the parahydrogen conversion associated with the catalyzed hydrogenation. Table 10 shows the half-life values $\tau_c$ and $\tau_h$, respectively, of parahydrogen conversion and catalyzed hydrogenation from 0 to $27^\circ C$. We see from the table that the presence of ethylene retards the parahydrogen conversion as in the case of nickel and that $\tau_c$ and $\tau_h$ are the same in the presence of excess ethylene, whereas $\tau_c$ is much greater in the presence of excess hydrogen, or the relative rate of parahydrogen conversion is much smaller than that of hydrogenation.

The optimum temperature was found at $160^\circ C$ for 20 mm Hg ethylene and 40 mm Hg hydrogen, and the activation heat of the catalyzed hydrogenation below the optimum 10 $\sim$ 11 kcal [85], which equaled the activation heat of parahydrogen conversion in the absence of ethylene [85]. The activation heat of the exchange was given as 22 kcal by them.

<table>
<thead>
<tr>
<th>Reaction temp. °C</th>
<th>Initial partial pressures, mm Hg</th>
<th>Half-life time, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{E,O}$</td>
<td>$P_{H,O}$</td>
<td>Parahydrogen conversion, $\tau_c$</td>
</tr>
<tr>
<td>25</td>
<td>40</td>
<td>21</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>0</td>
<td>19</td>
<td>40</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>24</td>
<td>42.5</td>
<td>17.5</td>
</tr>
<tr>
<td>27</td>
<td>0</td>
<td>12.5</td>
</tr>
<tr>
<td>27</td>
<td>36.5</td>
<td>12.5</td>
</tr>
</tbody>
</table>

TABLE 11. Exchange equilibrium between ethylene and hydrogen in course of catalyzed deuteration over platinized platinum foil [85]

\[ P_{E,O} = 20 \text{ mm Hg}, P_{H,O} = 40 \text{ mm Hg} \]

$x_{H,\text{obs}}$: Deuterium atom fraction in residual hydrogen at the exhaustion of ethylene.

$x_{H,\text{calc}}$: Deuterium atom fraction in equilibrium distribution between hydrogen and ethylene.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>% Deuterium in residual hydrogen</th>
<th>% exchange $1 - x_{H,\text{obs}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>99</td>
<td>37</td>
</tr>
<tr>
<td>54</td>
<td>95</td>
<td>40</td>
</tr>
<tr>
<td>79</td>
<td>80</td>
<td>41</td>
</tr>
<tr>
<td>100</td>
<td>75</td>
<td>40</td>
</tr>
<tr>
<td>120</td>
<td>63</td>
<td>41</td>
</tr>
<tr>
<td>146</td>
<td>59</td>
<td>42</td>
</tr>
<tr>
<td>187</td>
<td>51</td>
<td>43</td>
</tr>
<tr>
<td>235</td>
<td>48</td>
<td>44</td>
</tr>
</tbody>
</table>
5.1.4. Farkas and Farkas [85] observed the hydrogen exchange associated with deuteration of light ethylene in the presence of platinized platinum foil. Since, however, the deuteration was quite rapid under the conditions where the hydrogen exchange proceeded with measurable rate, the deuterium content in residual hydrogen was measured on exhaustion of ethylene. Starting from a deuterium content in residual hydrogen was measurable under the conditions where the hydrogen exchange proceeded with a measurable rate, the deuterium content in residual hydrogen was measured on exhaustion of ethylene. Starting from a mixture of 20 mm Hg ethylene and 40 mm Hg deuterium, they obtained the results shown in Table 11. The values \( x_{H, \text{calc}} \) are atom percent of deuterium in the residual hydrogen, \( x_{H, \text{calc}} \) those in exchange equilibrium calculated allowed for the isotopic effect, and percent exchange is the percent amount of exchange accomplished. Since there occurs no hydrogen exchange between hydro- gen and ethane under the experimental conditions [85], one can take from Table 11 that the exchange between ethylene and hydrogen is so rapid at around 230 °C that they practically attain the exchange equilibrium.

### 5.2. Modern Observations

5.2.1. Twigg [116] has catalytically hydrogenated 107 mm Hg light ethylene over nickel-kieselguhr catalyst at \(-78^\circ C\) either with 120 mm Hg equimolar mixture of \(^1\text{H}_2\) and \(\text{D}_2\) or with 120 mm Hg equili- brated mixture of \(^1\text{H}_2\), \(^1\text{HD}\), and \(\text{D}_2\) to the exhaustion of the light ethylene. He thus found that the infrared adsorption spectrum of the product, (A), of hydrogenation of the light ethylene with equimolar mixture of \(^1\text{H}_2\) and \(\text{D}_2\) was identical with that of the product, (B), of hydrogenation with an equilibrated mixture of \(^1\text{H}_2\), \(^1\text{HD}\), and \(\text{D}_2\), and that the identical spectra of (A) and (B) were different from the infrared absorption spectrum of an equimolar mixture, (C), of \(\text{C}_2\text{H}_4\) and \(\text{C}_2\text{H}_4\text{D}_2\). He found [116], moreover, that the conversion of 75.8 mm Hg para- hydrogen over the same catalyst at the same temperature was almost inhibited by coexistent 48.9 mm Hg ethylene and that deuteroethylene was scarcely pro- duced by catalyzed deuteration of light ethylene at \(-37^\circ C\) over the same catalyst.

The result that (A) and (B) have the same infrared absorption spectra but that of (C) is different ex- cludes the possibility of hydrogenation being effected by a single act of addition of a hydrogen molecule to ethylene but verifies the mechanism of hydrogenation through dissociated hydrogen atoms. 5.2.2. Turkevich, Bonner, Schissler, and Irsa [117] followed the catalyzed deuteration of light ethylene over nickel wire by mass-spectrometric analysis of the product in several stages of the progress of deuteration. The catalyst of nickel wire was mounted in a reaction vessel, oxidized at 600 °C, reduced at 330 °C and, before every run, pretreated in deuterium gas at 300 °C. The reaction vessel was kept at 0 °C, deuterium was first, light ethylene subsequently admitted over the catalyst. The reaction was started by applying an appropriate current to the wire to keep it at 90 °C for a recorded time, and the product thus obtained was analyzed. The results are shown in Figure 18, where any curve, \( A_n \) or \( E_n \), gives the partial pressure of ethane-\( d_n \) or ethylene-\( d_n \) against percent of ethylene deuterated. \( \text{C}_2\text{H}_4\text{H}_6 \) was the predominant initial product of deuteration, as seen in the figure, contrary to the expectation of the authors [117] of finding \( \text{C}_2\text{H}_4\text{D}_2 \) instead.

5.2.3. Kemball [76] followed the deuteration of light ethylene at \(-100^\circ C\) over films of Ni, Fe, Rh, and W, respectively, evaporated on glass wall kept at liquid nitrogen temperature, by analyzing the reacting gas that leaked steadily through a capillary into a mass spectrometer. Table 12 shows the relative
amounts of different ethylenes-\(d_n\) and ethanes-\(d_n\) in the initial stage of the deuteration. In case of tungsten, deuterium is hardly taken up at all by ethylene and the result is marked by the maximum abundance of \(C_2H_4D_2\) among the ethanes-\(d_n\).

It was found [76] that the total number of moles of ethane as well as the number of deuterium atoms taken up by a definite amount of ethylene increases proportional to the time of reaction. Table 13 [76] shows initial values of rate of ethane formation, \(v_h\), and exchange rate of ethylene, \(v_{ex,E}\). The kinetics of both reactions was found to correspond to \(m=0\) and \(n=0.5\). The activation heats derived as usual from both rates are approximately uniformly 5-6 kcal for W and 7 kcal for Ni, Fe, and Rh. Table 14 shows the relative amounts of ethanes-\(d_n\) on exhaustion of ethylene by deuteration [76].

5.2.4. Miyahara and Narumi [114] conducted a complete analysis of the product of catalyzed deuteration of light ethylene in the initial stage of deuteration over freshly evaporated nickel surface F (cf. 2.8.3) as shown in tables 15 and 16. “Deuterated percent \(C_2H_4\)” is the amounts of ethane in percent of the initial amount of ethylene which were identified with the decreases of total pressure in percent of the initial partial pressure of ethylene. Tables 15(b) and 16(b) show the mass spectra of run 2 in table 15(a) and run 12 in table 16(a), respectively, as observed at various stages of deuteration. The first column of these tables shows the mass spectra of gases sampled immediately after the introduction of the reactant mixture into the reaction vessels, which were assured free from ethane. The considerably high values of \(M_2\) and \(M_3\) are interpreted as due to an appreciable dehydrogenated adsorption of light ethylene on the fresh surface, \(F\), as described in section 2, which is enhanced at the higher temperature in the latter case.

It is concluded from tables 15 and 16 with reference to the optimum temperature, 137 °C, as inferred from the result in figure 19 (cf. 6.2), (1) that the predominant product of deuteration at 0 °C, amply below the optimum, is \(C_2H_4H_2\); as in the case of Turkevich et al. [117], but switches over to \(C_2H_4D_2\) as the partial pressure of deuterium is increased, (2) that \(H_2\) or \(HD\) is hardly evolved at all in course of the catalyzed deuteration of 10 mm Hg light ethylene with equimolar deuterium below the optimum, as seen from table 15(b), or, in other words, that protium atoms from light ethylene hardly enter hydrogen gas, (3) that at 200 °C, in contrast with the latter result, the predominant initial product of deuteration is \(C_2H_2D_2\), while great quantities of \(H_2\) and \(HD\) are evolved from the beginning of catalyzed deuteration as seen from tables 16(a) and 16(b), and (4) that an appreciable amount of deuteroethylene is evolved both at 0 and 200 °C.

5.2.5. Data are compiled in table 17 from table 3 with special reference to the catalyzed deuteration over an S surface of nickel [26], where the dehydrogenated adsorption of ethylene is substantially inhibited. Parenthesized figures show the percentages of the respective compounds-\(d_n\) in a random distribution of isotopes as calculated on the basis of the total deuterium atom fraction in ethylene or in hydrogen. It is concluded from table 17, referring to the fact that the observed value 0.992 of \(y_H\) is just that of original deuterium gas, (1) that hardly any protium appears in hydrogen gas in course of the catalyzed deuteration at -45 or -23 °C, temp.

<table>
<thead>
<tr>
<th>Metal</th>
<th>React. temp., °C</th>
<th>(v_h)</th>
<th>(v_{ex,E})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-100</td>
<td>1.54</td>
<td>3.60</td>
</tr>
<tr>
<td>Ni</td>
<td>-100</td>
<td>2.30</td>
<td>5.25</td>
</tr>
<tr>
<td>Rh</td>
<td>-104</td>
<td>18.0</td>
<td>18.2</td>
</tr>
<tr>
<td>W</td>
<td>-99</td>
<td>3.42</td>
<td>0.26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial partial pressures</th>
<th>React. temp., °C</th>
<th>Ethanes-(d_n), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(P_{E,0}) mm Hg</td>
<td>(P_{H,0}) mm Hg</td>
<td>(A_0)</td>
</tr>
<tr>
<td>Rh</td>
<td>2.7</td>
<td>8.1</td>
<td>-104</td>
</tr>
<tr>
<td>Fe</td>
<td>2.7</td>
<td>8.1</td>
<td>104</td>
</tr>
<tr>
<td>W</td>
<td>2.7</td>
<td>8.1</td>
<td>-99</td>
</tr>
<tr>
<td>Ni</td>
<td>2.7</td>
<td>8.1</td>
<td>-100</td>
</tr>
<tr>
<td>Ni</td>
<td>2.7</td>
<td>24.3</td>
<td>-92</td>
</tr>
<tr>
<td>Ni</td>
<td>8.1</td>
<td>24.3</td>
<td>-81</td>
</tr>
</tbody>
</table>
temperatures which are amply below the optimum at ca. 30 °C as gathered from the table, whereas above the optimum, $^1$H$_2$ and $^1$HD appear approximately in accordance with a random distribution of isotopes, (2) that ethylenes-$d_n$ appear in accordance with the random distribution of isotopes irrespective of temperature and (3) that the activation heat of catalyzed deuteration varies only slightly with the total pressure as indicated by its value

| TABLE 15(a). Relative amounts of ethylenes-$d_n$ = $E_n$ and ethanes-$d_n$ = $A_n$ in the deuteration product of 10 mm Hg light ethylene at 0 °C over a freshly evaporated surface $F$ of nickel film [114] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. of run | Initial partial pressure of D$_2$ mm Hg | Deuterated % C$_2$H$_4$ | Relative amounts of hydrocarbons-$d_n$, % | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $A_6$ |
| 2 | 10 | 33 | 13 | 1 | 0 | 0 | 45 | 23 | 18 | 0 | 0 | 0 | 0 |
| 3 | 45 | 12 | 1 | 0 | 0 | 35 | 28 | 19 | 4 | 1 | 0 | 0 |
| 4 | 107 | 29 | 27 | 3 | 0 | 0 | 40 | 24 | 3 | 2 | 0 | 0 | 0 |
| 5 | 107 | 29 | 29 | 5 | 2 | 0 | 23 | 19 | 13 | 4 | 2 | 1 | 0 |
| 7 | 138 | 36 | 14 | 1 | 0 | 0 | 27 | 10 | 36 | 7 | 2 | 1 | 1 |

| TABLE 15(b). Mass spectrum of reacted hydrogen gas of run 2 in table 15(a) |
|---|---|---|---|---|---|---|
| Deuterated % C$_2$H$_4$ | 0 | 15 | 20 | 27 | 33 |
| Relative heights of peaks | $M_2$ | 4 | 5 | 5 | 7 | 5 |
|                         | $M_3$ | 2 | 2 | 2 | 2 | 2 |
|                         | $M_4$ | 94 | 93 | 93 | 91 | 93 |

| TABLE 16(a). Relative amounts of ethylenes-$d_n$ = $E_n$ and ethanes-$d_n$ = $A_n$ in the deuteration product of 10 mm Hg light ethylene with equimolar deuteration at 200 °C over a freshly evaporated surface $F$ of nickel film [114] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. of run | Deuterated % C$_2$H$_4$ | Relative amounts of hydrocarbons-$d_n$, % | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $A_6$ |
| 11 | 20 | 38 | 27 | 13 | 0 | 4 | 6 | 7 | 4 | 2 | 0 | 0 |
| 12 | 31 | 25 | 25 | 11 | 3 | 3 | 8 | 12 | 7 | 4 | 1 | 0 |

| TABLE 16(b). Mass spectrum of reacted hydrogen of run 12 in table 16(a) |
|---|---|---|---|
| Deuterated % C$_2$H$_4$ | 0 | 13 | 31 |
| Relative heights of peaks | $M_2$ | 11 | 35 | 47 |
|                         | $M_3$ | 5 | 31 | 27 |
|                         | $M_4$ | 84 | 34 | 26 |

7.2 kcal at 0.1 mm Hg total pressure, derived from its rate given in table 17, and 8.4 kcal at 20 mm Hg total pressure, as indicated in figure 19.

5.2.6. Kazanskii and Voevodskii [119] analyzed mass-spectrometrically the products of catalyzed deuteration of ethylene at 90, 135, and 185 °C in the presence of palladium plate. Deuteroethylenes were hardly found at all at 90 °C but at higher temperature they were present in large amounts, as shown in figures 20(a), 20(b), and 20(c). The amounts of deuteroethylenes produced at 135 °C, if repres-
TABLE 17. Relative amounts of ethylenes-$d_{n} = E_{n}$ and hydrogens-$d_{n} = H_{n}$ in the reaction product of equimolar mixture of $C_{2}^{1}H_{4}$ and $D_{2}$ of 0.1 mm Hg initial total pressure over S surface of nickel [26, 118] (compiled from table 3 [26])

<table>
<thead>
<tr>
<th>React. temp. $^\circ$C</th>
<th>Deuterated $%$ $C_{2}H_{4}$</th>
<th>Rate of hydrogenation deuterated $%$ $C_{2}H_{4}$ min$^{-1}$</th>
<th>$E_{n}, %$</th>
<th>H$_{n}, %$</th>
<th>Deuterium atom fraction in $C_{2}H_{4}$ $H_{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-45</td>
<td>2</td>
<td>3.5</td>
<td>E$<em>{0}$ 7 E$</em>{1}$ 6 E$<em>{2}$ 8 E$</em>{3}$ 0 E$_{4}$ 0</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.017 0.992</td>
</tr>
<tr>
<td>-23</td>
<td>10</td>
<td>18.2</td>
<td>(93 7 0 0 0) (90 10 0 0 0)</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.025 0.992</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>56.9</td>
<td>(64 10 8 0 0) (64 29 2 0)</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.105 0.970</td>
</tr>
<tr>
<td>28</td>
<td>43</td>
<td>98.0</td>
<td>(66 28 5 0 0) (65 30 5 0 0)</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.103 0.930</td>
</tr>
<tr>
<td>32</td>
<td>41</td>
<td>107.1</td>
<td>(40 36 20 4 0) (37 42 18 3 0)</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.220 0.805</td>
</tr>
<tr>
<td>75</td>
<td>38</td>
<td>97.0</td>
<td>(29 38 24 7 2) (30 42 20 5 3)</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.263 0.555</td>
</tr>
<tr>
<td>110</td>
<td>21</td>
<td>50.2</td>
<td>(21 29 37 10 2) (19 30 38 10 2)</td>
<td>0 1.6 98.4</td>
<td>0 1.6 98.4 0.340 0.665</td>
</tr>
</tbody>
</table>

Parenthesized figures show the relative amounts of $E_{n}$ and $H_{n}$ calculated assuming random distribution of deuterium. Those of $E_{n}$ were calculated according to eq (12.32) with $x_{E0}$ derived from observed values of $X_{E0}$'s by eq (12.21.x). Those of $H_{n}$ were similarly calculated.
TABLE 18. Relative amounts of ethanes-\(d_n\) = \(A_n\) in the product of catalyzed deuteration of 50 mm Hg \(C_2H_4\) with 200 mm Hg \(D_2\) over Pd plate at 135 °C [119]

<table>
<thead>
<tr>
<th>Deuterated % (C_2H_4)</th>
<th>Relative amounts of ethanes-(d_n), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A_0)</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
</tr>
</tbody>
</table>

ethane was not involved in the catalyzed hydrogenation.

5.2.8. Kowaka [121] has investigated the effect of protium and deuterium diffused through palladium, in advance of Apel'baum and Temkin [91], upon \(C_2H_4\), or a mixture of \(C_2H_4\) and \(^1H_2\), or a mixture of \(C_2H_4\) and \(D_2\), respectively, contained inside a palladium thimble, by analyzing mass-spectrometrically the product. The palladium thimble was evacuated, before use, at 800 °C for 2 hr, corroded with \(aqua regia\) on both sides and again evacuated at 800 °C with the aim of removing occluded hydrogen. Protium or deuterium were now let diffuse toward the inside by electrolyzing protium or deuterium oxide, using the external surface of the thimble as a cathode.

Table 19, figure 21(a) and figure 21(b) show the effects of diffused deuterium upon 100 mm Hg \(C_2H_4\) and upon a mixture of 100 mm Hg \(C_2H_4\) and 50 mm Hg \(^1H_2\) inside the thimble, and figure 21(c) that of diffused protium upon a mixture of 100 mm Hg \(C_2H_4\) and 50 mm Hg \(D_2\). An appreciable amount of protium, to be traced back to light ethylene, is evolved as \(^1H_2\) or \(^1HD\), as seen in table 19, although the \(^1HD\)-evolution is suppressed at lower temperature. As shown by figures 21(b) and 21(c), diffused hydrogen is considerably active, and it is remarkable that in the former case the maximum abundance switches over from \(C_2H_4\) to \(C_2H_4D_2\) through the decrease of temperature just by 25 °C.
6. Isotopic Effect on Hydrogenation Rate

The isotopic effect on hydrogenation is defined as

\[ \alpha = \frac{v_h(\text{H}_2)}{v_h(D_2)} \]

where \( v_h(\text{H}_2) \) and \( v_h(D_2) \) are the rates of hydrogenation of \( \text{C}_2\text{H}_4 \) with pure protium and deuterium, respectively, of the same partial pressure under otherwise identical conditions.

6.1. Tucholski and Rideal [67] observed the rates, \( v_h(\text{H}_2) \) and \( v_h(D_2) \), of catalyzed hydrogenation with \( \text{H}_2 \) and \( D_2 \), respectively, in the presence of nickel wire oxidized at 600 °C and reduced at 330 °C. Activity lost by prolonged use was restored by keeping it at 200 °C in ca. 0.1 mm Hg protium or deuterium. The results are shown in Table 20. The optimum temperature is around 139 °C both in the cases of \( v_h(\text{H}_2) \) and \( v_h(D_2) \), as seen from the table, whereas the optimum of \( v_h(D_2) \) was reproducibly located at 160 °C in another series [67] of experiments by the same authors [67].

Table 20. Isotopic effect \( \alpha = v_h(\text{H}_2)/v_h(D_2) \) on hydrogenation rate of light ethylene on Ni wire [67]

<table>
<thead>
<tr>
<th>React. temp., °C</th>
<th>0</th>
<th>17</th>
<th>120</th>
<th>139</th>
<th>165</th>
<th>180</th>
<th>198</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_h(\text{H}_2) ) mm Hg min(^{-1} )</td>
<td>0.40</td>
<td>0.58</td>
<td>3.1</td>
<td>3.36</td>
<td>1.90</td>
<td>1.01</td>
<td>0.81</td>
</tr>
<tr>
<td>( v_h(D_2) ) mm Hg min(^{-1} )</td>
<td>0.24</td>
<td>0.38</td>
<td>2.25</td>
<td>2.54</td>
<td>1.84</td>
<td>1.34</td>
<td>0.54</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1.66</td>
<td>1.52</td>
<td>1.38</td>
<td>1.32</td>
<td>1.03</td>
<td>0.75</td>
<td>1.5</td>
</tr>
</tbody>
</table>

shows that \( \alpha \) decreases gradually with rise of temperature down to unity or below around the optimum and increases with temperature above it.

6.2. Miyahara and Narumi [114] and Miyahara [118] observed the initial rates, \( v_{h,0}(\text{H}_2) \) and \( v_{h,0}(D_2) \), of hydrogenation of light ethylene with equimolar protium or deuterium over a surface of evaporated nickel film at surface state, F, S, or C (cf. 2.8.3), at different temperatures and at different initial total
pressures. Figures 19 and 22 show the results obtained at 20 mm Hg [114] and 0.1 mm Hg [118] initial total pressure, respectively. The values of α derived in both cases of total pressure are shown in figure 23, with curves marked with S, 0.1 mm Hg, etc., which indicate the surface states of the evaporated nickel film and the initial total pressures. The optimum temperatures of hydrogenation with $^1\text{H}_2$, respectively, appropriate to the surface states and the total pressures are shown by vertical chain lines traced, respectively, up to the relevant α-curves. The values of α over the S surface decrease with temperature down to a minimum at the optimum and then increase qualitatively in accordance with the result 6.1. The α-values of carbided film are much higher than those over S surfaces as seen in figure 23.

Table 21. Activation heat and optimum temperature of catalyzed hydrogenation of light ethylene with equimolar protium or deuterium over evaporated nickel films [26, 114, 118]

<table>
<thead>
<tr>
<th>Surface state of evaporated Ni film</th>
<th>Initial total pressure mm Hg</th>
<th>Hydrogen</th>
<th>Activation heat kcal/mole</th>
<th>Optimum temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.1</td>
<td>$^1\text{H}_2$</td>
<td>4.8</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^2\text{D}_2$</td>
<td>7.2</td>
<td>50</td>
</tr>
<tr>
<td>S</td>
<td>20</td>
<td>$^1\text{H}_2$</td>
<td>6.0</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^2\text{D}_2$</td>
<td>8.4</td>
<td>137</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>$^1\text{H}_2$</td>
<td>2.5</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^2\text{D}_2$</td>
<td>2.5</td>
<td>110</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>$^1\text{H}_2$</td>
<td>11.0</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^2\text{D}_2$</td>
<td>11.0</td>
<td>165</td>
</tr>
</tbody>
</table>

Table 21 summarizes the results shown in figure 23. The optimum temperature of deuteration is 20 ~ 40 °C higher than that of hydrogenation with protium over either surface.

![Figure 23. Isotopic effect α versus temperature [118].](image)

![Figure 24a. Catalyzed hydrogenation of ethylene over Cu(+)MgO in four isotopically different cases [103].](image)

![Figure 24b. Catalyzed hydrogenation of ethylene over Cu(+)MgO in cases of C$_2$H$_4$+$^1\text{H}_2$ (broken line) and C$_3$D$_1$+$^1\text{H}_2$ (full line) at different temperatures [103].](image)
6.3. Table 22 shows the results obtained by Klar [104] with an iron catalyst prepared by thermal decomposition of iron oxalate followed by reduction at different temperatures, as shown in figure 24(b). The ratio of the initial rate of $C_2^1H_4 + ^1H_2$ to that of $C_2^1H_4 + D_2$ was found unity at 20 °C with a fresh catalyst but 0.75 over a catalyst whose activity had declined with 20 repeated uses. The activation heats of the reactions of $C_2^1H_4 + ^1H_2$ and $C_2^1H_4 + D_2$ were found to be 11.5 and 12 kcal/mole, respectively, over a fresh catalyst.

### Table 22. Ratio, $\alpha = \nu_\alpha(^1H_2)/\nu_\alpha(D_2)$, between the hydrogenation rates of light ethylene with protium $\nu_\alpha(^1H_2)$, and that with deuterium $\nu_\alpha(D_2)$ over iron catalyst [104]

<table>
<thead>
<tr>
<th>React. temp., °C</th>
<th>0</th>
<th>25</th>
<th>40</th>
<th>55</th>
<th>75</th>
<th>100</th>
<th>125</th>
<th>150</th>
<th>175</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_\alpha(H_2)$</td>
<td>0.005</td>
<td>0.0127</td>
<td>0.0253</td>
<td>0.0517</td>
<td>0.110</td>
<td>0.207</td>
<td>0.271</td>
<td>0.217</td>
<td>0.18</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>2.5</td>
<td>1.69</td>
<td>1.58</td>
<td>1.67</td>
<td>1.22</td>
<td>0.98</td>
<td>0.79</td>
<td>0.56</td>
<td>0.51</td>
</tr>
</tbody>
</table>

6.4. Table 23 shows the isotopic effect on the hydrogenation rate of light ethylene over copper catalyst [122]. The isotopic effect on the homogeneous hydrogenation rate is appended for reference. The catalyst $Cu(+MgO)$ was the reduction product of a mixture of oxides of Cu and Mg. In the presence of the latter catalyst, Joris, Taylor, and Jungers [103] observed the course of hydrogenation of ethylene in four isotopically different cases at 40 °C, as shown in figure 24(a), and also the course of hydrogenation of $C_2^1H_4 + ^1H_2$ and of $C_2D_4 + ^1H_2$ comparatively at catalyst but 0.75 over a catalyst whose activity had declined with 20 repeated uses. The activation heats of the reactions of $C_2^1H_4 + ^1H_2$ and $C_2^1H_4 + D_2$ were found to be 11.5 and 12 kcal/mole, respectively, over a fresh catalyst.

### Table 23. Ratio, $\alpha = \nu_\alpha(^1H_2)/\nu_\alpha(D_2)$, between the hydrogenation rates of light ethylene with protium, $\nu_\alpha(^1H_2)$, and that with deuterium, $\nu_\alpha(D_2)$ over copper catalyst [122]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>React. temp. °C</th>
<th>Initial partial pressure mm Hg</th>
<th>$C_2^1H_4$</th>
<th>$H_2$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu [123]</td>
<td>0</td>
<td>375</td>
<td>375</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cu (+ MgO) [103]</td>
<td>20</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Homogeneous reaction [123]</td>
<td>534 ~ 567</td>
<td>190</td>
<td>580</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

7. Supported Catalysts

7.1. Nickel-kieselguhr catalyst is of frequent practical use for hydrogenation but its behavior is remarkably different from that of unsupported nickel catalysts in the following points.

1. Ethylene or propylene does not polymerize over unsupported reduced nickel powder at 100 °C for several tens of hours but does perceptibly so over 15 percent nickel kieselguhr at 0 °C within 1 hr [124].

2. The exchange of hydrogen atoms between $C_2^1H_4$ and $C_2D_4$ at room temperature [24] is barely perceptible over nickel wire of 730 cm² area, and even at 300 °C it takes more than 3 hr to attain an exchange equilibrium over nickel wire of 990 cm² area [125], whereas the exchange is completed at room temperature within several minutes over 17 ~ 19 wt percent nickel-kieselguhr catalyst [125].

3. No deutoethylene was produced in course
of catalyzed deuteration of light ethylene over 60 wt percent nickel-kieselguhr catalyst both at -50 and +50 °C [126] as shown in table 24, in contrast with the result 5.2.4 (4), which showed that an appreciable amount of deuterioethylene was evolved over unsupported nickel. A mere 0.45 or 5.2 atom percent protium were found [126] in hydrogen gas at -50 or 50 °C, respectively, at the end of the experiments. The absence of deuterioethylene in the deuteration product of light ethylene was also observed by Twigg [116] in the presence of nickel-kieselguhr catalyst as mentioned in 5.2.1.

(4) Table 24 shows no preferential evolution of \( C_2^1H_6 \) in the initial stage of deuteration as found by Turkevich et al. [117] in the presence of unsupported catalyst but constant relative amounts of ethanes-\( d_n \) in the deuteration product, with a maximum at \( n=2 \) (\( C_2^1H_4D_2 \)) irrespective of temperature and extent of deuteration.

7.2. No such distinct differences are found between supported and unsupported catalysts of metals of the platinum group, which cause less dehydrogenated adsorption of ethylene as seen in section 2. Bond [88] investigated the kinetics and the distribution of compounds-\( d_n \) in the deuteration product of \( C_2^1H_4 \) in the presence of platinized Pt, 5 weight percent Pt-pumice, 1 weight percent Pt-alumina, 1 weight percent Pt-silica and 1 weight percent Pt-silica-alumina. One gram of each catalyst was dried in air, evacuated at 200 °C in a reaction vessel of 45 cm³ capacity, pretreated in hydrogen at 200 °C for 12 hr and evacuated. Admitting \( C_2^1H_4 \) first and \( D_2 \) subsequently over the catalyst, the deuteration was followed by total pressure decrease and by mass-spectrometric analysis of the product at different temperatures and partial pressures of reactants. The results indicated, as shown in table 25, that no significant difference exists between the five different platinum catalysts, except that \( C_2^1H_4D_2 \) is distinctly predominant only in the cases of 1 weight percent Pt-silica-alumina and 1 weight percent Pt-silica. Neither is there any distinct difference between the distributions of ethanes-\( d_n \) at 50 and 100 deuterated percents of ethylene under similar conditions of partial pressures as seen in table 24 of nickel-kieselguhr catalyst. Bond et al. [88, 89, 94], also dealt with rates of hydrogen exchange, which is not reviewed here, however, as this was quite unintelligible to the present writers.

| React. temp. °C | React. time min | deuterated % \( C_2^1H_4 \) | Relative amounts of hydrocarbons-\( d_n \), %
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>5</td>
<td>22</td>
<td>( E_0 )</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>87</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>39</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>94</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 24. Relative amounts of ethylene-\( d_n \) = \( E_n \) and ethanes-\( d_n \) = \( A_n \) in the product of catalyzed reaction of 1:10 molar mixture of light ethylene and deuterium over 60 percent Ni-kieselguhr [126].

\( P_{C_2^1H_4}=44.7 \) mm Hg (-50 °C), 64.8 mm Hg (50 °C) (partial pressures computed from reported experimental conditions).
TABLE 25. Relative amounts of ethanes-d~2 = A, in the deuteration product of light ethylene in the presence of platinum catalysts [88]-Continued

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Platinized-Pt</th>
<th>5 Wt % Pt-pumice</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp. °C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( P_{E,0} ) mm Hg</td>
<td>( P_{H,0} ) mm Hg</td>
<td>( P_{E,0} ) mm Hg</td>
</tr>
<tr>
<td>46.9</td>
<td>48.4</td>
<td>50.7</td>
</tr>
<tr>
<td>61.5</td>
<td>60.5</td>
<td>54.8</td>
</tr>
</tbody>
</table>

Relative amounts of A, %

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1 Wt % Pt-alumina</th>
<th>1 Wt % Pt-silica-alumina</th>
<th>1 Wt % Pt-silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp. °C</td>
<td>-18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( P_{E,0} ) mm Hg</td>
<td>( P_{H,0} ) mm Hg</td>
<td>( P_{E,0} ) mm Hg</td>
<td>( P_{H,0} ) mm Hg</td>
</tr>
<tr>
<td>48.8</td>
<td>52.3</td>
<td>52.3</td>
<td>51.3</td>
</tr>
<tr>
<td>70.0</td>
<td>56.0</td>
<td>56.0</td>
<td>60.2</td>
</tr>
</tbody>
</table>

Relative amounts of A, %

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A0</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{E,0} ) mm Hg</td>
<td>0.9</td>
<td>1.4</td>
<td>1.8</td>
<td>0.6</td>
<td>0.5</td>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
<td>( P_{H,0} ) mm Hg</td>
<td>27.1</td>
<td>28.4</td>
<td>30.1</td>
<td>30.6</td>
<td>29.6</td>
<td>31.0</td>
<td>20.9</td>
</tr>
</tbody>
</table>

Table continues with similar data for other catalysts and conditions.
TABLE 26. Relative amounts of ethanes-\(d_n\) = \(A_n\) and ethylene-\(d_n\) = \(E_n\) in

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pt</th>
<th>Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp. °C</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>(P_{H_2} 0) mm Hg</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>(P_{H_2} 0) mm Hg</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

Deuterated % \(C_2H_4\)

| \(A_0\) | 10.0 | 19.2 | 19.3 | 9.5 | 4.9 | 8.2 | 5.7 |
| \(A_1\) | 32.6 | 27.2 | 28.2 | 24.3 | 11.2 | 13.0 | 11.1 |
| \(A_2\) | 37.8 | 23.2 | 25.6 | 26.8 | 23.9 | 14.6 | 28.2 |
| \(A_3\) | 6.8 | 10.5 | 8.7 | 7.5 | 4.3 | 2.2 | 5.2 |
| \(A_4\) | 3.3 | 6.4 | 4.9 | 4.2 | 2.9 | 0.5 | 2.4 |
| \(A_5\) | 1.9 | 3.0 | 2.3 | 1.5 | 1.7 | 0.3 | 1.3 |
| \(A_6\) | 0.8 | 0.5 | 0.4 | 0.5 | 0.2 | 0.1 | 0.9 |

Less than 10 for all cases

| \(E_0\) | 6.0 | 7.4 | 9.2 | 19.6 | 36.5 | 44.0 | 32.8 |
| \(E_1\) | 0.8 | 2.7 | 1.2 | 4.5 | 8.6 | 11.4 | 6.6 |
| \(E_2\) | 0.0 | 0.8 | 0.2 | 1.3 | 3.9 | 4.7 | 3.4 |
| \(E_3\) | 0.0 | 0.0 | 0.3 | 2.1 | 1.0 | 2.4 |

Less than 15 for all cases

8. Carbided Catalysts

The activity of metallic catalysts, especially nickel, declines in general irreversibly, as mentioned in 2, on account of adsorbed complex produced by dehydrogenated adsorption of ethylene. Jenkins and Rideal [13] prepared a carbided surface by keeping an evaporated film in ethylene at 190 °C for 30 min. They found that the rate of hydrogenation over the carbided surface was quite reporducible, although smaller than that over the freshly evaporated surface by a factor of several tens. Taking advantage of this reporducibility they investigated the rate law on the carbided surface and discussed the mechanism of hydrogenation. This procedure has been extended to supported Ni [82, 83], Pd foil [87] and Pt wire [87], but it is questionable whether the carbided surface preserves any intrinsic property of the basic metal surface.

8.1. Miyahara [26, 118] observed the adsorption of ethylene and hydrogen by the catalyst in the course of the hydrogenation of light ethylene, the kinetics of the hydrogenation, the hydrogen exchange between ethylene molecules and the distribution of deuterium in the product of catalyzed deuteration over F (fresh), S (once used for a run of hydrogenation) and C (carbided) surfaces of evaporated nickel film; the conclusion was that F and S behaved similarly to each other, except that the dehydrogenated adsorption of ethylene was inhibited over S, while C behaved quite differently from both F and S. The activity of C is smaller than that of S by a factor of several tens; apart from that, C differs from S in the following points:

(a) Ethylene is adsorbed by S and C approximately to the same extent in course of the catalyzed

![Figure 25. Initial hydrogenation rate, \(v_{H_2} \text{protium}\), of light ethylene with equimolar protium over carbided surface versus \(10^9/T\) K [118].](attachment:image.png)

\(v_{H_2} \text{protium}\) is the initial value of \(v\) given in hydrogenated percent \(C_2H_4\) min\(^{-1}\). Figures attached to a curve indicate the initial total pressure and the activation heat determined from the part of the curve over the range of lower temperature.
the deuteration product of light ethylene over 5 mole % metal-\(\gamma\) alumina [89, 95]

<table>
<thead>
<tr>
<th>Ru</th>
<th>Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>54</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>54</td>
<td>165</td>
</tr>
<tr>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

hydrogenation, whereas hydrogen is appreciably adsorbed only by S but not by C (cf. table 2) [26].
(b) The optimum temperature of hydrogenation over C is ca. 30 °C higher than that over S (cf. figs. 13, 19, and 22 and table 21) [118].
(c) The activation heat over S at temperatures below the optimum is 5~6 kcal/mole and practically independent of the total pressure of the reactant gas mixture, whereas that on C below the optimum increases from 2.5 to 11 kcal/mole with increase of the total pressure from 0.1 to 20 mm Hg [118] (cf. table 21 and figs. 19, 22, and 25).
(d) The distribution of deuterium in hydrogen in course of the catalyzed deuteration of light ethylene is equilibrated over C, whereas it is not over S, although the deuterium in ethylene is of random distribution in both the cases [118] (cf. tables 17 and 27).

<table>
<thead>
<tr>
<th>Deuterated</th>
<th>Rate of deuteration deutereated % C(_2)H(_4)·min(^{-1})</th>
<th>E(_n), %</th>
<th>H(_n), %</th>
<th>Deuterium atom fraction in</th>
<th>React. temp. °C</th>
<th>Deuterated % C(_2)H(_4)</th>
<th>Rate of deuteration deutereated % C(_2)H(_4)·min(^{-1})</th>
<th>E(_n), %</th>
<th>H(_n), %</th>
<th>Deuterium atom fraction in</th>
</tr>
</thead>
<tbody>
<tr>
<td>-23</td>
<td>1.2</td>
<td>0.86</td>
<td>88</td>
<td>12</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2 (0.1)</td>
<td>5.8 (94.1)</td>
<td>0.032 (0.970)</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>1.26</td>
<td>80</td>
<td>18</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3 (0.2)</td>
<td>6 (91.4)</td>
<td>0.055 (0.956)</td>
</tr>
<tr>
<td>70</td>
<td>6.4</td>
<td>3.16</td>
<td>16</td>
<td>32</td>
<td>32</td>
<td>15</td>
<td>4</td>
<td>53 (53.0)</td>
<td>40 (39.6)</td>
<td>0.368 (0.272)</td>
</tr>
<tr>
<td>110</td>
<td>3.1</td>
<td>3.75</td>
<td>19</td>
<td>32</td>
<td>32</td>
<td>14</td>
<td>3</td>
<td>53 (53.0)</td>
<td>40 (39.6)</td>
<td>0.340 (0.272)</td>
</tr>
<tr>
<td>160</td>
<td>3.1</td>
<td>2.12</td>
<td>21</td>
<td>32</td>
<td>31</td>
<td>13</td>
<td>3</td>
<td>50 (50.0)</td>
<td>42 (41.4)</td>
<td>0.323 (0.293)</td>
</tr>
</tbody>
</table>
9. Reaction Mechanisms

Representative mechanisms are here reviewed which have been selected from those put forward up to now for the catalyzed hydrogenation in the presence of metals, especially nickel. It is the concept of the rate-determining step, that is indispensable in dealing with mechanisms. Confusions arise often, however, by giving it an ambiguous definition and unconvincing applications. Therefore, a definition of the rate-determining step is advanced and its application illustrated by mechanisms here.

9.1. Dissociative Mechanism

Farkas and Farkas put forward a mechanism on the basis of experimental results of the catalyzed hydrogenation as well as of the associated reactions, i.e., parahydrogen conversion and $^{1}H_2$–$D_2$ equilibration, over nickel [2] and platinum catalysts [85]. They assumed that the rate-determining step of the catalyzed hydrogenation as well as of parahydrogen conversion was the dissociative adsorption of hydrogen molecules, i.e.,

$$H_2 \rightarrow 2\text{H(a)}, \quad (9.1)$$

on the grounds that hydrogenation and parahydrogen conversion had activation heats of the same magnitude, i.e., 10–11 kcal/mole, and a constant ratio of rates throughout in spite of a widely varying activity of platinum catalysts [85]. Ethylene was assumed, on the other hand, to be adsorbed as

$$C_2\text{H}_4 \rightarrow C_2\text{H}_4(a) \quad (9.2)$$

and combine with 2H(a) so as to complete the hydrogenation thus

$$C_2\text{H}_4(a) + 2\text{H(a)} \rightarrow C_2\text{H}_6. \quad (9.3)$$

The exchange reaction of ethylene was assumed by them to occur separately, through a step of dissociation of ethylene, i.e.,

$$C_2\text{H}_4(a) \rightarrow C_2\text{H}_3(a) + \text{H(a)}, \quad (9.4)$$

(hence the name "dissociative mechanism"), on the grounds that the activation heat of exchange was greater than that of catalyzed hydrogenation both over nickel [2] and platinum [85] as reviewed in 5.1.2 and 5.1.3, respectively.

They attributed parahydrogen conversion and $^{1}H_2$–$D_2$ equilibration to step (9.1) and its reverse, on the one hand, and their inhibition to the preoccupation of sites of these reactions by ethylene, on the other hand. However, the inhibition follows necessarily from the proposed rate-determining step (9.1) irrespective of the preoccupation, since ethylene consumes the "moving spirits," H(a)'s, of the reverse of step (9.1) at a rate greater than that of the proposed rate-determining step (9.1).

9.2. Associative Mechanism

9.2.1. Horiuti and Polanyi [7] found that the rate of exchange between ethylene and water was smaller than that between ethylene and hydrogen by a factor of ca. $10^{5}$ and that the exchange rate between ethylene and benzene under the same conditions was still smaller [7] by orders of magnitude. On this experimental basis, they discussed step (9.4) as proposed to be responsible for the exchange. Let step (9.4) be in partial equilibrium; $C_2\text{H}_4(a)$ is admitting H(a)'s through its reverse including such ones originating from other molecules. The rate of the picking up is that of the reverse of step (9.4), i.e., a "unimolecular" dissociation; the rate of the latter is constant irrespective of the activity of H(a), apart from the effect of adsorption, hence the rate of picking up H(a) is constant as well. Step (9.4) can hence not be responsible for the exchange, insofar as the absorption does not make a difference of orders of magnitude such as observed.

Horiuti and Polanyi [7], thus put forward with reference to the experimental results [7], of the wandering of the double bond, the scheme

$$C_2\text{H}_4 \rightarrow C_2\text{H}_4(a) \xrightarrow{I_3} C_2\text{H}_5(a) \xrightarrow{II} C_2\text{H}_5(a) \xrightarrow{III} C_2\text{H}_6, \quad (9.5)$$

where $C_2\text{H}_4(a)$ represents so-called associatively adsorbed ethylene, in which the $\pi$-bond of ethylene is broken and two carbon-metal bonds are formed, and $C_2\text{H}_5(a)$, termed "half-hydrogenated state" by them [7], is an ethyl radical linked with the metal by its methylene radical. The two hydrogen atoms...
from a methylene radical of C2H4(a) and one from H(a) assume equivalent positions in the methyl radical of C2H5(a), so that the exchange results on reversal of steps II.

Step II in partial equilibrium is accelerated by increase of the activity of H(a), hence its backward act must be likewise accelerated. The rate of C2H4(a) embodying hydrogen atoms from H(a) depends in consequence on the activity of H(a), in distinction from the case where dissociation (9.4) is responsible for exchange. The exchange rate of hydrogen atoms between ethylene and water or benzene is hence by far smaller than that between ethylene and hydrogen, as observed, owing to their widely divergent capacities of sustaining the activity of H(a).

9.2.2. Scheme (9.5) is now discussed with special reference to the rate-determining step of the relevant overall reaction. The rate-determining step is defined only for such an overall reaction where each of the constituent steps has unique, definite stoichiometric number [127]. The constituent step r of a stoichiometric number different from zero, is defined as rate-determining if the steady rate of the overall reaction is given practically as that in the equilibria of all constituent steps but r. These partial equilibria determine the activity products, a1 and a2, of the initial and the final system of r, irrespective of the kinetic particulars of any step. The net rate of r is \( k_{a1} - k_{a2} \) or \( k_{a1} - k_{a2}/K \), where K = \( k_{a1}/k_{a2} \) is the equilibrium constant of r, which is thermodynamically definite irrespective of the kinetic particulars of r. The steady rate of the overall reaction is thus proportional to \( k_i \), which alone involves the kinetic particulars of r, while the other factor, \( a_1 - a_2/K \), of the net rate is thermodynamically defined by the system of step r and the conditions of the assembly in which the reaction in question is going on. Step r thus literally determines the steady rate of the overall reaction through its kinetic particulars which are exclusively incorporated in \( k_i \).

9.2.2.1. A rate-determining step cannot be defined in this way, e.g., for parahydrogen conversion in gear with the overall reaction. Neither is it necessary to assign a similar concept to this conversion, as seen later. We should admit a wording like “the rate-determining step of parahydrogen conversion,” if this occurs in gear with the hydrogenation, as designating a step assumed (by the broacher of the wording) to have the same rate as the parahydrogen conversion in question.

The rate-determining step of scheme (9.5) is now discussed on this basis. It is noted that step III may be rate-determining, but it can never be in partial equilibrium since it practically lacks backward acts, as verified by result 5.2.7 that ethane is never involved in any constituent step of the catalyzed hydrogenation of ethylene. Nevertheless, any step other than III, e.g., Ia may be qualified as rate-determining, if \( k_{a1}/k_{a2} \) is diminished by an amount which is ignorable as compared with \( k_{a1}/k_{a2} \), by reducing all steps but Ia (inclusive of III) from the actual steady state to equilibria.

9.2.2.2. Let III be rate-determining, leaving the other three steps in their respective partial equilibria. A step is kept in partial equilibrium notwithstanding the progress of the overall reaction, which of course imposes a finite amount of net rate upon the step, insofar as its forward and backward rates are large enough as compared with their difference, i.e., the net rate. There hence occurs a lively exchange of hydrogen atoms between gaseous ethylene and hydrogen, as seen readily by tracing scheme (9.5) with step III supposed to be arrested. Parahydrogen conversion and \(^1\text{H}_2\text{D}_2\) equilibration proceed just as in the absence of ethylene, apart from the effect, if any, of preoccupation of sites by adsorption. Deuterium atoms are randomly distributed over C2H4, H2 and C2H6 composed of the former two throughout.

9.2.2.3. If step II is to determine the rate, leaving steps Ia and Ib in their partial equilibria, transfer of hydrogen atoms between gaseous ethylene and gaseous hydrogen is retarded in either direction. Parahydrogen conversion and \(^1\text{H}_2\text{D}_2\) equilibration proceed as lively as in 9.2.2.2.

9.2.2.4. In case of Ib determining the rate, leaving Ia and II in their partial equilibria, admission of hydrogen atoms originating from gaseous ethylene into gaseous hydrogen, is retarded whereas the reverse transfer occurs. Parahydrogen conversion and \(^1\text{H}_2\text{D}_2\) equilibration are practically inhibited.

9.2.2.5. If Ia determines the rate, leaving Ib and II in their partial equilibria, parahydrogen conversion and \(^1\text{H}_2\text{D}_2\) equilibration will occur as in the absence of ethylene and hydrogen atoms from ethylene penetrate hydrogen while the reverse transfer is retarded on the contrary to the case of 9.2.2.4. Hydrogen atoms are randomly distributed over gaseous hydrogen and C2H4(a), but not over gaseous ethylene and C2H4(a) throughout; in the particular case of hydrogenation of light ethylene with pure deuterium C2H4(a) is exclusively C2D4(a) so that gaseous ethylene should consist in the beginning of the hydrogenation only of C2^1H4 and C2D4 but not of ethylene-dn of intermediate composition.

9.2.3. Tables 3 and 17 show that deuterium in gas keeps its atom fraction of 0.992 at -23 and -45 °C, amply below the optimum at 28 °C, during the catalyzed deuteration of light ethylene. Protium of ethylene got thus hardly into gaseous hydrogen, whereas an appreciable amount of deuterium atoms entered gaseous ethylene and became distributed randomly there as seen by comparison of the observed percentage of ethylenes-dn with calculated value shown in parentheses. The tables show, on
the other hand, that above the optimum there occur a rapid exchange between gaseous ethylene and deuterium and a lively $^1$H$_2$–D$_2$ equilibration, the results below the optimum fit in exclusively with the conclusions of 9.2.2.4, while those above the optimum fit in exclusively with those of 9.2.2.2. We are thus inevitably led to the conclusion that the rate-determining step switches over from $I_0$ below the optimum to III above.

The same conclusion has previously been arrived at by Horiuti [9] from the analysis of experimental results of zur Strassen [64]. It may be noted that the switchover in the rate-determining step is necessarily connected with the appearance of an optimum, the excess of activation heat of exchange over that of hydrogenation and other profiles of the reaction, as shown by a statistical mechanical theory developed in section 12.

The term “associative mechanism” will be used in what follows just to signify the kinetic theory of scheme (9.5) without specializing in any particular rate-determining step.

9.2.4. The chemisorbed states, H(a) etc., included in scheme (9.5), are experimentally verified as follows. Parahydrogen conversion and $^1$H$_2$–D$_2$ equilibration proceed over evaporated nickel films perceptibility around $-100\, ^\circ\mathrm{C}$ with a rate increasing with temperature [128], whereas the transition from “normal” to “activated” adsorption with low or high adsorption heat respectively occurs around $-150\, ^\circ\mathrm{C}$ as traced on an isobar [129] of hydrogen adsorption over the same catalyst. These experimental results afford the basis for accepting the existence of H(a) under the conditions in question.

Pliskin and Eischens [130] demonstrated infrared-spectrometrically the existence of associatively adsorbed ethylene, C$_2$H$_4$(a), and the formation of ethyl radical, C$_2$H$_3$(a), from C$_2$H$_4$(a) on admission of hydrogen gas over adsorbed ethylene. Ethylene and hydrogen are adsorbed simultaneously on S-film without dehydrogenated adsorption of ethylene as referred to in 2.E.1, which further confirms the existence of three intermediates H(a), C$_2$H$_4$(a), and C$_2$H$_3$(a) there.

9.2.5. The experiment of Apelbaum and Temkin [91] on palladium indicates unambiguously a definite fall of fugacity from gaseous hydrogen to adsorbed hydrogen on the catalyst at 22 °C but none at 176 °C. Step $I_0$ is thus rate-determining at lower temperatures and in partial equilibrium at higher temperatures, in accord with a similar conclusion in 9.2.3 in the case of nickel.

### 9.3. Twigg and Rideal’s Mechanism

9.3.1. Twigg and Rideal [68] contradicted the dissociative adsorption (9.4) of ethylene as responsible for the exchage reaction on the ground of Conn and Twigg’s experiment [23] referred to in 9.7, which showed that C$_2$H$_4$ and C$_2$D$_4$ did not exchange hydrogen atoms at 76 °C. Twigg and Rideal [68] found, as reviewed in 5.1.2, that $^1$H$_2$–D$_2$ equilibration was inhibited by the presence of ethylene, and that the plot of the nonequilibrium fractions $1-u$ of hydrogen gas against its deuterium atom fraction, $x_H$, converted into a single straight line for temperatures below and including 156 °C, as seen in figure 16. From these experimental results they gathered [68] that $^1$H$_2$–D$_2$ equilibration was not effected by step (9.1) but, as suggested by the latter close connection between equilibration and exchange, was alternatively in gear with steps resulting in the exchange between ethylene and hydrogen, as

\[ C_2H_4 \rightleftharpoons C_2H_3(a), \]

\[ C_2H_4(a) + H_2(a) \rightleftharpoons C_2H_3(a) + H(a), \tag{9.6} \]

and

\[ C_2H_3(a) \rightleftharpoons C_2H_4(a) + H(a), \tag{9.7} \]

where H(a) is the physically adsorbed hydrogen molecule.

They attributed the hydrogenation, on the other hand, to a single step

\[ C_2H_4(a) + H_2(a) \rightarrow C_2H_6 \tag{9.8} \]

on the ground that the activation heat of exchange exceeded appreciably that of hydrogenation [68, 69]. This mechanism of hydrogenation should lead, however, to different products when light ethylene is hydrogenated, in one case with an equimolar mixture of $^1$H$_2$ and D$_2$, and in the other case with an equilibrated mixture of $^1$H$_2$, $^1$HD, and D$_2$. This is contrary to the observation of Twigg [116] in 5.2.1, provided that the peculiarities of nickel-kieselguhr used in the latter observation are ignored.

9.3.2. Twigg has thus revised the mechanism as [116]

\[
\begin{align*}
C_2H_4 & \overset{\frac{1}{2}}{\underset{x}{\rightarrow}} C_2H_3(a) \\
C_2H_4(a) + H_2(a) & \overset{\frac{1}{4}}{\underset{x}{\rightarrow}} C_2H_3(a) + H(a) \overset{x}{\rightarrow} C_2H_6 \\
C_2H_3(a) & \overset{\frac{5}{6}}{\underset{x}{\rightarrow}} C_2H_4(a) + H(a)
\end{align*}
\tag{9.9}
\]

with the aim to account for the observed difference between the activation heats of hydrogenation and of exchange, by ascribing, respectively, different rate-determining steps to them similarly to the proposal of Twigg and Rideal [68] reviewed in 9.3.1. The rate-determining steps of hydrogenation and
exchange were thus indicated to be steps 7 and 4, respectively, which have the same initial system, hence give rise to the same rate law for both the reactions, as observed.

Twigg [116] assumed next that below the optimum, step 7 was overwhelmingly faster than step 4. If, then, the system $\text{C}_2\text{H}_3(a) + \text{H}(a)$ is once created by step 3, it should be converted with predominant probability into $\text{C}_2\text{H}_4$ rather than reconverted into $\text{C}_2\text{H}_3(a) + \text{H}(a)$ through step 4. Step 3 thus determines the rate of hydrogenation, rather than step 7, in conflict with Twigg's statement. This is, however, just a contradiction in terms and, remaining true to the postulated predominance of step 7, his arguments apply just by terminological revision. The rate of rate-determining step 3 is $k_3\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$, denoting the rate constant of step $n$ by $k_n$ and the respective coverages by adsorbates $\text{C}_2\text{H}_4(a)$ etc. by $\theta_{\text{C}_2\text{H}_4}$ etc. The latter rate is written, admitting the proportionality of $\theta_{\text{H}}$ to $P_\text{H}$, as $k_3\theta_{\text{C}_2\text{H}_4}P_\text{H}$, which just reproduces the rate expression of the catalyzed hydrogenation given by Twigg himself. The steady state condition of hydrogenation is now

$$k_3\theta_{\text{C}_2\text{H}_4}P_\text{H} - k_4\theta_{\text{C}_2\text{H}_4}\theta_\text{H} = k_7\theta_{\text{C}_2\text{H}_4}\theta_\text{H}. \quad (9.10)$$

Hence, we have below the optimum

$$k_3\theta_{\text{C}_2\text{H}_4}P_\text{H} = k_7\theta_{\text{C}_2\text{H}_4}\theta_\text{H}, \quad (9.11)$$

ignoring the rate of step 4 as compared with that of 7 according to the postulate. The rate of exchange is similarly $k_3\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$ or, according to eq (9.11), $k_3(k_4/k_7)\theta_{\text{C}_2\text{H}_4}P_\text{H}$, which assures the rate law of exchange to be the same as that of hydrogenation.

Above the optimum, it follows from postulate $k_4 \gg k_7$ and eq (9.10) that the forward and backward rates of step 3 are balanced with each other, hence that step 7 functions as the rate-determining step, provided that step 1 is also in partial equilibrium. We are thus led to concluding from the kinetic postulates of Twigg that the part of determining the rate of hydrogenation is switched over from step 3 below the optimum to step 7 above.

As shown by Twigg [116], the activation heat of exchange exceeds that of hydrogenation above and below the optimum by $E_4 - E_7$ throughout, where $E_i = RT\Delta \ln k_i/oT$ and $E_7 = RT\Delta \ln k_7/oT$. The difference $E_4 - E_7$ below the optimum is the difference of the activation heat of the reverse of step 3 from that of rate-determining step 3 as seen from the above expression for the exchange rate, $k_3(k_4/k_7)\theta_{\text{C}_2\text{H}_4}P_\text{H}$; the forward flow of the exchange rate, $k_3\theta_{\text{C}_2\text{H}_4}P_\text{H}$, is sparingly reversed, to a ratio of $k_4$ to $k_7$, to form the backward flow giving rise to the exchange. The ratio $k_4/k_7$ in the expression for the backward flow is connected with the difference between heights of the two energy humps which enclose $\text{C}_2\text{H}_3(a) + \text{H}(a)$ as $RT\Delta \ln(k_4/k_7)/oT = E_4 - E_7$. Above the optimum, $k_4/k_7$ equals directly the ratio of exchange rate to hydrogenation rate, the latter now being governed by step 7, hence the difference is once again $E_4 - E_7$.

The above inference would illustrate that the difference of activation heats provides no ground to exclude the reverse of step (9.1), assigned to be the rate-determining step of hydrogenation, as done by Farkas et al. [2], from being the "rate-determining step of exchange." It may be noted, however, that the switchover of the rate-determining step that follows from the postulate of Twigg, can only occur, according to the statistical mechanical theory of the reaction developed in 11 and 12, between steps having systems of different materials, such as steps I_b and III of scheme (9.5), but it can scarcely occur otherwise, cf. steps 3 and 7 in scheme (9.9).

### 9.4. Jenkins and Rideal's Mechanism

Jenkins and Rideal [13] revised the above mechanism supposing that the catalyst's surface was complex covered or carbided and capable of adsorbing further hydrogen but no more ethylene.\(^{18}\)

\(^{15}\) The initial and final systems of a step are its system, respectively, in the state before and after the occurrence of the step.

\(^{16}\) Equation (9.10) is expressed for $k_3 \ll k_4$ as

$$\theta_{\text{C}_2\text{H}_4}P_\text{H} = k_4\theta_{\text{C}_2\text{H}_4}\theta_\text{H} \gg k_4\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$$

\(^{17}\) The $\Delta s$ are adsorbate coverages defined in the text; the first and the third member are the rates of step 3 and 4, respectively, which are by no means balanced, hence step 3 is by far not in partial equilibrium. We can bring the latter step up to equilibrium by increasing $\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$ by a factor $k_4/k_6$. The rate of step 7 thus increases $k_4/k_6$ fold. Since the latter increased rate does not approximate by any means the steady rate, step 7 is excluded from being rate-determining according to 9.2.2.

Step 3 is now similarly examined. By reducing step 7 to its partial equilibrium, $\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$ vanishes when the rate of hydrogenation is $k_3\theta_{\text{C}_2\text{H}_4}P_\text{H}$ rather than $k_4\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$. The rate of step 7 thus increases $k_4/k_6$ fold. Since $k_4\theta_{\text{C}_2\text{H}_4}\theta_\text{H}$ is negligibly small by premise, the steady rate is closely approximated by that in equilibrium of step 7, i.e., $k_3\theta_{\text{C}_2\text{H}_4}P_\text{H}$.

Step 3 is thus duly rate-determining according to 9.2.2, provided that step 1 is also practically in equilibrium.

An actual example of the similar rate-determining step is given in 13.4.2.

\(^{18}\) Materials of systems of step I_b and III of scheme (9.5) are $\text{H}_2$ and $\text{C}_2\text{H}_4 + \text{H}_2$, respectively, whereas those of steps 3 and 7 are commonly $\text{C}_2\text{H}_3 + \text{H}_2$.

\(^{19}\) Just contrary to result 8.1(a).

The exchange was postulated to occur under these conditions through a step

$$\text{C}_2\text{H}_4 + 2\text{H}(a) \rightleftharpoons \text{C}_2\text{H}_3(a) + \text{H}(a),$$

in which one of the two adjacent adatoms is picked up, whereas both of them are captured to complete the hydrogenation as

$$\text{C}_2\text{H}_4 + 2\text{H}(a) \rightarrow \text{C}_2\text{H}_6. \quad (9.12)$$

They postulated further that the reverse of step (9.1) occurs slower than step (9.12) at temperatures below and faster above the optimum, respectively. Below the optimum, 2H(a) once formed by step (9.1) should be converted almost certainly into $\text{C}_2\text{H}_3$ by step (9.12) rather than reconverted into $\text{H}_2$, so that step (9.1) is essentially rate-determining for hydrogenation, while above the optimum step (9.12) determines the rate, as shown by arguments.
similar to those on steps 3 and 7 in 9.3.2. The rate-determining step of hydrogenation thus switches over from step (9.1) below the optimum to step (9.12) above, which is something in common with the associative mechanism outlined in 9.2.1.

Beeck [6] proposed, in advance of the above revision [13], that the hydrogenation proceeded through step (9.12) and its rate-determining step was the evacuation by hydrogenated desorption of sites for adsorption of $2\text{H(a)}$ preoccupied by acetylenic complex, although this is inapplicable as remarked in 3.1.3.

9.5. Redistribution Mechanism

We have seen in 7.1.3 that hardly any deuterium enters the ethylene in gas in course of its catalyzed deuteration over Ni-kieselguhr catalyst, while deuterium is abundantly contained and randomly distributed in the ethane molecules thus evolved. This result admitted, according to Wilson, Otvos, Stevenson, and Wagner [126], of no explanation by mechanisms proposed up to that time. They put forward, for an explanation, the redistribution mechanism in which a rapid exchange of hydrogen atoms among "adsorbed hydrocarbon fragments," e.g., $\text{C}_2\text{H}_4(\text{a})$ or $\text{C}_2\text{H}_5(\text{a})$, on the catalyst effected an exchange equilibrium or random distribution of deuterium atoms among them as well as the hydrogenation through steps such as

$$2\text{C}_2\text{H}_5(\text{a}) \rightarrow \text{C}_2\text{H}_4(\text{a}) + \text{C}_2\text{H}_6.$$ 

They [126] reproduced the fractions of ethanes-$d_n$ at $-50 \degree C$ in table 24 approximately by its probability $\left\{6!/(n!(6-n)!\right\}x^n(1-x)6-n$ in random distribution, but the peak of distribution at $n=2$ observed in $50 \degree C$ was not thus reproduced. They similarly calculated the fraction of butane-$d_2$ in the deuteration product of light butylene, but the calculated abundance of butane-$d_2$ fell appreciably short of observation.

9.6. Adsorbed State of Intermediates

With special reference to the adsorbed state of the intermediates implied, Semenov [131] proposed the constituent steps of catalyzed hydrogenation in terms of free valencies, $V$, furnished by metal atoms of the catalyst. Ethylene is thus combined with $V$ to form a free radical as

$$\text{C}_2\text{H}_4 + V \rightarrow V\text{CH}_2\text{CH}_2.). \quad (9.13)$$

The free radical reacts upon $H_2$ to form $\text{C}_2\text{H}_5(\text{a})$ or upon another $V$ to form a stable $\text{C}_2\text{H}_4(\text{a})$ as

$$V\text{CH}_2\text{CH}_2+ + H_2 \rightarrow V\text{CH}_2\text{CH}_3 + H \quad (9.14)$$

or

$$V\text{CH}_2\text{CH}_2+ + V \rightarrow V\text{CH}_2\text{CH}_2V.$$ 

The $H$ formed by step (9.14) is so unstable that it attacks $\text{C}_2\text{H}_5(\text{a})$ to form ethane as

$$H + V\text{CH}_2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + V.$$ 

In the case where sufficient $\text{C}_2\text{H}_4(\text{a})$ and $\text{C}_2\text{H}_5(\text{a})$ are present, there occur frequently forward and backward acts of the steps

$$H + V\text{CH}_2\text{CH}_2V \rightarrow V\text{CH}_2\text{CH}_3 + V$$

and

$$VH + V\text{CH}_2\text{CH}_2V \rightarrow V\text{CH}_2\text{CH}_3 + V.$$ 

and the $V\text{CH}_2\text{CH}_2V$'s react upon each other to form polymer, which poisons the catalyst. Semenov [131] did not refer to step (9.1) of hydrogen chemisorption in this connection.

Bond et al. [132], has recently advanced the view that the bonds which link ethylene to metal are not $\sigma$-bonds as admitted so in 3.1.2, but $\pi$-bonds between surface metal atoms and ethylene, with the double bond of $\text{C}_2\text{H}_4$ left intact, as in the case of complex compounds between olefine and metal salts, which is, however, not verified thus far and, if it should be at all, makes no difference in the kinetic treatments.

10. Current Theoretical Treatments

10.1. Outline

The rate $v$ of combination, e.g., of species A and B distributed homogeneously in a macroscopic phase is expressed according to the mass action law in terms of the concentrations, $[A]$ and $[B]$, of the respective species as

$$v = k_{AB} [A][B].$$
\[ v \propto [A][B]. \] (10.1)

If either or both of species A and B are adsorbed, as denoted by appendix (a), i.e., as A(a) or B(a), the rate of combination is usually expressed by

\[ v \propto \theta_A[A] \] (10.2.A)

or

\[ v \propto \theta_A\theta_B, \] (10.2.B)

where \( \theta_A \) and \( \theta_B \) are the fractions of the catalyst surface covered by A and B, respectively.

Schwab [133] expressed the rate of the step

\[ H_2(a) + C_2H_4(a) \rightarrow C_2H_6, \]

assumed by him to be rate-determining in the catalyzed hydrogenation of rate \( v_h \) according to eq (10.2.B) as

\[ v_h = k_h b_E b_H P_H (1 + b_E P_E)^{-1}, \] (10.3)

substituting \( \theta_{C_2H_4} \) in eq (10.2.B) from Langmuir's adsorption isotherm:

\[ \theta_{C_2H_4} = b_E P_E (1 + b_E P_E)^{-1}, \] (10.4)

and similarly for \( \theta_H \):

\[ \theta_H = b_H P_H (1 + b_H P_H)^{-1}, \]

but ignoring \( b_H P_H \) as compared with unity, where \( k_h \) is the so-called "true" rate constant. Schwab [133] assumed that \( b_E P_E \gg 1 \) above the optimum and \( b_E P_E \ll 1 \) above the optimum, hence according to eq (10.4) that \( \theta_{C_2H_4} \approx 1 \) or \( \theta_{C_2H_4} \approx 0 \), respectively, or in words that ethylene saturates the catalyst's surface below the optimum but is desorbed as the temperature is raised past the optimum, \( T_X \). The rate laws below and above the optimum are, in consequence,

\[ v_h = k_h b_H P_H \quad (T < T_X) \]

and

\[ v_h = k_h b_E b_H P_E P_H \quad (T > T_X), \]

and the activation heats below the optimum, \( E_{T < T_X} \), and above the optimum, \( E_{T > T_X} \), are

\[ E_{T < T_X} = E_0 + \Delta H_H \] (10.5.a),

and

\[ E_{T > T_X} = E_0 + \Delta H_H + \Delta H_E = E_{T < T_X} + \Delta H_E, \] (10.5.b)

respectively, where

\[ E_0 = RT^2 \frac{\partial}{\partial T} \ln k_h \] (10.6.k)

is the so-called "true" activation heat and

\[ -\Delta H_E = -RT^2 \frac{\partial}{\partial T} \ln b_E \] (10.6.E),

and

\[ -\Delta H_H = -RT^2 \frac{\partial}{\partial T} \ln b_H \] (10.6.H)

are the adsorption heats of ethylene and hydrogen, respectively. Schwab [133] determined, from the plot of \( v_h/PH \) against \( P_E \) by zur Strassen [64] as shown in figure 26, \( k_h b_H \) and \( b_E \) and hence \( ET<TX \) and \( \Delta H_E \) as

\[ FIGURE 26. Proportional constant \( v_h/PH \) of \( v_h \) to \( P_H \) versus \( P_E \) [64]. \]

<table>
<thead>
<tr>
<th>( P_E ) (mmrHg)</th>
<th>( v_h/PH )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>( x )</td>
</tr>
<tr>
<td>0.04</td>
<td>( O )</td>
</tr>
<tr>
<td>0.06</td>
<td>( + )</td>
</tr>
<tr>
<td>0.08</td>
<td>( - )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( v_h/PH )</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>( 0 )</td>
</tr>
<tr>
<td>92</td>
<td>( x )</td>
</tr>
<tr>
<td>67</td>
<td>( O )</td>
</tr>
<tr>
<td>45</td>
<td>( + )</td>
</tr>
</tbody>
</table>

\( E_{T < T_X} = 7.3 \text{ kcal/mole}, \) (10.7.E),

\( E_{T > T_X} = 17.3 \text{ kcal/mole}. \) (10.7.H)

He [133] thus described the optimum as the point of desorption of ethylene. This theory of optimum does not, however, fit in with new results as shown in what follows. The quantity of ethylene adsorbed on an S surface of evaporated nickel film in course of the progress of hydrogenation (cf. table 2) was found approximately constant and corresponded to the coverage of \( \theta_{C_2H_4} = 0.33 \) over the temperature range from -50 to 110 °C [61], which comprises the optimum temperature, 35 °C; the above value of \( \theta_{C_2H_4} \) was calculated from the observed quantity of adsorption by geometric considerations on the basis of 10^{15} surface metal atoms per unit BET area, any two neighboring atoms among them being taken as available for occupation by one adsorbed ethylene molecule. This disproves the hypothesized desorption of ethylene, provided that the observed amount of adsorption directly represents those and only those molecules occupying the sites of critical complex.\(^{19}\)

The above provision might be questioned with regard to the active center theory, in the sense that just a minute fraction of the observed amount of ethylene adsorbed may block the active centers and evaporate at the optimum to release them, while the observation of the total adsorbed quantity

\(^{19}\) Cf. footnote 5 to 3.1.6.
would be quite insensitive to this fraction. It is, however, established [38] that the number of sites of critical complex involved amounts to around $10^{15}$ cm$^{-2}$, as referred to in 3.1.6. Therefore, if ethylene is desorbed at the optimum to set these sites free, according to Schwab's hypothesis, then the desorbed amount must be of about this magnitude, which is by no means negligible as compared with the amount of adsorbed ethylene observed, and would never escape detection; the approximately constant $\theta_{20}$ over the above temperature range thus excludes the possibility of the desorption as responsible for the optimum.

The above hypothesis is further contradicted by the observed dependence of the optimum temperature upon the partial pressure of ethylene. Assigning the optimum to the point where $\{\ln v_{20}/(1/T)\}_P$, $r_{20} = 0$, we have, on substitution of $v_{20}$ from eq (10.3),

$$RT^2 \partial \ln k_{20}/\partial T + \{RT^2/(1 + b_{P}P_{E})\} \partial \ln b_{P}/\partial T + RT^2 \partial \ln b_{hi}/\partial T = 0.$$  

The value of $\log_{10} b_{P}$ at $T = T_{X}$ is obtained by integrating eq (10.6.E) for constant $\Delta H_{E}$, as

$$\log_{10} b_{P} = \log_{10} b_{P,0} - \Delta H_{E}/2.303RT_{X},$$

where $\log_{10} b_{P,0}$ is the integration constant. Eliminating $RT^2 \partial \ln k_{20}/\partial T$, $RT^2 \partial \ln b_{P}/\partial T$, $RT^2 \partial \ln b_{hi}/\partial T$ and $b_{P}$ from the two above equations and eqs (10.6.k), (10.6.E), and (10.6.H), we have

$$\frac{1}{T_{X}(^\circ K)} = \frac{2.303R}{\Delta H_{E}} \left\{ \log_{10} \frac{-\Delta H_{E} - \Delta H_{H} - E_{0}}{b_{P,0}(E_{0} + \Delta H_{H})} - \log_{10} P_{E} \right\}$$

(10.8)

The constant $\log_{10} b_{P,0}$ is evaluated from the above linear relation as

$$\log_{10} b_{P,0} = -9.1.$$  

(10.9)

The value of $(E_{0} + \Delta H_{H})$ is given by eqs (10.5.a) and (10.7.E), while that of $-\Delta H_{H}$ is given by eq (10.7.H). Substituting these values of $(E_{0} + \Delta H_{H})$, $\Delta H_{E}$, and that of $\log_{10} b_{P,0}$ from eq (10.9) into eq (10.8), we have

$$1/T_{X} = (1/3760)(9.3 - \log_{10} P_{E}),$$

(10.10)

($T_{X}$ in °K, $P_{E}$ in mm Hg) which deviates considerably from eq (4.3) as observed by Sato and Miyahara [80].

Jenkins and Rideal [13] expressed the rate of catalyzed hydrogenation as $v_{h} = k_{3}P_{E}\theta_{H_{2}}$ according to their mechanism (which was reviewed in 9.4), where $k_{3}$ is the rate constant of step (9.12). Denoting the rate constants of step (9.1) and of its reversal with $k_{1}$ and $k_{2}$, respectively, one can write the steady condition of the reaction, as regards the intermediates $2H(a)$, as

$$k_{1}P_{H}(1 - \theta_{H_{2}}) = k_{2}\theta_{H_{2}} + k_{3}P_{E}\theta_{H_{2}}$$

or neglecting the rate of repulse of hydrogen adsorption, $k_{1}P_{H}\theta_{H_{2}}$, as compared with the sum of the rate of adsorbed hydrogen leaving the adsorbed state both by desorption $(k_{2}\theta_{H_{2}})$ and by hydrogenation $(k_{3}P_{E}\theta_{H_{2}})$, as

$$k_{1}P_{H} = k_{2}\theta_{H_{2}} + k_{3}P_{E}\theta_{H_{2}}.$$  

Eliminating $\theta_{H_{2}}$ from this equation and the above expression for the hydrogenation rate, $v_{h} = k_{3}P_{E}\theta_{H_{2}}$, we have

$$v_{h} = k_{1}k_{3}P_{E}P_{H}/(k_{2} + k_{3}P_{E}),$$

(10.11)

which is of the same form as eq (10.3) due to Schwab and agrees with the rate law observed by Jenkins and Rideal [13] at the optimum temperature, 165 °C, as given in table 7. They assumed, as reviewed in 9.4, that $k_{2} \ll k_{3}P_{E}$ at temperatures below and $k_{2} \gg k_{3}P_{E}$ above the optimum, hence $v_{h} \propto P_{H}$ or $v_{h} \propto P_{H}P_{E}$, respectively, from eq (10.11), in accordance with experiments. The rate-determining step is in consequence (9.1) at temperatures below but (9.12) above the optimum, as discussed in 9.4. The change of activation heat may occur, hence, by switchover in the rate-determining step at the optimum because of the difference in materials of the systems [20] of step (9.1) ($H_{2}$) and that of step (9.12) ($H_{2} + C_{2}H_{4}$) as mentioned in 9.8.2, whereas there exists then little difference from the associative mechanism, insofar as the hydrogenation is concerned.

10.2. Critical Review of Current Treatments

The formulation of rate of steps by the mass action law referred to in 10.1. is applicable only in cases where the system (see footnote 20) of the step is statistically independent, i.e., the system assumes any state under given macroscopic constraints, e.g., confinement to a definite volume, as if it were alone under the same constraints. The statistical independence is secured in cases where the species of variable concentrations concerned are sparse enough, whether the step be homogeneous or heterogeneous. 21 The covered fraction of one-tenth might be thought of as moderate, but the corresponding three-dimensional concentration is, for $10^{15}$ cm$^{-2}$ sites and the appropriate thickness of $10^{-8}$ cm, $10^{15} \times 10^{-1} \times (10^{-8})^{-1}$ cm$^{-3} = 10^{22}$ cm$^{-3}$, which matches the molecular concentration of liquids. The applicability of the mass action law is

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20 Set of particles involved in the step.

21 A step is called homogeneous or heterogeneous according as its critical complex [cf. footnote 5 to 3.1.6] is situated in a macroscopic phase or in a surface phase. A macroscopic phase will be called simply phase in what follows.
thus a problem which is rather more serious in case of heterogeneous steps than in case of homogeneous steps, just because of the different concentrations of species in the state of interest.

The applicability must of course be decided on the basis of a general theory of reaction rates which does not rest upon the statistical independence of the system of the given step. Readers are referred, in this regard, to an article “On the Theory of Heterogeneous Catalysis” by Horiuti and Nakamura [134].

There exist two kinds of deviations from the statistical independence of a system of a step in case of heterogeneous steps [134]. First, a species is not admissible to a site of adsorption if the site is preoccupied by another species. Secondly, there exist in general repulsive or attractive interactions between species which occupy their respective sites exclusively. In the semiquantitative treatments presented in this monograph, we will be content to take account of the former kind of deviation only, ignoring the latter throughout. Under this limitation, the current treatments referred to in 10.1 are critically reviewed on the basis of the general theory [134]; conclusions only are cited, leaving out any detailed arguments.

(A) Equation (10.2.B) is exact, if the critical complex\(^{22}\) of the step occupies the combined sites of A and B.

(B) If the critical complex occupies a single site, either of A or B, the exact equations is

\[ v_+ \propto \theta_A[B] \quad (10.12.A) \]

or

\[ v_+ \propto [A] \theta_B, \quad (10.12.B) \]

respectively. Equations (10.12) are applicable when A and B are alternative occupants of one kind of sites, or when A and B occupy different kinds of sites exclusively, or when either one of them is the exclusive occupant of any sites. The necessary and sufficient condition for eqs (10.12.A) and (10.12.B) to be valid is that the critical complex occupies a single site, either of A or of B, respectively [134]; it is not necessary that either of A and B is adsorbed and collided with by the other from the gas phase. On the other hand, eqs (10.12.A) and (10.12.B) do not apply even if the one from the gas phase collides with the other one which is adsorbed, provided that the critical complex thus formed occupies combined sites of A and B; in the latter case eq (10.2.B) holds instead.

It may be noted that eq (10.12.A) is identical with eq (10.2.A).

11. Statistical Mechanical Formulation of Rates

Rates are statistical mechanically formulated under the premise mentioned in 10.2 with the aim of formulating the catalyzed hydrogenation of ethylene statistical mechanically on the basis of the associative mechanism.

11.1. Outline

The general theory assures, under the premise in 10.2, that an exact result is obtained by the procedure of Glasstone, Laidler, and Eyring, which treats sites of adsorption as if they were constituent species of a statistically independent system of the step. We start from eq (72) on p. 378 of “The Theory of Rate Processes” by Glasstone, Laidler, and Eyring, McGraw-Hill Book Company, 1941, for the rate \( v \) of a bimolecular step in case of sparse coverage, i.e.,

\[ v = \frac{sC_1C'_2C_s}{kT} \frac{f_1}{hF_gF'_{g's}} \]

by which two molecules of different kinds in gas, of concentrations \( C \) and \( C' \), respectively, are combined on the catalyst; the catalyst provides sites of adsorption for the molecules, each of them being occupied by any of them at a given time, and the activated complex\(^{23}\) of the step occupies adjacent two-sites. \( C_1 \) is the number of available single sites per unit area, and \( s \) is the number of sites adjacent to each site. \( F_g \) and \( F'_{g's} \) are the complete partition functions of molecules of the respective kinds per unit volume, which are substituted for the partition functions in the original equation in Glasstone, Laidler and Eyring’s book, so that the Boltzmann factor of the total elevation, \( e_0 \), of the ground state in the original equation is absorbed into the partition functions. The factor \((1/2)sC_s\) represents the total number, \( N_t \), of sites of the activated complex per unit area under the above premise of a sparse coverage. The quantities \( f_1 \) and \( f_s \) are termed, by the book’s authors, the partition functions of the activated complex and of the reaction sites, respectively, whereas partition functions are defined in this book only for a statistically independent assembly and not for an adsorbed species or a site which are not statistically independent. This amounts to a leap of argument but can be reconciled by an alternative interpretation of \( f_1 \) and \( f_s \) as follows.

\(^{22}\) Cf. footnote 5 to 3.1.6.

\(^{23}\) Under the present approximation, activated complex may be taken synonymous with the critical complex referred to in 3.1.6.

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The factor \( f \) in the above equation is read for the partition function (complete) of the catalyst with a single activated complex attached to a definite site, and \( f \) for the partition function (complete) of the bare catalyst. These definitions are acceptable since both subjects may be taken to be statistically independent. Since \( F_g \) and \( F_{g'} \) are partition functions of molecules A and B, both detached from the catalyst, the product \( F_g F_{g'} f_s \) is the partition function of an assembly consisting of the bare catalyst, A and B, all separated from each other. The factor \( f_s / F_g F_{g'} f_s \) is hence the ratio of the probabilities of the state where the activated complex is attached to a definite site and that where the assembly is in the separated state; this ratio, when multiplied by the universal frequency, \( kT/h \), gives the specific rate of the step in question, which pertains to a single pair of A and B on the definite site; the transmission coefficient is assumed unity throughout the present treatment. Assuming the physical identity of all sites of the activated complex on the catalyst, the last-mentioned specific rate times the number, \( N \), of sites of the activated complex gives the specific rate of the step which occurs to this single pair of A and B per unit area. The overall rate of the step per unit area is now the last mentioned specific rate times the number of pairs of A and B, i.e., the product of the numbers of both kinds of molecules. This product is reduced to the product, \( C_g C_{g'} \), of the concentrations, with regard to the above equation of \( v \), by referring \( F_g \) and \( F_{g'} \) respectively to unit volume. This equation is readily generalized for any type of step under the condition that its initial system is a set of gas molecules and the catalyst surface is just sparsely covered, as

\[
v = (kT/h)N q^i a_i, \tag{11.1.v}
\]

where

\[
q^i = f_i / f_s, \quad a_i = \prod_i a_i^v, \quad a_i = C_i / F_i
\]

(11.1.q), (11.1.l), (11.1.i)

and \( \nu_i \) is the number of \( i \)th constituents of the initial system, I, in gas. The quantity \( q^i \) is by definition the Boltzmann factor of the work required to add a system of the step in question to a definite site on the catalyst as an activated complex, keeping the whole assembly involved in statistical mechanical equilibrium throughout the process [134, 135].

### 11.2. Function \( a_i \)

Function \( a_i \) in eq (11.1.v) is now developed for the sake of an expedient application. Equation (121) in the same monograph of Glasstone et al., states that

\[
K_c = \frac{F_g F_{g'} F_s}{F_{A} F_{B} F_{C}} \ldots
\]

for the concentration equilibrium constant \( K_c \) of the reaction in gas,

\[aA + bB + cC + \ldots = lL + mM + nN + \ldots \]

defined as

\[
K_c = \frac{C_l C_m C_n \ldots}{C_A C_B C_C \ldots}
\]

in terms of equilibrium concentrations, \( C_l \), etc., in gas. We have, equating the above alternative expressions of \( K_c \) to each other

\[
\left( \frac{C_A}{F_A} \right)^a \left( \frac{C_B}{F_B} \right)^b \left( \frac{C_C}{F_C} \right)^c \ldots = \left( \frac{C_L}{F_L} \right)^l \left( \frac{C_M}{F_M} \right)^m \left( \frac{C_N}{F_N} \right)^n \ldots
\]

or with reference to eq (11.1.i)

\[
a^l a^m a^n \ldots = a^l a^m a^n \ldots
\]

It follows, if a set of molecules in gas, \( I = \sum_i \nu_i I_i \), is in equilibrium with another set of molecules in gas, \( I' = \sum_i' \nu_i' I_i' \), that

\[
a_i = a_{i'}, \tag{11.2.eq}
\]

where

\[
a_i = \prod_i a_{i}^{\nu_i}, \quad a_{i'} = \prod_{i'} a_{i'}^{\nu_{i'}}
\]

(11.2.I), (11.2.I')

\( a_i \) and \( a_{i'} \) are called by Fowler and Guggenheim [136] the absolute activities of species \( I_i \) and \( I_i' \) respectively; the \( a_i \) and \( a_{i'} \) are those of the sets \( I \) and \( I' \).
12. Statistical Mechanical Formulation of the Associative Mechanism

The statistical mechanical theory of rates in section 11 is applied to the associative mechanism in order to derive the steady rate of catalyzed hydrogenation on the basis of associated reactions. Functions \( k(s) \) appropriate respectively to steps \( s \) of scheme (9.5) are first derived; \( k(s) \) is the forward, unidirectional rate of step \( s \), under the supposition that all other constituent steps are in equilibrium.

12.1. Formulation of \( k(s) \)'s

The formulation of \( k(s) \) is exemplified with step II. The relevant activated complex is in equilibrium with the initial system, \( C_2H_4(a) + H(a) \), which determines the concentration of the activated complex, hence the rate. Suppose now the presence of hypothetical molecules \( C_2H_4(g) \) and \( H(g) \) in gas which are, respectively, in equilibrium with \( C_2H_4(a) \) and \( H(a) \). The activated complex is then in equilibrium with \( C_2H_4(g) \) and \( H(g) \). The forward rate of step II, \( \nu(\Pi) \), is thus expressed according to eqs (11.1) as

\[
\nu(\Pi) = \frac{kT}{h} N_{\text{II}} q^{\text{II}} \alpha_{C_2H_4(g)} \alpha_{H(g)}. \tag{12.1}
\]

The rate \( k(\Pi) \) is now by definition the particular value of \( \nu(\Pi) \) in the case where all other constituent steps of scheme (9.5) are in equilibria. \( C_2H_4 \) in gas is thus in equilibrium with \( C_2H_4(a) \), hence with \( C_2H_4(g) \) and \( H_2 \) in gas with \( H(a) \), hence with \( H(g) \). We have in consequence according to eq (11.2)

\[
\nu(\Pi) = k(\Pi) = \frac{kT}{h} N_{\text{II}} q^{\text{II}} \alpha_{C_2H_4(g)} \alpha_{H(g)}. \tag{12.1}
\]

The statistical mechanical theory of rates in order to derive the steady rate of catalyzed hydrogenation on the basis of associated reactions.

12.2 Expressions for \( \alpha_E \) and \( \alpha_H \)

The functions \( \alpha_E \) and \( \alpha_H \) can be written according to eq (11.1.i), developing \( F \) and \( F_H \) statistical mechanically and substituting 1333\( P_i kT \) (\( P_i \) in mm Hg) for \( C_i \), as

\[
a_E = \frac{kt}{1333P_E} \frac{(2\pi m_E kT)^{3/2}}{h^3} 2\pi^2 (2\pi I_E kT)^{3/2} \frac{j=1}{12} \left\{ 1 - \exp \left( -\frac{h\nu_j}{kT} \right) \right\}^{-1} \exp \left( -\frac{\epsilon_E}{RT} \right)
\]

and

\[
a_H = \frac{kt}{1333P_H} \frac{(2\pi m_E kT)^{3/2}}{h^3} 4\pi^2 I_H kT \frac{h^2}{h} \exp \left( -\frac{\epsilon_H}{RT} \right),
\]

where \( m_E \) and \( m_H \) are the masses of ethylene and hydrogen, \( I_E \) is the geometric mean of the three principal moments of inertia of ethylene, \( I_H \) the moment of inertia of hydrogen.

This postulate of the theory of absolute rate is often criticized (General Discussion "Reaction Kinetics," Trans. Faraday Soc. 34, 57, 71, 75 (1938)). Of course the equilibrium of such sort, could not always be established in the thermodynamic sense. It has been shown [135], however, that, in case where the transmission coefficient is unity, the unidirectional rate may be exactly deduced according to the postulate even in the absence of such thermodynamic equilibrium.
can simply be replaced with $T_N$, since it varies little with temperature. $T_N$ is taken to be 373.15 °K in the present treatment. We have thus

$$a_E = P_E/Q_E, \quad a_H = P_H/Q_H.$$  

(12.3.E), (12.3.H)

where

$$Q_E = Q_{E,0} \exp \left( -\frac{\epsilon_E + 4RT_N}{RT} \right),$$  

(12.4.E),

$$Q_H = Q_{H,0} \exp \left( -\frac{\epsilon_H + \frac{1}{2}RT_N}{RT} \right),$$  

(12.4.H)

$$Q_{E,0} = \frac{kT_N}{1333} \frac{(2\pi m_k kT_N)^{3/2}}{h^3} \frac{2\pi^2(2\pi I_k kT_N)^{3/2}}{h^3} \cdot \prod_{j=1}^{12} \left( 1 - \exp \left( -\frac{hf_{ij}}{kT_N} \right) \right)^{-1} \epsilon^4 = 3.939 \times 10^{14} \text{ mm Hg}. \quad (12.5.E)$$

and

$$Q_{H,0} = \frac{kT_N}{1333} \frac{(2\pi m_k kT_N)^{3/2}}{h^3} \frac{4\pi^2 I_k kT_N}{h^2} e^{7/2}$$

It may be noted that the chemical potential $\mu_i$ of species $i$ is given as $\mu_i = RT \ln a_i$, from which the partial molar enthalpy of species $i$, $H_i = \mu_i - T(\partial \mu_i / \partial T)_p$, is derived particularly for ethylene and hydrogen as

$$H_E = \epsilon_E + 4RT_N, \quad H_H = \epsilon_H + \frac{7}{2}RT_N, \quad (12.6.E), (12.6.H)$$

and the partial molar entropy, $\tilde{S}_i = - (\partial \mu_i / \partial T)_p$, follows as

$$\tilde{S}_E = R \ln Q_{E,0}/P_E, \quad \tilde{S}_H = R \ln Q_{H,0}/P_H. \quad (12.7.E), (12.7.H)$$

The factor $q^{s(s)}$ in eqs (12.2) is approximated as

$$q^{s(s)} = \exp \left( -\frac{\epsilon^{s(s)}}{RT} \right), \quad (12.8)$$

where $\epsilon^{s(s)}$ is the ground state energy of the activated complex of step $s$, ignoring the Boltzmann factors of excited states, which may be fairly high on account of the narrow space of the site to which the system of the step is confined.

### 12.3. Practical Expressions of $k(s)$'s

Substituting $a_E$, $a_H$ and $q^{s(s)}$ from eqs (12.3) and (12.8) into eqs (12.2) and further $T$ in the factor $kT/h$ by $T_N \exp (1 - N_{10}/T)$, identifying all $N_{10}$'s with each other and referring to eqs (12.6), we have

$$k(I_a) = \rho(P_E/Q_{E,0}) \exp (-\Delta^1 H(I_a)/RT), \quad (12.9.I_a)$$

$$k(I_b) = \rho(P_H/Q_{H,0}) \exp (-\Delta^1 H(I_b)/RT), \quad (12.9.I_b)$$

$$k(II) = \rho(P_E/Q_{E,0})(P_H/Q_{H,0})^{1/2} \exp (-\Delta^1 H(II)/RT) \quad (12.9.II)$$

and

$$k(III) = \rho(P_E/Q_{E,0})(P_H/Q_{H,0}) \exp (-\Delta^1 H(III)/RT), \quad (12.9.III)$$

where

$$H_{(I_a)} = \bar{H}_E, \quad H_{(I_b)} = \bar{H}_H, \quad H_{(II)} = \bar{H}_E + \bar{H}_H/2, \quad H_{(III)} = \bar{H}_E + \bar{H}_H. \quad (12.12.I_a), (12.12.I_b), (12.12.II), (12.12.III)$$

Equations (12.9) are...
The function $\rho$, as defined by eq (12.10.$\rho$), is the partition function of activated complexes, with energies referred to the appropriate ground states, which transit the activated state unidirectionally once within unit time.$^{26}$ $\Delta^i S(s)$ and $\Delta^i G(s)$ thus defined are the increments of Gibbs energy and of entropy, respectively, of the whole assembly, caused by bringing up the set $I(s)$ of reactants to the state where it is transiting the activated state unidirectionally once within unit time through steps other than $s$, all supposed to be in equilibrium.

12.4. Rate Equations in Terms of $k(s)$'s

The forward and backward rates, $v_+(s)$ and $v_-(s)$, of the constituent steps of scheme (9.5) are given according to eqs (11.1.v) and (11.1.I) as

$$v_+(I_a) = (kT/h)N_t q^{h(l)} a_{E},$$

$$v_+(I_b) = (kT/h)N_t q^{h(l)} a_{H},$$

$$v_+(II) = (kT/h)N_t q^{h(l)} a_{C_2H_4(a)} a_{H(a)},$$

$$v_+(III) = (kT/h)N_t q^{h(l)} a_{C_2H_5(a)} a_{H(a)},$$

where $a_{C_2H_4(a)}$, $a_{H(a)}$ and $a_{C_2H_5(a)}$ are the absolute activities of $C_2H_4(a)$, $H(a)$ and $C_2H_5(a)$ defined as those of hypothetical gas molecules, $C_2H_4(g)$, $H(g)$ and $C_2H_5(g)$ respectively in equilibrium with $C_2H_4(a)$, $H(a)$, and $C_2H_5(a)$. Referring to eqs (12.2), the above expressions of $v_+(s)$ and $v_-(s)$ are written in the form

$$v_+(I_a) = k(I_a) \gamma(C_2H_4),$$

$$v_+(I_b) = k(I_b) \gamma(H)^2,$$

$$v_+(II) = k(II) \gamma(C_2H_5),$$

$$v_+(III) = k(III) \gamma(C_2H_6),$$

where

$$\gamma(C_2H_4) = a_{C_2H_4(a)}/a_E,$$

$$\gamma(H) = a_{H(a)}/a_H^{1/2},$$

$$\gamma(C_2H_5) = a_{C_2H_5(a)}/a_E a_H^{1/2},$$

$$\gamma(C_2H_6) = a_{C_2H_6(a)}/a_E a_H;$$

$\gamma(C_2H_4)$ etc., may be called the activity coefficients of the relevant species.

12.5. Steady State of Catalyzed Hydrogenation

The steady state is formulated by equating the algebraic sum of rates of formation of each intermediate to zero. The stoichiometric number 26 of each step of scheme (9.5) is thus found to be unity commonly with reference to reaction (4.1), without any isotopic discrimination. Formulating the steady state individually with respect to $E_n(a) = C_2H_4-nD_n(a)$ ($n = 0, 1, 2, 3, 4$), $H(a)$, $D(a)$ and $A_n(a) = C_2H_5-nD_n(a)$ ($n = 0, 1, \ldots, 5$), one can determine the relative amounts of $E_n(a)$ etc., and the evolution rates of ethylenes-$d_n$, hydrogens-$d_n$ and ethanes-$d_n$ as shown in what follows.
12.5.1. The rate $V_s$ of steady hydrogenation in the associative mechanism is given in terms of $v_+(s)$'s and $v_-(s)$'s, on account of unit stoichiometric numbers for every constituent step, as

$$V_s = v_+(s) - v_-(s), \quad s = I_a, I_b, II, III \quad (12.18)$$

or, substituting $v_+(s)$'s and $v_-(s)$'s from eqs (12.16), as

$$V_s = k(I_a)(1 - \gamma(C_2H_4)) - k(I_b) + k(I)$$

$$= k(II)(\gamma(C_2H_4)y(H) - \gamma(C_2H_3))$$

$$= k(III)(\gamma(C_2H_3)y(H) - \gamma(C_2H_4)). \quad (12.19)$$

Eliminating $\gamma(C_2H_4)$, $\gamma(H)$ and $\gamma(C_2H_3)$ from eq (12.19), we have

$$\gamma(C_2H_3) = \left(\frac{v_s}{k(I_a)}\right) \left(1 - \frac{v_s}{k(I_b)}\right)$$

$$- \frac{v_s}{k(II)} \left(1 - \frac{v_s}{k(I_b)}\right)^{1/2} - \frac{v_s}{k(III)}. \quad (12.20)$$

Rates of the catalyzed hydrogenation of diverse definitions have been introduced in reviewing the treatments of various authors, symboling them commonly with $v_h$. These $v_h$'s are related with $V_s$ as

$$v_h = (kT/1333V)V_s,$$

if $v_h$ is given in the rate of partial pressure decrease of either reactant in mm Hg in a closed space of constant volume, $V$. We have

$$v_h = (kT/1333P_E)V_s,$$

if $v_h$ is the increasing rate of hydrogenated fraction of ethylene of partial pressure, $P_E$, in mm Hg or

$$v_h = (kT/1333P_H)V_s,$$

if $v_h$ is the first order rate with respect to hydrogen, which is referred to particularly as the rate constant, $k_h$.

These $v_h$ differ from $V_s$ by a factor which depends on temperature and hence makes a difference between the activation heat derived at constant partial pressures of reactants from $v_h$ and that from $V_s$ commonly as

$$RT^2\ln v_h/\partial T = RT^2\ln V_s/\partial T + RT.$$

The common difference $RT$ is about within experimental errors of observation. We deal exclusively with the steady hydrogenation for which $V_s > 0$. It is inferred from eqs (12.19), that

(i) \( 0 < \gamma(C_2H_4), \gamma(H), \gamma(C_2H_3), \gamma(C_2H_6) < 1 \),

(ii) \( 0 < v_s/(1 - \gamma(C_2H_6)) < k(s), (s = I_a, I_b, II, III) \), and also that,

(iii) as one of the functions $k(s)$, say $k(r)$, lies sufficiently below all other $k(s')$, every step other than $r$ approaches equilibrium so that $r$ tends to be rate-determining according to 9.2.2. Conversely, as step $r$ tends to be rate-determining, all other rates, $k(s')$, get greater than $k(r)$.

Inference (i) is readily seen from eq (12.19), noting that $V_s, k(s)$'s, $\gamma(C_2H_4), \gamma(H), \gamma(C_2H_3), \gamma(C_2H_6)$ are all positive. It follows from eq (12.19) and (i) that

$$1 > 1 - V_s/k(I_a) = \gamma(C_2H_4) > 0, \quad 1 > 1 - V_s/k(I_b) = \gamma(H)^2 > 0,$$

hence according to eq (12.20)

$$\gamma(C_2H_3) < 1 - V_s/k(I_b), \quad \gamma(C_2H_6) < 1 - V_s/k(I_b)$$

$$\gamma(C_2H_6) < (1 - V_s/k(I_a)) - (1 - V_s/k(I_b))^{1/2} \gamma(H)$$

$$(1 - V_s/k(I_b))^{1/2} (1 - V_s/k(I_b))^{1/2} \gamma(H) = 1 - V_s/k(II)$$

and $\gamma(C_2H_3) < 1 - V_s/k(III)$, which are summarized in (ii).

It follows from (i) and (ii) that $V_s < k(s)$. As $k(r)$ of step $s = r$ gets smaller than $k(s')$ of the other steps, $s$ \neq r, the coefficient of every $k(s')$ in eq (12.19) tends to zero or, according to eqs (12.16), every step $s$ approaches equilibrium. As to the converse it is seen readily from eq (12.19) that the coefficient of $k(r)$ approaches $1 - \gamma(C_2H_6)$ while those of $k(s')$ tend, respectively, to zero. The $k(s')$ should hence get greater than $k(r)$, by the same equation, as $r$ tends to be rate-determining.

It may be noted that $\gamma(C_2H_6)$ is extremely small under the usual condition of experiments; $\gamma(C_2H_6)$ is $3.6 \times 10^{-27}$ at 200 °K and $2.7 \times 10^{-6}$ at 500 °K for $P_E = P_H = P_A = 10$ mm Hg.\(^{28}\)

12.5.2. The steady state is formulated with respect to $E_n(a) = C_{2H_4}^a D_n(a)$ in accordance with the mechanism of exchange specified in 9.2.1., ignoring isotopic differences in rates, as

$$X_{En}v_+(I_a) - X_{En}(a)v_-(I_a) - X_{En}(a)v_+(II)$$

$$+ \left[\frac{5 - n}{x_{H(a)}X_{En}}, \frac{6 - n}{X_{En}}, \frac{1 - v}{n} \right]$$

$$\gamma = 0, 1, 2, 3, 4, \quad (12.21)$$

where $X_{En}$ is the mole fraction of $E_n = C_{2H_4}D_n$.\(^{20}\)

2. Correction on page 44 under Section 12.5. Steady State of Catalyzed Hydrogenation

First column, four lines from the bottom reads: where suffix equation signifies....

Should read: where suffix eq. signifies....
over $C_2H_4$ in gas, $X_{E_n(a)}$ the mole fraction of $E_n(a)$
$= C_2^2H_{4-n}D_n(a)$ over $C_2H_2(a)$ and $x_{H(a)}$ the atom
fraction of $D(a)$ over $H(a)$. The first two terms give the
net rate of creation of $E_n(a)$ by step I$_a$ and its
reverse, and the third term the rate of consumption
of $E_n(a)$ by step II. The last term gives the rate of
regeneration of $E_n(a)$ by the reverse of step II,
which is elucidated as follows.

The first term in curly brackets provides, when multiplied
by $v_+(II)$, the rate of formation of $E_n(a)$ from $E_{n-1}(a)$
and $D(a)$ by step II and its reverse; two out of three hydrogen
atoms on the methyl radical of the half-hydrogenated state
originate from the methylene radical of $E_n(a)$, so that these
two contain as an average $(n-1)/2$ deuterium atoms; the third
hydrogen atom being deuterium, we have $(n-1)/2 + 1 = (n+1)/2$ deuterium
atoms in the methyl radical of the half-hydrogenated state, as
an average. The number of protium atoms is thus $3 \frac{n - n + 1}{2} = (5 - n)/2$,
one of which has to be given off by the reverse
of step II, which occurs with the probability of $\frac{5-n}{2} \times \frac{1}{3} = \frac{5-n}{6}$.

hence the first term. The second term in curly brackets represents
the regeneration of $E_n(a)$ from $A_n(a)$, which acquired
one protium atom by step II. The methyl radical of the $A_n(a)$ has $n/2$
deuterium atoms and $3 - n/2$ protium atoms as an average; one
of the latter has to be given off for the regeneration of $E_n(a)$,
which occurs with the probability of $(3-n/2)/3 = (6-n)/6$, hence
the second term. The third term represents the regeneration of
$E_n(a)$ which acquired one deuterium atom on reaching the half-
hydrogenated state; its methyl radical has thus $n/2 + 1$ deuterium
atoms, and one of them has to be given off in order to regenerate
$E_n(a)$, which occurs with the probability of $(n+2)/6$, hence
the third term. The fourth term is referred to the half-hydrogenated
state formed by combination of $E_{n+1}(a)$ with $H(a)$. The methyl
radical, hence, keeps $(n+1)/2$ deuterium atoms exclusively
originating from the methylene radical of $E_{n+1}(a)$. One of $(n+1)/2$
deuterium atoms on the methyl radical has to be released by the
reverse of step II, which occurs with the probability of $(n+1)/6$,
hence the fourth term in curly brackets.

12.5.3. The steady state is formulated with respect
to $H(a)$ and $D(a)$ similarly as

$$2(1-x_{H(a)})v_+(I_b) - 2(1-x_{H(a)}v_-(I_b) - (1-x_{H(a)})v_+(II)$$

$$+ \frac{2}{3}X_{E_n(a)}v_-(II) - (1-x_{H(a)})v_+(III) = 0$$

(12.21.1H)

and

$$2x_{H(a)}v_+(I_b) - 2x_{H(a)}v_-(I_b) - x_{H(a)}v_+(II)$$

$$+ \frac{2}{3}X_{E_n(a)}v_-(II) - x_{H(a)}v_+(III) = 0$$

(12.21.D)

where $x_{E_n(a)}$ is the atom fraction of deuterium in
$C_2H_2(a)$, and the coefficient of $v_-(II)$ in eqs (12.21.H)
and (12.21.D) is the probability of $H(a)$ or $D(a)$ being
yielded, respectively, by the reverse of step II. Terms comprising $v_-(III)$ have been ignored according
to conclusions 13.4.

12.5.4. The steady state is formulated with respect
to $A_n(a) = C_2^2H_{3-n}D_n(a)$ as

$$(x_{H(a)}X_{E_n(a-1)} + (1 - x_{H(a)})X_{E_n(a)})v_+(II)$$

$$- X_{A_p(a)}v_-(II) - X_{A_p(a)}v_+(III) = 0$$

(12.21.A)

where $X_{A_n(a)}$ is the mole fraction of $A_n(a)$ over
$C_2H_2(a)$. The first term gives the rate of $A_n(a)$ formation by combination both of $E_{n-1}(a)$ with $D(a)$
and of $E_n(a)$ with $H(a)$, as represented by the two
in curly brackets, while the second and third
terms give the rates of consumption by the reverse
of step II and step III, respectively. Terms comprising $v_-(III)$ have been ignored similarly, according
to 13.4.

12.5.5. The fraction $x_{E_n(a)}$ in eqs (12.21.H) and
(12.21.D) is related with $X_{E_n(a)}$'s as

$$4x_{E_n(a)} = \sum_{n=1}^{5} nX_{E_n(a)}$$

(12.21.x)

by definition. $X_{E_n(a)}$ and $X_{A_n(a)}$ satisfy, by definition, the equations,

$$\sum_{n=0}^{5} X_{E_n(a)} = 1, \quad \sum_{n=0}^{5} X_{A_n(a)} = 1.$$

(12.21.XE), (12.21.XA)

Equations (12.21) provide 16 equations for 13
unknowns, i.e., $X_{E_n(a)}(n = 0, \ldots, 4)$, $x_{H(a)}$, $x_{E_n(a)}$
and $X_{A_n(a)}(n = 0, \ldots, 5)$. The 16 equations are not
all independent. Summation of eqs (12.21.E) over
$n$ yields, with reference to eq (12.21.XE),

$$v_+(I_a) - v_-(I_a) - v_+(II) + v_-(II) = 0,$$

(12.22.E)

summation of eqs (12.21.H) and (12.21.D) gives

$$2v_+(I_b) - 2v_-(I_b) - v_+(II) + v_-(II) - v_+(III) = 0,$$

(12.22.H)

and summation of eqs (12.21.A) over $n$ with reference
to eq (12.21.XA) gives

$$v_+(II) - v_-(II) - v_+(III) = 0.$$
$4x_1^e v_+ (I_a) - 4x_1^e v_-(I_a) - 4x_2^e v_+ (II)$

$+ \left( \frac{2}{3} x_H(a) + \frac{10}{3} x_2^e(a) \right) v_-(II) = 0,$ \hspace{1cm} (12.23.b)

where $x_E = \sum_{n=1}^{4} n x_{E_n}/4$ is the atom fraction of deuterium in $C_2H_4$ in gas. We have, eliminating $v_-(I_a) + v_+(II)$ from eqs (12.23.b) and (12.22.E),

$6(x_1^e - x_1^e(a))v_+(I_a) + (x_H(a) - x_1^e(a))v_-(II) = 0.$ \hspace{1cm} (12.23.c)

Equations (12.23.a) and (12.23.c) are solved simultaneously for $x_1^e(a)$ and $x_H(a)$ as

$X_{E} = \frac{6x_1^e v_+(I_a) + x_H(a) v_-(II)}{6v_+(I_a) + v_-(II)}$ \hspace{1cm} (12.24.E)

and

$x_H(a) = \frac{2x_1^e v_+(I_a) v_-(II) + x_H(a)(6v_+(I_a) + v_-(II))}{2v_+(I_a) v_-(II) + v_+(I_b)(6v_+(I_a) + v_-(II))}.$ \hspace{1cm} (12.24.H)

The mole fraction of $A_n(a)$ over $C_2H_5(a)$, $X_{A_n(a)}$, is obtained by eliminating $(v_-(II) + v_+(III))/v_+(II)$ from eqs (12.21.A) and (12.22.A) as

$X_{A_n(a)} = x_H(a) X_{E_{n-1}(a)} + (1 - x_H(a)) X_{E_n(a)}.$ \hspace{1cm} (12.24.A)

## 12.6. Rates of Reaction Associated With the Catalyzed Hydrogenation

The rates of the associated reactions are derived as follows, ignoring the isotopic differences in rates.

### 12.6.1. Exchange rate in course of hydrogenation

is defined respectively for ethylene and hydrogen as follows.

### 12.6.1.1. Let $n_E$ be the total number of hydrogen atoms comprised in gaseous ethylene and $x_E$ their fraction of deuterium. The rate of increase of deuterium atoms in gaseous ethylene, $d(n_1^e x_1^e)/dt$, is given in terms of the rate of penetration into gaseous ethylene of hydrogen atoms originating from gaseous hydrogen, $V_+ E$, and the rate of hydrogen atoms driven out from gaseous ethylene to gaseous hydrogen.

$V_+ E$ should exceed $V_+E$ by the rate with which constituent hydrogen atoms of gaseous ethylene are lost by hydrogenation, $-n_E$, i.e.,

$V_+ E = V_{ex. E} - n_E.$

We have from the above two equations

$V_{ex. E} = \frac{n_\overline{E} x_\overline{E}}{(x_\overline{E} - x_H)}.$ \hspace{1cm} (12.25.E)

$V_{ex. E}$ thus defined is called the exchange rate of ethylene.

Similarly, the exchange rate of hydrogen is defined as

$V_{ex. H} = \frac{n_\overline{H} x_\overline{H}}{(x_\overline{H} - x_H)},$ \hspace{1cm} (12.25.H)

where $n_H$ is the number of hydrogen atoms comprised in gaseous ethylene.

### 3. Correction on page 46 under Section 12.6. Rates of Reaction Associated With the Catalyzed Hydrogenation

First column, first footnote, line two reads: $= -x_H$ at $x_\overline{E} = 0$ and

Should read: $= -x_H$ at $x_\overline{E} = 0$ and

transferred counter from gaseous ethylene to gaseous hydrogen and ethane. $V_+ E$ should exceed $V_{ex. E}$ by the rate with which constituent hydrogen atoms of gaseous ethylene are lost by hydrogenation, $-n_E$, i.e.,

$V_+ E = V_{ex. E} - n_E.$

The factor, $1/n_H$, is given as $k T \times 1333 P_H^v$ in terms of the partial pressure of hydrogen, $P_H$, in mm Hg and the volume, $V$, in which the gas mixture in question is confined. This factor makes difference between the activation heats derived at constant $P_H$ and $V_{ex. E}$ as

$RT log \frac{V_{ex. E}}{P_{ex. E}} = RT log \frac{P_H}{V_{ex. E}}.$

similar to the case of $v_1$ and $P_1$, referred to in footnote 27 to 12.5.1.
Substituting \( n_E \dot{x}_E \) from the above equation into (12.25.E), \( V_{ex,E} \) is given as

\[
V_{ex,E} = 4 \frac{x_E(a) - x_E}{x_E - x_E} v_-(I_a). \tag{12.26.E}
\]

Equation (12.25.H) is similarly transformed as

\[
V_{ex,H} = 2 \frac{x_H(a) - x_H}{x_E - x_H} v_-(I_b). \tag{12.26.H}
\]

12.6.2. Parahydrogen conversion is effected according to scheme (9.5), in course of catalyzed hydrogenation, by step I_b and its reverse. Let \( X_p \) be the mole fraction of parahydrogen over hydrogen in gas, i.e.,

\[
X_p = \frac{N_p^p}{N_H},
\]

where \( N_p^p \) is the number of parahydrogen molecules and \( N_H \) the total number of hydrogen molecules. We have by differentiation

\[
\dot{X}_p = \frac{\dot{N}_H}{N_H} - X_p \dot{N}_H/N_H.
\]

\( \dot{N}_H \) and \( \dot{N}_H \) are expressed in terms of \( v_+(I_b) \) and \( v_-(I_b) \) as

\[
\dot{N}_H = X_p v_+(I_b) - X_p v_-(I_b), \quad \dot{N}_H = v_-(I_b) - v_+(I_b),
\]

where \( X_p \) is the particular value of \( X_p \) reached in equilibrium of parahydrogen conversion.\(^{30}\) Eliminating \( \dot{N}_H \) and \( \dot{N}_H \) from the above three equations, we have

\[
V_p = N_H \frac{\dot{X}_p}{X_p} = v_-(I_b), \tag{12.27}
\]

which states that the rate of parahydrogen conversion, \( V_p \), as defined by the second member of eq (12.27) equals \( v_-(I_b) \).

12.6.3. The rate of \(^1\)H_2-D_2 equilibration, \( V_q \), is defined as

\[
V_q = N_H \dot{u} \tag{12.28.q}
\]

where

\[
u = N_{HD,eq}/N_{HD} \tag{12.28.u}
\]

and \( N_{HD,eq} \) is the number of \(^1\)HD molecules, which would exist if hydrogen concerned were equilibrated. \( V_q \) is developed as follows.

For a supposed equilibration of the hydrogen present

\[
N_H = N_{1H_2,eq} + N_{1HD,eq} + N_{D_2,eq}
\]

and

\[
x_H = (2N_{D_2,eq} + N_{1HD,eq})/2N_H,
\]

where suffix eq signifies particular values in the equilibration. Besides,

\[
N_{1HD,eq}^2 N_{1H_2,eq} N_{D_2,eq} = 4
\]

in the absence of isotopic difference of rates.

On elimination of \( N_{1H_2,eq} \) and \( N_{D_2,eq} \) from the above three equations, we have

\[
N_{1HD,eq}^2 = 2x_H(1 - x_H)N_H. \tag{12.28.N}
\]

The ratio \( u \) is expressed by substituting \( N_{1HD,eq} \) from the above equation into eq (12.28.u) as

\[
u = N_{1H_2}/2x_H(1 - x_H)N_H. \tag{12.29}
\]

hence, by logarithmic differentiation,

\[
\dot{u}/u = \frac{\dot{N}_{1H_2}/N_{1H_2} - \dot{N}_H/N_H}{N_{1H_2}/N_H} + \frac{1}{1 - x_H} \frac{1 - x_H}{x_H} \dot{x}_H.
\]

\( \dot{N}_H \) in the above equation is expressed as

\[
\dot{N}_H = v_-(I_b) - v_+(I_b)
\]

and \( \dot{N}_{1H_2} \) as

\[
\dot{N}_{1H_2} = 2x_{1H_2}(1 - x_{1H_2})v_-(I_b) = \frac{N_{1H_2}}{N_H} v_-(I_b).
\]

Hydrogen evolved by the reverse of step I_b must be perfectly equilibrated in the absence of isotopic difference of rates. The rate of \(^1\)HD formation by the reverse of I_b is thus its rate, \( v_-(I_b) \), times the fraction, \( x_H(1 - x_H) \), hence the first term of the above equation. The second term gives the rate of consumption of \(^1\)HD molecules by step I_b, i.e., its rate, \( v_+(I_b) \), times the fraction of the number of \(^1\)HD over \( N_H \). Eliminating \( N_{1H_2}, N_{1HD} \) and \( N_H \) from the above four equations, we have, referring to eq (12.28.q).

\[
V_q = N_H \dot{u} = \frac{x_{1H_2}(1 - x_{1H_2})}{x_H(1 - x_H)} \left\{ v_-(I_b) - \left( \frac{1}{x_H(1 - x_H)} \right) \right\} \dot{x}_H N_H u. \tag{12.30}
\]

12.6.4. The rates of evolution, \( V_{E_n}, V_{H_n}, V_{1HD}, V_{D_2}, \) and \( V_{A_n} \) of ethylene-\(d_n \), \(^1\)H_2, \(^1\)HD, D_2 and ethane-\(d_n \), \( A_n \), are given in terms of \( X_{E_n(a)}, X_{H_n(a)}, X_{1H_2(a)}, x_{1H_2} \)'s and \( v_-(s)'s \) and \( v_+(s)'s \), as

\[
V_{E_n} = X_{E_n(a)} v_-(I_a), \quad n = 0, 1, 2, 3, 4, \tag{12.31.E}
\]

\[
V_{H_2} = (1 - x_{1H_2})^2 v_-(I_b), V_{1HD} = 2x_{1H_2}(1 - x_{1H_2}) v_-(I_b),
\]

\[
V_{D_2} = x_{1H_2}^2 v_-(I_b) \tag{12.31.H}
\]

and

---

\(^{30}\)Hydrogen evolved by the reverse of step I_b must be of equilibrium composition, insofar as para- and orthohydrogen enter step I_b with equal chance since, otherwise, the catalyst should shift the equilibrium.
\[ V_n = \{ x_{H(a)} x_{\Lambda_{n-1}(a)} + (1 - x_{H(a)}) x_{\Lambda_n(a)} \} v_+(III), \]

\[ n = 0, 1, \ldots, 6. \quad (12.31.A) \]

12.6.5. Let us assume that deuterium atoms are randomly distributed over \( E_n \) and \( E_{\Lambda_n} \), which is realized, where the associative mechanism is concerned, when \( v_+(I_a) \) and \( v_-(I_a) \) are large enough to give every ethylene molecule, be it in the gas or in the surface phase (adsorbed), an equal chance of acquiring deuterium. We have then

\[ X_{E_n} = X_{E_{\Lambda_n}(a)} = \left( \frac{4}{n} \right) x_{E_{\Lambda_n}}^n (1-x_{E_{\Lambda_n}})^{4-n}. \quad (12.32) \]

Substituting \( X_{\Lambda_n(a)} \) and \( X_{\Lambda_{n-1}(a)} \) from eq (12.24.A) into eq (12.31.A), we have

\[ V_n = \{ x_{H(a)}^2 x_{E_{\Lambda_n}(a)} + 2 x_{H(a)} (1-x_{H(a)}) x_{E_{n-1}(a)} + (1-x_{H(a)}) x_{E_{n}(a)} \} v_+(III), \]

\[ n = 0, \ldots, 6. \quad (12.33.a) \]

13. Estimate of \( k(s)'s \)

Rates of steady hydrogenation and various associated reactions were given in section 12. in terms of \( v_+(s)'s \) and \( v_-(s)'s \), which in their turn are determined by \( k(s)'s \) according to eqs (12.16) and (12.19). The rates, \( k(s)'s \), are evaluated in this section by adapting the theoretical relations to experimental results. It may be noted that the steady rate, \( V_s \), of the catalyzed hydrogenation is practically given by \( k(r) \) of the rate-determining step itself, according to 9.2.2 and 12.5.1, and that the rates of \( k(s)'s \) are given by eq (12.9) in the form of \( k(s) = k_0 \exp (-\Delta H(s)/RT) \), where \( k(s)_0 \) and \( \Delta H(s) \) are constants appropriate to step \( s \) which are independent of temperature at constant partial pressures of reactants; the former was already statistical mechanically evaluated, the latter alone remaining to be determined. The rates \( k(s)'s \) are thus estimated in what follows.

13.1 Estimates of \( k(I_a) \)

It is inferred, as shown below, that \( k(I_a) \) is practically infinite or inestimably higher than \( V_s \), so that \( \gamma(C_2H_4) \) is practically unity according to eq (12.19), i.e.,

\[ \gamma(C_2H_4) = 1. \quad (13.1) \]

13.1.1. Table 17 shows that at 110 °C deuterium atoms in ethylenes-\( d_4 \) are in perfectly random d' - ' with \( \gamma \) and \( \gamma(H) \) near \( \gamma(H) = \gamma(H)_{\Lambda_n} \), which is the coefficient of \( \gamma(C_2H_4) \) and \( \gamma(H)_{\Lambda_n} \) in eq (12.19), i.e.,

\[ \gamma(C_2H_4) = 1. \quad (13.1) \]

13.1.2. It is read from the results of Turkevich et al. [17], as reviewed in 5.2.2, that

\[ \gamma(C_2H_4) = 1. \quad (13.1) \]

Second line of second column reads: coefficient of \( v_-(I_a) \) in eq (12.33.c) to be zero, while that of

Should read: coefficient of \( v_+(I_a) \) in eq (12.23.c) to be zero, while that of

x_E or substituting \( X_{E_{\Lambda_n}(a)} \) etc. from eq (12.32) into eq

(12.33.a),

\[ V_n = \left( \frac{4}{n-2} \right) x_{E_{\Lambda_n}(a)}^n (1-x_{E_{\Lambda_n}(a)})^{n-2} + 2 \left( \frac{4}{n-1} \right) x_{H(a)} (1-x_{H(a)}) x_{E_{\Lambda_n}(a)}^n (1-x_{E_{\Lambda_n}(a)})^{n-3} \]

\[ + \left( \frac{4}{n} \right) (1-x_{H(a)})^2 x_{E_{\Lambda_n}(a)}^n (1-x_{E_{\Lambda_n}(a)})^{n-4} \} v_+(III), \]

\[ n = 0, \ldots, 6. \quad (12.33.b) \]

where combination \( \left( \frac{4}{n} \right) \) vanishes, of course, for \( n > 4. \) In the special case where \( x_{H(a)} \) = \( x_{E_{\Lambda_n}(a)} \) = \( x_{\Lambda_n} \), eq (12.33.b) is reduced identically to the equation

\[ V_n = \left( \frac{6}{n} \right) x_{\Lambda_n}^n (1-x_{\Lambda_n})^6 - n v_+(III), \quad (12.33.c) \]

which indicates the random distribution of deuterium over ethane evolved."
\[ V_5; V_{E_1}; V_{E_{n+1}} = 1:2.33:0 \quad (13.2.E) \]

and

\[ V_{A_0}; V_{A_1}; V_{A_2}; V_{A_{n+1}} = 1:0.69:0.154:0 \quad (13.2.A) \]

at the very beginning of the catalyzed deuteration of light ethylene over nickel wire at 90 °C. Equation (13.2.E) states that \( E_1 \) is the only deuteroethylene evolved at the very beginning, which shows that the reverse of step \( I_a \) is rapid enough to carry away \( E_1(a) \) once formed by step II and its reverse before \( E_1(a) \) enters step II again to acquire another deuterium atom. Equation (13.2.A) states, on the other hand, that the only deuteroethanes evolved are \( A_1 \) and \( A_2 \). It follows, since ethane is formed by two consecutive additions of \( H(a)'s \) to \( C_2H_4(a) \) according to scheme (9.5), that practically only light \( C_2H_4(a) \) are subject to two consecutive additions, endorsing the statement of eq (13.2.E) and, in conjunction with the latter, confirming the conclusion of 13.1.1.

\[ \Delta^H(I_b) = 4.7 \text{ kcal/mole} \quad (13.3) \]

is adopted; this is the mean of the two observations, \( \Delta^H(I_b) = 4.60 \text{ kcal/mole} \) [64] and \( \Delta^H(I_b) = 4.80 \text{ kcal/mole} \) [26].

### 13.2 Estimate of \( k(I_b) \)

It has been concluded in 9.2.3, that the rate-determining step below the optimum is \( I_b \). The quantity \( \Delta^H(I_b) \) is thus determinable from observations of \( V_s \) below the optimum identifying \( V_s \) with \( k(I_b) \) of eq (12.9.I_b); the value

\[ \Delta^H(I_b) = 4.7 \text{ kcal/mole} \quad (13.3) \]

is adopted; this is the mean of the two observations, \( \Delta^H(I_b) = 4.60 \text{ kcal/mole} \) [64] and \( \Delta^H(I_b) = 4.80 \text{ kcal/mole} \) [26].

### 13.3. Estimate of \( k(II) \) and \( k(III) \)

There are three methods of determining \( k(III) \) through \( \Delta^H(III) \). One is quite similar to that of determining \( \Delta^H(I_b) \) in 13.2 on the basis of the conclusion in 9.2.3; this method has not, however, been adopted, since the appropriate observations above the optimum are not sufficiently reliable.

The second method consists in comparing a theoretical relation between \( T_x \) and \( P_e \) with the observed relation (4.3); its result, described in 13.3.2, is used for checking that of the third method adopted here, which determines \( k(II) \) and \( k(III) \) coherently from the experimental results of eq (13.2), as described in 13.3.1.

#### 13.3.1. The experimental results of eq (13.2) are stated in conjunction with the appropriate condition as

\[ x_E = 0, \quad x_{E(a)} = 1, \quad x_H = 1, \quad (13.4.E), (13.4.E(a)), (13.4.H) \]

from which \( X_{E(a)} \) and \( X_{A(a)} \) are deduced according to eq (12.24.A) as

\[ X_{E(a)} = 1 - x_{H(a)} \quad \text{and} \quad X_{A(a)} = x_{H(a)} = 0. \]

ignoring \((1 - x_{H(a)})X_{E(a)} \), inasmuch as \( x_{E(a)} \) must be quite small according to eq (13.4.E(a)). We have, from the above equations and eq (12.31.A)

\[ V_{A_0} = (1 - x_{H(a)})v_-(III), \quad V_{A_1} = 2x_{H(a)}(1 - x_{H(a)})v_+(III), \quad V_{A_2} = x_{H(a)}^2v_+(III) \quad (13.5.a) \]

and

\[ V_{A_{n+2}} = 0, \quad (13.5.b) \]

from which the most probable value of \( x_{H(a)} \) is determined by eq (13.2.A) as

\[ x_{H(a)} = 0.264. \quad (13.6) \]

The fraction \( x_{H(a)} = \sum x_{H(a)} / 4 \) may be ignored as compared with the above value of \( x_{H(a)} \), since the fractions \( X_{E(a)} X_{A(a)} \) are extremely small according to eq (13.4.E(a)). We have thus from eqs (12.23.a) and (12.31.H)

\[ v_-(II) = 3 \left(1 - x_{H(a)}\right) v_+(I_b). \]

hence by eq (13.6)

\[ v_-(II) = 8.36 v_+(I_b). \quad (13.7.b) \]

We have, on the other hand, from eq (12.21.E) for \( n = 1 \)

\[ -X_{E(a)}v_-(I_a) + X_{E(a)}v_-(II) = 0; \quad (13.8) \]

the last term of eq (12.21.E) vanishes because of eq (13.4.E), since \( x_{E} = \sum x_{E(a)} / 4 \); eq (13.8) is arrived at by ignoring all terms containing the factors \( X_{E(a)} \) and \( X_{A(a)} \), which are small according to eqs (13.4.E(a)) and (12.21.x), except for the term \( -X_{E(a)} v_-(I_a) \), on account of the practically infinite magnitude of \( v_-(I_a) \), as concluded in 13.1.

\[ V_{E_1} \text{ is given by eqs (13.8) and (12.31.E) as} \]

\[ V_{E_1} = (2/3)x_{H(a)}v_-(II) \]

hence by eqs (13.2.E) and (13.6)

\[ V_s = \frac{2}{3} \times 2.33 \times x_{H(a)}v_-(II) = 0.0755 v_-(II) \quad (13.9) \]

or, substituting \( v_-(II) \) from eq (13.7.b) into eq (13.9),

\[ V_s = 0.632 v_+(I_b). \]

Noting that \( v_+(I_b) \) equals \( k(I_b) \) by eq (12.16.I_b), we have from the first and third members of eq (12.19) and the above equation

\[ y(H) = 0.607. \quad (13.10.H) \]
Writing eq (12.18) with special reference to step II as \( V_s = (v_s(\text{II})/ v_s(\text{II} - 1)) v_s(\text{II}) \) or, according to eq (12.16.11), as \( V_s = (\gamma(C_2H)_4/ \gamma(C_2H)_3 - 1) v_s(\text{II}) \), we evaluate \( \gamma(C_2H)_3 \) using eqs (13.9), (13.10.1) and (13.1) as

\[
\gamma(C_2H)_3 = 0.564. \tag{13.10.A}
\]

Equations (13.1) and (13.10) give, by eq (12.19), the ratio between \( k(s)'s \) at 90 °C as

\[
k(I_b) : k(II) : k(III)
= (1 - \gamma(H)^{\text{II}})^{-1} : (\gamma(C_2H)_3)^{-1} : (\gamma(H)\gamma(C_2H)_3)^{-1}
= 1 : 14.7 : 1.84. \tag{13.11}
\]

The quantities \( \Delta^i H(\text{II}) \) and \( \Delta^j H(\text{III}) \) are now determined according to eqs (13.3), (12.5), (12.9) and (13.11), noting that \( P_e = 10 \text{ mm Hg} \) and \( P_H = 20 \text{ mm Hg} \) in the experiment [117] in question, as

\[
\begin{align*}
\Delta^i H(\text{II}) &= -12.6 \text{ kcal/mole}, \tag{13.12.II} \\
\Delta^j H(\text{III}) &= -18.3 \text{ kcal/mole}. \tag{13.12.III}
\end{align*}
\]

13.3.2. The rate-determining step is switched over from step I_b to III, when the temperature rises past the optimum, according to 9.2.3. An equation for the optimum temperature, \( T_X \), is thus obtained by equating \( k(I_b) \) to \( k(\text{III}) \) at \( T = T_X \) in accordance with eqs (12.9) as

\[
\Delta^i H(I_b) - \Delta^j H(\text{III}) = 2.3 \text{ RT}_X \log_{10} Q_{E, \phi}/P_e,
\]

which gives, on comparison with the observation of eq (4.3),

\[
\Delta^i H(I_b) - \Delta^j H(\text{III}) = 24.2 \text{ kcal/mole} \tag{13.13.H}
\]

and

\[
\log_{10} Q_{E, \phi} = 14.5. \tag{13.13.Q}
\]

We have, from eqs (13.3) and (13.13.H),

\[
\Delta^i H(\text{III}) = -19.5 \text{ kcal/mole},
\]

which agrees tolerably well with the value of (13.13.III), confirming it thus, while the value of eq (13.13.Q) is in excellent agreement with the theoretical value \( \log_{10} Q_{E, \phi} = 14.596 \) of eq (12.5.E).

13.4. Rates Based on the Estimated \( k(s)'s \)

We have from eqs (12.9.I_b), (12.5.H) and (13.3)

\[
\log_{10} k(I_b) = \log_{10} \rho \frac{P_H}{0.575 \times 10^{10}} - \frac{1027}{T} \tag{13.14.I_b}
\]

and similarly from eqs (12.9), (12.5) and (13.12) for steps II and III

\[
\begin{align*}
\log_{10} k(II) &= \log_{10} \rho \left( \frac{P_H}{0.575 \times 10^{10}} \right)^{1/2} \left( \frac{P_E}{3.939 \times 10^{14}} \right) + \frac{2751}{T} \tag{13.14.II} \\
\log_{10} k(III) &= \log_{10} \rho \left( \frac{P_H}{0.575 \times 10^{10}} \right) \left( \frac{P_E}{3.939 \times 10^{14}} \right) + \frac{4008}{T} \tag{13.14.III}
\end{align*}
\]

The rates \( k(s) \) determine \( V_s, \gamma(H) \) and \( \gamma(C_2H)_3 \) by eq (12.19) with reference to the values of \( \gamma(C_2H)_3 \) given in 12.5 and \( \gamma(C_2H)_4 \) of eq (13.1). These values of \( k(s)'s \) and of \( \gamma(C_2H)_4, \gamma(H), \gamma(C_2H)_3 \) and \( \gamma(C_2H)_4 \) determine \( v_+(s)'s \) and \( v_-(s)'s \) by eqs (12.16) as shown in figure 27.

The rates \( V_s, V_{in}, V_{en}, V_H, V_e \) and \( V_q \) are hence developed in terms of \( v_+(s)'s \) and \( v_-(s)'s \) by eqs (12.18), (12.26), (12.27), and (12.30); \( x_{H(a)b} \), as required for the calculation of \( V_q \), for \( x_E = 0, x_H = 1/2 \) and \( u = 0 \), is determined by an equation obtained from eq (12.24.H) for infinite \( v_+(I_a) = k(I_a) \).

The results are shown in figure 28, side by side with \( k(s) \).

We see from figure 27 that \( v_+(II) = v_+(I) \) throughout, i.e., step II is practically in equilibrium. The rates \( v_+(I_b) \) and \( v_+(I) \) coincide at lower temperatures but diverge above the optimum which is located around the intersection of \( k(I_b) \) and \( k(III) \) in figure 28; \( v_+(I_b) \) coincides above the optimum with \( v_+(I_a) \) indicating an equilibrium of \( I_b \), while \( v_+(I) \) gives practically the steady rate of hydrogenation governed by step III in accordance with 12.5.1(iii) and figure 28, \( v_+(III) \) being vanishingly small as seen in figure 27.

The following is inferred from the above numerical results.

13.4.1. Figure 27 shows that at or below 200 °C, \( v_+(III) \) is smaller than \( v_+(I) \) by a factor of at least 10^6. Such a small rate, \( v_+(III) \) is hardly traceable, insofar as methods reviewed here are concerned. This accounts for the results obtained by Matsuzaki and Nakajima [120] in 5.2.7 that ethane was not perceptibly involved in the catalyzed hydrogenation.

13.4.2. Figure 27 shows that step III is far from being in equilibrium over the temperature range where \( I_b \) determined the rate, according to 9.2.3.

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Figure 27. Rates of steps $s_1, v_s(s)$, and of their reverses, $v_r(s)$, at the steady state of hydrogenation over nickel; $s = I_b, II, III$. 

$P_e - P_a = P_s = 10$ mm Hg. $p = sT_N^2$. 

It is inferred below that $I_b$ actually satisfies the conditions, advanced in 9.2.2, for a step determining the rate, notwithstanding a departure of some other constituent step from equilibrium. Comparison is made in this regard between the magnitude of $v_{-}(I_b)$ in the steady state and that in perfect equilibria of all steps other than $I_b$. The rate $v_{-}(I_b)$ in the respective case is given according to eq (12.16.1b) as $v_{-}(I_b) = \gamma(H)^2 \kappa(I_b)$ or $v_{-}(I_b)_{eq} = \gamma(H)^2 \kappa(I_b)$, where suffixes $s$ and $eq$ signify the particular values in the steady state and in the state of perfect equilibria of all steps but $I_b$, respectively.
The coefficient $\gamma(H)$ is determined by eqs (12.19) and (13.14), referring to eq (13.1), whereas $\gamma(H)^{eq}=\gamma(C_2H_6)$, as follows readily from eqs (12.16) by equating $v_+(s)$ with $v_-(s)$ for all steps but $I_b$.

We have thus, e.g., at $T=250^\circ K$ and $P_E=P_H=10$ mm Hg, where $I_b$ governs the rate according to 12.5.1(iii), $\gamma(H)^2=10^{-8}$ and $\gamma(H)^{eq}=10^{-18}$, so that $v_-(I_b)$ is greater than $v_-(I_b)^{eq}$ by a factor of ca. $10^{10}$. This makes, however, practically no difference in the net rate, $V_s=k(I_b)(1-\gamma(H)^2)$, as given by eq (12.19), illustrating the argument in 9.2.2.1.

5. Correction on page 52 under legend of Figure 28

Legend reads: .....$^1H_2$-$D_2$ mixture.

Should read: .....$^1H_2$-$D_2$ mixture. $P_E=P_H=10$ mm Hg.

Various phenomena concerned with the catalyzed hydrogenation of ethylene will be accounted for systematically on the basis of the theory of the associative mechanism developed in the foregoing sections.

14.1. Switchover in the Rate-Determining Step

At the switchover temperature, $T_X$, of the rate-determining step from $I_b$ to III, we have $k(I_b)=k(III)$, as mentioned in 13.3.2, and hence from eqs (12.14)

$$\Delta G(I_b) = \Delta G(III),$$

the other below $T_X$ but lower than the other above $T_X$. No such switchover in the relative magnitudes of $k(\cdot)$'s can take place without a difference in activation entropies. This difference arises now only through difference in the systems $I(s)$ of the

6. Correction on page 53 under Section 14.1. Switchover in the Rate-Determining Step

First column, ninth line from the bottom reads: for $P_E=10$ mm Hg. This......

Should read: for $P_E=10$ mm Hg and $T_X=373^\circ$K. This.....

$$\Delta S(I_b) - \Delta S(III) = R \ln \left( \frac{Q_{E,0}}{P_E} \right),$$

which amounts to 62.2 e.u. according to eq (12.5.E) for $P_E=10$ mm Hg. This difference of activation entropy originates from the ethylene molecule that $I(s)$ of step III possesses in excess over that of $I_b$, and compensates for the difference in activation heats which amounts to 24 kcal, leveling $k(I_b)$ and $k(III)$ at $T_X$.

We see that, while $k(s_1)$ and $k(s_2)$ for steps $s_1$ and $s_2$ of different activation entropies equal each other at a certain temperature $T_X$, one of them is higher than on equal terms with the activation heats, that the activation entropy must be algebraically smaller in case of an heterogeneous step which amounts to a restriction of a system initially in a three dimensional phase to a surface phase such as to reduction its phase volume by a factor of 10^8 and that heterogeneous steps, which are thus destined to have algebraically smaller activation entropies, have smaller activation heats, or even negative ones, in accordance with the so-called compensation effect, in as far as rates accessible to our measurements are limited to a narrow compass of magnitude.


The activation heat of exchange of hydrogen has been observed definitely to be greater than that of hydrogenation, which disposed a number of authors [2, 13, 68, 116] to attribute to the exchange of hydrogen some different sequence of steps from that of hydrogenation, as reviewed in section 9. Figure 28 shows that the one and the same sequence of steps of the associative mechanism leads necessarily to an excess of the activation heat of exchange, $RT^2 \ln V_{ex,H}/\partial T$, over that of hydrogenation; the excess amounts to 23 kcal below $T_X=373$ K and 5.7 kcal at 200 °C, qualitatively in accordance with the experimental results of Twigg and Rideal [68].

The necessity of having this excess is qualitatively demonstrated on the basis of the associative mechanism as follows. The exchange rate, $V_{ex,H}$, is given in general by substitution of $x_{H(a)}$ from eq (13.15) into eq (12.26.H) as

$$V_{ex,H} = 2v_-(II)v_-(I_b)/(v_-(II) + 3v_+(I_b)), \quad (14.1)$$

which will be discussed now for the respective cases below and above the optimum.

The rate-determining step being either $I_b$ or III in accordance with 9.2.3, we have partial equilibrium of step II throughout, as verified by figure 27, hence according to eqs (12.16.II) and (13.1)

$$\gamma(H) = \gamma(C_2H_5). \quad (14.2)$$

Equations (12.22.H) and (12.22. A) yield, on the other hand, $v_+(I_b) = v_+(III)$ or, substituting $v_+(I_b)$ etc. from eq (12.16) and referring to eq (14.2), $k(I_b) = \gamma(H)^2(k(I_b) + k(III))$.

In the temperature range below the optimum we have ignoring $k(I_b)$ as compared with $k(III)$,

$$\gamma(H)^2 = k(I_b)/k(III). \quad (14.3)$$

Figure 27 shows, on the other hand, that $v_+(II) = v_+(II)$ is far greater than $v_+(I_b)$ while $v_+(III)$ equals $v_+(III)$, i.e.,
Ignoring thus $v_+(I_b)$ in comparison with $v_-(II)$, we can reduce eq (14.1) to the form

$$V_{ex, H} = 2v_-(I_b)$$  \hspace{1cm} (14.5.a)$$
or, according to eqs (12.16,1a) and (14.3),

$$V_{ex, H} = 2k(I_b)^2/k(III).$$  \hspace{1cm} (14.5.b)$$

Equation (14.5.b) is interpreted as follows. Equation (14.4) shows that an H(a) formed by the forward act of $I_b$ passes rapidly between the initial and final states of step II until it finally enters step III to finish the hydrogenation or the reverse of $I_b$ to revert to H$_2$ in gas. $V_{ex, H}$ counts those H(a) (cf. eq (14.5.a)) which get back into hydrogen molecules in gas per unit time, i.e., the rate of overall supply of H(a), $2v_-(I_b)$, multiplied by $v_-(I_b)/(v_-(I_b) + v_+(III))$ which is the fraction of them getting back into H$_2$, or by $v_-(I_b)/v_+(III)$, according to eqs (12.16,1a), (14.4), (14.3), which state that $v_-(I_b) = \gamma(H)^2k(I_b) = v_+(III)k(I_b)/k(III)$ \(\ll v_+(III)\). This fraction equals $k(I_b)/k(III)$ while $v_+(I_b)$ is given by $k(I_b)$, hence eq (14.5.b).

The activation heat of exchange of hydrogen, $RT^2\gamma \partial \ln V_{ex, H}/\partial T$, is hence necessarily greater than that of hydrogenation, $RT^2\gamma \partial \ln k(I_b)/\partial T$, by $RT^2\gamma \partial \ln k(I_b)/\partial T - RT^2\gamma \partial \ln k(III)/\partial T$ (below the optimum), which is inevitably positive as shown in 14.1.

Above the optimum, where step III governs the rate as concluded in 9.2.3, we have from eq (12.19), according to inferences (i) and (ii) in 12.5.1 and to eq (13.1), that

$$\gamma(H) = \gamma(C_2H_5) = 1,$$  \hspace{1cm} (14.6.a)$$
hence

$$v_+(s) = v_-(s) = k(s), \hspace{1cm} s = I_a, I_b, II \hspace{1cm} (14.6.b)$$

and

$$v_+(III) = k(III)$$  \hspace{1cm} (14.6.c)$$

according to eqs (12.16), i.e., all steps but III are in partial equilibrium. We observe the higher extremum of temperature, where $k(I_b) \gg k(II)$ as seen in figure 28. Equation (14.1) then assumes the form,

$$V_{ex, H} = (2/3)v_-(II)$$  \hspace{1cm} (14.7)$$

if we ignore $v_-(II) = k(II)$ as compared with $3v_-(I_b) = 3k(I_b)$ and identify $v_-(I_b)$ with $v_+(I_b) = k(I_b)$.

We have from eq (12.24,E), for the predominance of $v_+(I_a)$ inferred in 13.1,

$$x_{(a)} = x_e$$  \hspace{1cm} (14.8.E)$$

and from eq (13.15), for the predominance of $v_+(I_b)$ over $v_-(II)$,

$$x_{(a)} = x_{(a)}$$  \hspace{1cm} (14.8.H)$$

Equations (14.8) state that the “fall” of deuterium content occurs across step II so that the rate of exchange is proportional to $v_-(II) = v_+(II) = k(II)$, as seen from eq (14.7); the proportionality factor 2/3 represents the number of hydrogen atoms transferred from the state where they belong to C$_2$H$_5$(a) back to that of H(a) for every reversal of step II; this transfers either of the two hydrogen atoms in the methyl radical originating from C$_2$H$_5$(a) with the probability of 1/3; two out of three times does the reversal bring hydrogen atoms from C$_2$H$_5$(a) to the state of H(a) as given by the proportionality factor.

The activation heat of exchange of hydrogen is thus $RT^2\gamma \partial \ln k(II)/\partial T = \Delta H(II) = -12.6$ kcal which is algebraically greater than that of hydrogenation, $-18.3$ kcal, but by an excess appreciably smaller than that below the optimum.

### 14.3. Retardation of Parahydrogen Conversion and °H$_2$-D$_2$ Equilibration by the Presence of Ethylene

It may be noted that eq (12.27) for the parahydrogen conversion and eq (12.30) for the equilibration apply irrespective of the presence or absence of ethylene, insofar as these associated reactions are caused by step $I_b$ and its reverse and the hydrogen desorbed is in equilibrium with respect to parahydrogen conversion or to °H$_2$-D$_2$ equilibration.

The rate of parahydrogen conversion in the presence or absence of ethylene is equal according to eq (12.27), to $v_-(I_b)$. This assumes, in the absence of ethylene, its particular value, $k(I_b)$, in equilibrium of $I_a$ according to eq (12.16.1a). It follows that the ratio of the rates of parahydrogen conversion in the presence of ethylene, $V_p(P)$, and in its absence, $V_p(A)$, equals $v_-(I_b)/k(I_b)$ or, according to eq (12.16.1a),

$$V_p(P)/V_p(A) = \gamma(H)^2$$  \hspace{1cm} (14.9)$$

where $\gamma(H)$ is the activity coefficient of hydrogen adatom in the presence of ethylene.

In the temperature range where $I_b$ governs the hydrogenation rate, $\gamma(H)^2$ is, according to eq (14.3), extremely small as compared with unity, hence the retardation of parahydrogen conversion by ethylene according to eq (14.9). Above the optimum $\gamma(H)^2 = 1$, according to eq (14.6.a), hence no retardation. These

The rate of $^1$H$_2$D$_2$ equilibration, $V_q$, is given, under the special condition where $v = 0$ and $x_e = 0$, according to eq (12.30), as

$$V_q = \frac{x_{H(a)}(1 - x_{H(a)})}{x_H(1 - x_H)} v_-(I_b).$$

The value of $x_{H(a)}$ in the absence of ethylene is nothing but $x_H$. We have thus, denoting the rates in the presence and absence of ethylene by suffixes (P) and (A), respectively:

$$V_q(P)/V_q(A) = \frac{x_{H(a)}(1 - x_{H(a)})}{x_H(1 - x_H)}.$$  \hspace{1cm} (14.10)

The value of $x_{H(a)}$ for $x_e = 0$ is given by eq (13.15) as

$$x_{H(a)} = \frac{3v_+(I_b)}{v_- + 3v_+(I_b)} x_H.$$  \hspace{1cm} (14.11)

Below the optimum, $x_{H(a)}$ is extremely small as compared with unity according to equations (14.11) and (14.4), hence retardation; above the optimum, where $k(I_b)$ predominates over $k(II)$, $x_{H(a)}$ equals $x_H$ according to equations (14.11) and (14.6.b), hence no retardation. The former conclusions explain the experimental result [68] reviewed in 5.1.2.

### 14.4. The Relation Between Equilibrium Fraction, $u$, and Deuterium Atom Fraction, $x_H$, of Hydrogen

The theory of the associative mechanism leads to the expression for $u$ in terms of $x_H$ and $x_{H(a)}$:

$$\exp \left( \int_1^u \frac{dx_H}{x_H x_{H(a)} - x_{H(a)}} \right) = \int_1^u \frac{x_{H(a)}(1 - x_{H(a)})}{x_H x_{H(a)} - x_{H(a)}} dx_H$$

$$\cdot \exp \left( \int_{x_H}^{x_{H(a)}} \frac{dx_H}{x_H x_{H(a)} - x_{H(a)}} \right) dx_H$$

as derived in the following.

On elimination of $V_{x_H}$ and $u(I_b)$ from eqs (12.25.H), (12.26.H) and (13.30), one obtains, noting $n_H = 2N_H$ by definition,

$$\frac{du}{dx_H} = \frac{x_{H(a)}(1 - x_{H(a)})}{x_{H(a)} - x_{H(a)}} - \left( \frac{1}{x_{H(a)} - x_H} - \frac{1}{1 - x_H} + \frac{1}{x_H} \right) u,$$

which is solved as

$$\exp \left( \int_1^u \frac{dx_H}{x_H x_{H(a)} - x_{H(a)}} \right) = \left\{ \int_1^{x_H} \frac{x_{H(a)}(1 - x_{H(a)})}{x_H x_{H(a)} - x_{H(a)}} dx_H \right\}$$

$$\cdot \exp \left( \int_{x_H}^{x_{H(a)}} \frac{dx_H}{x_H x_{H(a)} - x_{H(a)}} \right) dx_H + C,$$

the integration constant, $C$, is determined by substituting $u$ from eq (12.29) into the above equation thus

$$\frac{N_{HHD}}{2N_H} = \exp \left( \int_1^{x_H} \frac{dx_H}{x_H x_{H(a)} - x_{H(a)}} \right) \left\{ \int_1^{x_H} \frac{x_{H(a)}(1 - x_{H(a)})}{x_H x_{H(a)} - x_{H(a)}} dx_H \right\}$$

$$\cdot \exp \left( \int_{x_H}^{x_{H(a)}} \frac{dx_H}{x_H x_{H(a)} - x_{H(a)}} \right) dx_H + C,$$

Since $N_{HHD} = 0$ for $x_H = 1$, we have $C = 0$, hence eq (14.12) above.

Equation (14.12) leads to the following limiting values of $u$ as $x_H$ tends to unity or to $x_{H(a)}$, respectively:

$$\lim_{x_H \to 1} u = x_{H(a)}, \quad \lim_{x_H \to x_{H(a)}} u = 1.$$  \hspace{1cm} (14.13.a), (14.13.b)

Equation (14.13) applies in the case of deuteration of ethylene with pure deuterium, as in the experiment of Twigg and Rideal [68] reviewed in 5.1.2; part (a) shows that $u$ starts from the initial value of $x_{H(a)}$, while part (b) indicates the situation, which is finally arrived at along with the progress of reaction.

It is now required to find $x_{H(a)}$ as a function of $x_H$ in order to determine the relation between $u$ and $x_H$ by eq (12.12). The relation is given for an equimolar mixture of reactants as

$$x_H - x_{H(a)} = F \exp \left\{ \int_{P_0}^{P} (F/V_q) [(v_+(I_b) + v_-)(I_b)/2 + v_- (I_b)] dP \right\}.$$  \hspace{1cm} (14.14.x)

where

$$F = v_-(II)(v_-(II) + 3v_+(I_b))^{-1}.$$  \hspace{1cm} (14.14.F)

and $P$ and $P_0$ are the current and the initial partial pressures of either reactant. The fraction $x_H$ is given as a function of $P$, as

$$1 - x_H = \int_{P_0}^{P} (F_{V_-(I_b)/V_q}) \exp \left\{ \left[ \int_{P_0}^{P} (F/V_q) \right. \cdot (v_+(I_b)/2 + v_-(I_b)) \right\} dP \right\} d\ln P.$$  \hspace{1cm} (14.15)

Equations (14.14) and (14.15) are derived as follows.

Equation (12.25.x) is written, replacing $v_-(I_a)$ with $v_+(I_a)$ according to equations (12.16.1a) and (13.1), as

$$n_{x_H} = 4(x_{H(a)} - x_H)v_+(I_a).$$

Eliminating $(x_H - x_{H(a)})v_+(I_a)$ and $(x_{H(a)} - x_H)v_-(II)$ from the above equation, eq. (12.25.a) and (12.23.c), we have

$$N_{x_H} = \frac{1}{2} \cdot (x_H - x_{H(a)})v_+(I_b).$$  \hspace{1cm} (14.16)
where $N = n_F/4 = n_H/2$ is the number of molecules of either reactant. The fraction, $x_{\text{H(a)}}$, is substituted from eq (13.15) into eq (14.16) with reference to eq (14.14.F) as

$$N\dot{x}_E = 1/2 \cdot (x_H - x_E)Fv_+(I_b). \quad (14.17)$$

We have, on the other hand, from equations (12.25.H) and (12.26.H)

$$N\dot{x}_H = (x_{\text{H(a)}} - x_H)\nu_-(I_b) \quad (14.18)$$
or, substituting $x_{\text{H(a)}}$ from eq (13.15) with reference to eq (14.14.F),

$$N\dot{x}_H = (x_E - x_H)Fv_-(I_b). \quad (14.19)$$

Equations (14.17) and (14.19) lead to the differential equation

$$-\left(\frac{\dot{x}_H - x_H}{x_E - x_H}\right) = \left(\frac{F}{N}\right)\left(\nu_+(I_b)/2 + \nu_-(I_b)\right),$$

or by integration to the equation

$$x_E - x_H = C \exp \left\{ -\int \left(\frac{F}{N}\right)\left(\nu_+(I_b)/2 + \nu_-(I_b)\right) dt \right\},$$

where $C$ is the integration constant as determined for the initial conditions, i.e., $x_E = 0$ and $x_H = 1$ at $t = 0$, as

$$-1 = C \exp \left\{ -\int_0^t \left(\frac{F}{N}\right)\left(\nu_+(I_b)/2 + \nu_-(I_b)\right) dt \right\},$$
hence

$$x_H - x_E = \exp \left\{ -\int_0^t \left(\frac{F}{N}\right)\left(\nu_+(I_b)/2 + \nu_-(I_b)\right) dt \right\}.$$

The value $x_H - x_E$ thus obtained is substituted into eq (14.19) as

$$\dot{x}_H = -(F/N)(I_b)\exp \left\{ -\int_0^t \left(\frac{F}{N}\right)\left(\nu_+(I_b)/2 + \nu_-(I_b)\right) dt \right\}.$$

On integration we have

$$1 - x_H = \int_0^t \left(\frac{F}{N}\right)\left(\nu_+(I_b)/2 + \nu_-(I_b)\right) dt,$$
determining the integration constant by the initial condition that $x_H = 1$ at $t = 0$.

The last two equations are written, changing the variable of integration for an expedient calculation according to the identity,

$$\frac{d N}{N} = \frac{d \ln P}{dt} dt, \quad \frac{d N}{N} = -\frac{d \ln P}{N} = -\frac{d \ln P}{V_s},$$

based on the proportionality between $P$ and $N$ and the relation, $V_s = -dN/dt$, as

$$\dot{x}_H = -(F/N)(I_b)\exp \left\{ -\int_0^t \left(\frac{F}{V_s}\right)\nu_+(I_b)/2 + \nu_-(I_b) d\ln P \right\}.$$

### 14.5. Changes in $V_{A_\alpha}$'s With Temperature and Partial Pressures of the Reactants

We have from eq (13.5)

$$V_{A_0} : V_{A_1} : V_{A_2} : V_{A_{n>2}} = (1 - x_{\text{H(a)}})^2$$

$$: 2x_{\text{H(a)}}(1 - x_{\text{H(a)})} : x_{\text{H(a)}}^2 : 0,$$

which shows that the relative magnitudes of $V_{A_n}$ depend solely on $x_{\text{H(a)}}$. The fraction $x_{\text{H(a)}}$ is now uniquely defined, according to eq (13.7.a), by the ratio $\nu_+(I_b)/\nu_-(II) = \kappa$ as

$$\frac{x_{\text{H(a)}}}{3(1 - x_{\text{H(a)}})} = \frac{\nu_+(I_b)}{\nu_-(II)} = \kappa, \quad (14.21.a)$$

while $\kappa$ is expressed by eqs (12.16) as

$$\kappa = k(I_b)/\gamma(C_2H_3)k(II). \quad (14.21.b)$$

Figure 29 shows the relation between $1 - u$ and $x_H$ calculated by eqs (14.12), (14.14), and (14.15) for $P_{E_0} = P_{H_0} = 10$ mm Hg, which roughly reproduces the experimental results of Twigg and Rideal [68] in figure 16 on the one hand and predicts [8, 9, 10, 137] the rapid rundown of the curves at lower temperatures, on the other hand, which has been verified by Matsuzaki [115] as shown in figure 17.
The function $\kappa$ is determined by the values of $k(s)$ for the specified conditions according to eqs (13.14) and $\gamma(C_2H_3)$ derived from $k(s)$ by eq (12.19). The relative rates of eq (14.20) are thus calculated for different values of $P_E$, $P_H$ and temperature as shown in table 28. The values at $P_E = 10$ mm Hg, $P_H = 20$ mm Hg and 90 °C closely reproduce the observations, shown in parentheses, by Turkevich et al. [117], under the same conditions.

We see from table 28 that the maximum yield of ethanes-d$_3$ is shifted from $A_0$ through $A_1$ to $A_2$ by either increasing $P_H/P_E$ or raising the temperature. These conclusions have been experimentally verified semiquantitatively by Miyahara and Narumi [114] as shown in tables 15 and 16.

The dominating factor $\kappa$ is discussed in what follows. In case where $I_b$ determines the rate, we have $\gamma(C_2H_3) = \gamma(H) = \sqrt{k(I_b)/k(III)}$ from eq (14.2) and (14.3), hence by eq (14.21.b)

$$
\kappa = \sqrt{k(I_b)/k(II)} \quad (14.22.a)
$$

or, according to eqs (12.9) and (14.22.a),

$$
\kappa \propto \sqrt{P_H/P_E}. \quad (14.22.b)
$$

Equations (14.21.a) and (14.22.b) indicate that $x_H(a)$ increases to shift the maximum yield of ethanes-d$_n$ toward $A_2$ by increasing $P_H/P_E$ in accordance with table 28.

When the rate is determined by step III, at higher temperatures, we have from eqs (14.21.b) and (14.6.a) $\kappa = k(I_b)/k(II)$. The factor $\kappa$ increases with temperature, since $\Delta H(I_b) > \Delta H(II)$ as seen from eqs (13.3) and (13.12.11), so that at sufficiently high a temperature $x_H(a)$ tends to unity and the maximum yield shifts to $A_2$; there must, however, be a range of temperatures, as seen in figure 28, where step III determines the rate but $k(I_b) \ll k(II)$, hence $A_0$ predominate.

### 14.6. “Random Distribution” of Deuterium in Ethylene and Ethane in the Deuteration of Light Ethylene

Kemball [76] has observed the initial evolution rates of ethylenes-d$_n$ and ethanes-d$_n$ in deuteration of light ethylene over evaporated nickel film as referred to in 5.2.3. It is shown next that his results follow necessarily from the present theory for the associative mechanism.

The values of $\log_{10}(k(s)/\rho)$ are calculated for the specified experimental conditions, i.e., $-100$ °C, $P_E = 2.7$ mm Hg and $P_H = 8.1$ mm Hg by eqs (13.14) as

$$
\log_{10}(k(I_b)/\rho) = 16.9543, \quad \log_{10}(k(II)/\rho) = 2.1552,
$$

from which $\gamma(C_2H_4)$, $\gamma(H)$ and $\gamma(C_2H_3)$ are evaluated by eq (12.19), ignoring $\gamma(C_2H_6)$ and referring to eq (13.1), as

$$
\gamma(C_2H_4) = 1, \quad \gamma(H) = \gamma(C_2H_3) = 3.52 \times 10^{-8}.
$$

The forward and backward rates, $v_+(s)'s$ and $v_-(s)'s$, of steps $s$ are calculated from the above values of $k(s)'s$ and $\gamma(H)$ etc. according to eqs (12.16) as

$$
v_+ (II) = v_-(II) = 5.038 \times 10^{-11} \rho, \quad v_+(I_b) = v_+(III) = 9.002 \times 10^{-16} \rho, \quad v_-(I_b) = 1.118 \times 10^{-28} \rho,
$$

as given in the order of their magnitudes. Step II as well as step $I_a$, in accordance with 13.1, are thus occurring in both directions with rates far exceeding those of other steps, so that an isotopic exchange equilibrium is brought about among $C_2H_4$, $C_2H_4(a)$ and $H(a)$ according to the associative mechanism; the deuterium atoms in $C_2H_4(a)$ and $H(a)$ are in
consequence in random distribution, hence as well those in \( \text{C}_2\text{H}_6 \), which is composed of \( \text{C}_2\text{H}_4(a) \) and \( \text{H}(a) \) according to the mechanism. It follows that ethylenes-\( d_n \) are evolved with the relative rates given by eqs (12.31.E) and (12.32), and ethane-\( d_n \) by eq (12.33.c).

The above conclusion is compared with the experimental results of Kemball [76] in table 29 in terms of the percentages of ethylenes-\( d_n \), \( (100 - 36.7) \left\{ \sum_{n=1}^{4} \left( \frac{4}{n} \right) x_{\text{E}(a)}^n (1 - x_{\text{E}(a)})^{4-n} \right\} \), and of ethanes-\( d_n \), \( 36.7 \left\{ \sum_{n=1}^{6} \left( \frac{6}{n} \right) x_{\text{E}(a)}^n (1 - x_{\text{E}(a)})^{6-n} \right\} \), among the total ethanes, and excellent agreement is found; 36.7 in the above expressions is the percentage of ethane in the entire hydrocarbons excluding light ethylene, and \( \left( \frac{4}{n} \right) x_{\text{E}(a)}^n (1 - x_{\text{E}(a)})^{4-n} \) is the fraction of the amount of ethylene-\( d_n \) in the total amount of ethylene excluding light ethylene. The value of \( x_{\text{E}(a)} \) was thus taken to be 0.222.

Wagner et al. [126], conducted an experiment, as referred to in 7.1.3, on the catalyzed deuteration of light ethylene in the presence of nickel on kieselguhr and observed the distribution of ethanes-\( d_n \) in the product of the catalyzed deuteration. They tried to account for the experimental results assuming a random distribution of deuterium in ethane, i.e., in accordance with eq (12.33.c); the maximum yield of ethanes-\( d_n \) was thus located at \( n = 2 \) for \(-50^\circ \mathrm{C}\) but at \( n = 3 \) for \(50^\circ \mathrm{C} \), whereas the maximum was observed at \( n = 2 \) in both cases [126]. Wagner et al., calculated \( x_{\text{E}} \) to be 0.35 and 0.50 at \(-50^\circ \mathrm{C}\) and \(50^\circ \mathrm{C} \), respectively, as the fraction of the total number of deuterium atoms lost from hydrogen gas over the total number of hydrogen atoms in ethane evolved. Since no deuterium entered ethylene, this process of calculation would be correct, provided only that the supported catalyst did not exchange deuterium with reactants. Without relying on the assumption \( x_{\text{A}} \) is straightforwardly and necessarily given as \( x_{\text{A}} = \sum_{n=1}^{6} nX_{\text{A}n} / 6 \). The fraction, \( x_{\text{A}} \), is thus calculated as 0.331 and 0.422, respectively, at \(-50^\circ \mathrm{C}\) and \(50^\circ \mathrm{C} \). With these values, the observed peaks at \( n = 2 \) are reproduced at both temperatures.

### Table 29. Relative rates of evolution, \( V_{\text{E}n} \) and \( V_{\text{An}} \), of ethylenes-\( d_n \) = \( \text{E}_n \) and ethanes-\( d_n \) = \( \text{A}_n \) in the initial deuteration product of light ethylene over evaporated nickel film

<table>
<thead>
<tr>
<th>( x_{\text{E}(a)} )</th>
<th>( V_{\text{E}1} )</th>
<th>( V_{\text{E}2} )</th>
<th>( V_{\text{E}4} )</th>
<th>( V_{\text{A}2} )</th>
<th>( V_{\text{A}4} )</th>
<th>( V_{\text{A}6} )</th>
<th>( V_{\text{A}8} )</th>
<th>( V_{\text{A}10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs. [76]</td>
<td>0.222</td>
<td>46.7</td>
<td>13.2</td>
<td>2.7</td>
<td>0.7</td>
<td>7.8</td>
<td>12.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Calc.</td>
<td>41.8</td>
<td>17.9</td>
<td>3.4</td>
<td>0.3</td>
<td>8.1</td>
<td>13.9</td>
<td>9.9</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\* Reproduced from table 12.
\( ^b \) The percentages are calculated according to eqs (12.31.E), (12.32) and (12.33.c), and the experimental result that the total ethanes amounts to 36.7 percent of the total hydrocarbons except \( \text{E}_n \), as

\[
V_{\text{E}n} = (100 - 36.7) \left\{ \sum_{n=1}^{4} \left( \frac{4}{n} \right) x_{\text{E}(a)}^n (1 - x_{\text{E}(a)})^{4-n} \right\}
\]

and

\[
V_{\text{An}} = 36.7 \left\{ \sum_{n=1}^{6} \left( \frac{6}{n} \right) x_{\text{E}(a)}^n (1 - x_{\text{E}(a)})^{6-n} \right\} \]

\( x_{\text{E}(a)} \) is now given as \( x_{\text{E}(a)} = x_{\text{E}} = x_{\text{E}(a)} \).

### 14.7. Isotopic Effect on Hydrogenation Rate

We have seen in section 6 that the hydrogenation rate of light ethylene with light hydrogen exceeds the deuteration rate of light ethylene under similar conditions by a factor of 2 to 3 at temperatures below the optimum; the factor decreases down to unity around the optimum temperature but exhibits a tendency to increase again at higher temperatures as seen in figures 19, 22, and 23 or in table 20. The experimental results are accounted for by the present theory as follows.

We see from figure 28 that step \( \text{I}_b \) governs the rate below the optimum, hence the appropriate isotopic difference in rate. Above the optimum, the rate is governed by step \( \text{III} \), hence an isotopic difference in rate depending on \( x_{\text{E}(a)} \), while the fraction \( x_{\text{E}(a)} \) is kept equal to \( x_{\text{E}} = 0 \) as inferred in 13.1. The fraction \( x_{\text{H}(a)} \) for \( x_{\text{E}} = 0 \) is now given according to eq (14.11), which is written for temperatures above the optimum according to eq (14.6.b) as

\[
x_{\text{H}(a)} = \frac{3k(I_b)(k(II))}{3k(I_b) + 3k(II)} x_{\text{H}}.
\]

There are two phases, one at lower and one at higher temperatures in the region of rate-determining step \( \text{III} \), where \( k(\text{I}_b) < k(\text{II}) \) and \( k(\text{I}_b) > k(\text{II}) \), respectively, as seen from figure 28. The above equation states that at the lower temperatures in this region, \( x_{\text{H}(a)} \) is small even in the case of deuteration, and affects little the rate-determining step \( \text{III} \) isotopically, whereas at higher temperatures \( x_{\text{H}(a)} \) approaches \( x_{\text{H}} = 1 \) and hence makes an isotopic difference through the rate-determining step \( \text{III} \) in accordance with experimental results.
15. Application of the Theory of Absolute Rates

Laidler [138] applied the theory of absolute rates to the rate-determining step III of the associative mechanism and to a step

$$2 \text{C}_2\text{H}_4(\text{a}) \rightarrow \text{C}_2\text{H}_4(\text{a}) + \text{C}_2\text{H}_6,$$  \hspace{1cm} (15.1)

concluding that a tolerable agreement with experimental results is obtained in both cases. His procedure and conclusion are commented upon on the basis of the present theory.

15.1. Laidler expressed the concentration $C_{s_2}$ of dual sites, i.e., the number of pairs of adjacent bare sites per unit area of catalyst as

$$C_{s_2} = \frac{sC^2_s}{2L},$$

where $C_s$ is the concentration of bare single sites, $s$ the number of sites adjacent to a single site and $L$ the concentration of single sites when the surface is completely bare. This equation is derived expressing the probability that one of adjacent single sites to a bare single site is also bare, by $1-\theta$, where $\theta$ is given by $2C_d/L$ in terms of the concentration $C_a$ of adsorbed ethylene. This procedure would be exact, if $\text{C}_2\text{H}_4(\text{a})$ were dissociated into adsorbed methylene radicals, $\text{CH}_2(\text{a})$, and distributed over single sites independent of each other. Let 1 and 2 be the adjacent single sites, of which the above probability is in question. The probability that site 2 is occupied under the premised bareness of site 1 is $\left(\frac{s-1}{s}\right)\theta$, since the premised bareness of site 1 excludes one of $s$ cases where site 2 is occupied by an $\text{C}_2\text{H}_4(\text{a})$ lying across sites 1 and 2. The probability in question is thus $1 - \frac{s-1}{s}\theta$ rather than $1-\theta$. The approximation associated with the revised expression is that the probability of the remaining $s-1$ cases of site 2 being occupied is assumed unchanged by premising the bareness of site 1 thus excluding the one of $s$ cases. This correction changes, however, hardly the order of magnitude of the numerical factor in question below. We will remain, on that account, with Laidler's approximation in this regard.

15.2. A rather serious difficulty is associated with this treatment in the temperature change of rate. Laidler arrives at rate equations of step III of the associative mechanism and of step (15.1) respectively determining the rate, which contain numerical factors, $AB^2$ and $A^2B^2$, respectively, where

$$A = \frac{1 + x - (1 + 2x)^{1/2}}{2x}, \hspace{1cm} B = \frac{(1 + 2x)^{1/2} - 1}{x},$$

and

$$x = 2sKC_g,$$  \hspace{1cm} (15.4)

and

$$K = \frac{C_d}{C_gC_{s_2}},$$  \hspace{1cm} (15.5)

$K$ is the equilibrium constant of adsorption and $C_g$ is the concentration of ethylene in gas here given in terms of its partial pressure in mm Hg.

The procedure of Laidler to be questioned is this. He took arbitrarily the maxima of $AB^2$ and $A^2B^2$ with respect to $x$ for the calculation of reaction rates. Since $K$ varies with temperature, $x$ will too, so that the numerical factors necessarily slip off the maximum at a particular temperature, when varying the temperature. The result is that the temperature change of the numerical factor is superimposed upon that due to the Boltzmann factor of a constant energy increment included in the rate equation.

This superimposition is illustrated with the observation of Farkas, Farkas, and Rideal [2] at 120 ºC and $P_E = 12$ mm Hg with which Laidler compares his calculated rates. The last mentioned energy increment is taken to be 4.7 kcal/mole by Laidler. $AB^2$ and $A^2B^2$ have maximum values at around $x = 2$ according to eqs (15.3). These maxima are taken to be numerical factors in calculating the rates in the respective case. The $K$ value for $x = 2$ and $s = 4$ is according to eq (15.4)

$$K = \frac{1}{(4 \times 12)} \text{ (mm Hg)}^{-1}.$$

$K$ can be written, on the other hand, in terms of the heat of adsorption, $\epsilon_E$, and of the partition function of ethylene, $Q_{E,0}$, as done by Laidler with the adsorption of hydrogen, as

$$K = Q_{E,0}^{-1}e^{\epsilon_E/RT}.$$  \hspace{1cm} (15.6)

We have from the above equations and the numerical value of $Q_{E,0}$ of eq (12.5E)

$$\epsilon_E = 23.2 \text{ kcal/mole}.$$  \hspace{1cm} (15.7)

It follows from eqs (15.6) and (15.7) that $K$ and in consequence $x$ decrease according to eq (15.4) monotonously with increase of temperature.

It is readily deduced from eqs (15.3) that extreme values of the numerical factors are

$$AB^2 = x^{-1}, \hspace{0.5cm} A^2B^2 = (2x)^{-1} \hspace{0.5cm} \text{for} \hspace{0.5cm} x \gg 1,$$  \hspace{1cm} (15.8a)

and

$$AB^2 = x/4, \hspace{0.5cm} A^2B^2 = x^2/16 \hspace{0.5cm} \text{for} \hspace{0.5cm} x \ll 1.$$  \hspace{1cm} (15.8b)
We have from eqs (15.4), (15.6), (15.7), and (15.8) that
\[ RT^2 \partial \ln (AB^2)/\partial T = RT^2 \partial \ln (A^2B^2)/\partial T = 23.2 \text{ kcal/mole} \]
in the extreme of low temperature and
\[ RT^2 \partial \ln (AB^2)/\partial T = -23.2 \text{ kcal/mole}, \]
\[ RT^2 \partial \ln (A^2B^2)/\partial T = -46.4 \text{ kcal/mole} \]
in the extreme of high temperature. These amazing values are inevitably superimposed upon the constant energy increment mentioned above. The activation heat thus decreases from the low extreme of temperature to the high extreme by 46.4 kcal/mole in case of the rate determined by step III and by 69.6 kcal/mole in case of the rate determined by step (15.1).

Such a superimposition occurs, however, over not very wide a range of temperature; we have for example
\[ RT^2 \partial \ln (AB^2)/\partial T = 16.5 \text{ kcal/mole}, \]
\[ RT^2 \partial \ln (A^2B^2)/\partial T = 13.1 \text{ kcal/mole} \]
at 90 °C and
\[ RT^2 \partial \ln (AB^2)/\partial T = -14.9 \text{ kcal/mole}, \]
\[ RT^2 \partial \ln (A^2B^2)/\partial T = -33.9 \text{ kcal/mole} \]
at 150 °C as calculated by eqs (15.3), (15.4), (15.6), and (15.7) assuming \( x = 2 \) at 120 °C. This amounts to saying that nearly 70 percent of the overall decreases of activation heat mentioned above are got through within the temperature range of ±30 °C, which is far from being true.

15.3. One might try to elude the extravagant superimposition inherent to the Laidler’s procedure by localizing the phase of the numerical factor either to that of (15.8.a) or (15.8.b). In the former case we have according to eqs (15.4) and (15.6)
\[ AB^2 = \frac{Q_{E,0}}{2sC_g} \exp (-\varepsilon_E/RT), \]
\[ A^2B^2 = \frac{Q_{E,0}}{4sC_g} \exp (-\varepsilon_E/RT). \]

Incorporating the exponential factor in the above equation in that of the activation heat as did by Laidler with the adsorption heat of hydrogen, the numerical factor is now \((1/2s)(Q_{E,0}/C_g)\) or \((1/4s)(Q_{E,0}/C_g)\), which amounts to \(4.1 \times 10^{12}\) or \(21 \times 10^{12}\) respectively for \(s = 4\) and \(P_E = 12 \text{ mm Hg}\). In the latter case of eq (15.8.b), the numerical factor is respectively for step III or (15.1) determining the rate in place of the maximum value, 0.074 or 0.0156 used by Laidler. The agreement with experimental results is thus quite out of question.

One might see that the numerical factors are secured in the order of magnitude of unity by confining them to the intermediate phase, say to their maxima, where we encounter the difficulty described in 15.3.

15.4. The rate equation in case of step III determining the rate for \( x \leq 1 \) is given\(^{32}\) according to eq (15.9.a) as
\[ v = \frac{(kT/h)N_t}{(C_g/Q_{E,0})(H/2Q_{H,0})} \exp (-\Delta^s H(r)/RT), \]
where \( N_t \) represents \( (s/2)L \) i.e., the concentration of dual sites in case of a practically bare surface, \( Q_{E,0} \) or \( Q_{H,0} \) the partition function of ethylene or hydrogen and \( \Delta^s H(r) \) the activation heat. The difficulty, in particular, with eq (15.10) is that \( v \) is smaller than that observed by a factor ca. 10^12 provided that \( \Delta^s H(r) \) is fixed at 4.7 kcal/mole as assigned by Laidler. This difficulty is got over by excluding ethylene from \( I(r) \) of eq (12.13), which reduces the rate remarkably by decreasing \( \Delta^s S(r) \) as seen from eqs (12.14) and (12.15). We are thus just in line with the association mechanism, in which the rate is determined by the dissociative adsorption of hydrogen molecules, i.e., by step Ib, under the activation heat of the above magnitude.

The \( \Delta^s S(\text{III}) \) is lower than \( \Delta^s S(\text{Ib}) \) on account of an ethylene molecule comprised in I(III), in excess over I(III). Since \( k(\text{III}) \) must, however, be greater than \( k(\text{Ib}) \) in the temperature range, where \( I_t \) governs the rate according to 12.5.1.(iii), step III should have an activation heat sufficiently lower than step Ib in accordance with eq (12.14). Along with rise of temperature, however, the effect of the lower activation heat is reduced and sooner or later \( k(\text{III}) \) becomes lower than \( k(\text{Ib}) \) so that III governs the rate in place of Ib at higher temperature according to 12.5.1.(iii), hence the switchover in the rate-determining step described in 14.1.

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\(^{32}\) We have an extra factor \( s^2 \) by a direct substitution of \( AB^2 \) from eq (15.9.a) into eq (91) of the article of Laidler [130]. He identified the partition functions, \( f_{sw} \) and \( f_{sr} \), in the last-mentioned equation of him respectively with unity, which is not correct, since the appropriate states are respectively \( s^2 \)-fold degenerated. Equation (15.10) is obtained without the extra factor by identifying partition functions \( f_{sw} \) and \( f_{sr} \) respectively with a instead on this account. Detailed account will not be given on this point since the factor in question does not affect the conclusion.
16. Concluding Remark

As developed in the foregoing sections, the present theory based on scheme (9.5) accounts systematically for the experimental results on the catalyzed hydrogenation of ethylene in the presence of metallic catalysts especially nickel. But it may be mentioned in concluding this review that the present theory accounts for the experimental results of other olefines as well, e.g., the optimum temperatures observed in the catalyzed hydrogenation of propylene [139, 140] and butylene [141], the distribution of deuterium in their deuteration products [139], the migration of double bonds [141] etc.

17. References

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$$V_s: V_{E_1}; V_{E_{n+1}} = 1:2.33:0$$  \hspace{1cm} (13.2.E)$$
and
$$V_{A_0}: V_{A_1}: V_{A_2}: V_{A_{n+1}} = 1:0.69:0.154:0$$  \hspace{1cm} (13.2.A)$$
at the very beginning of the catalyzed deuteration of light ethylene over nickel wire at 90 °C. Equation (13.2.E) states that $E_1$ is the only deuterioethylene evolved at the very beginning, which shows that the reverse of step I$_a$ is rapid enough to carry away $E_1$ (a) once formed by step II and its reverse before $E_1$ (a) enters step II again to acquire another deuterium atom. Equation (13.2.A) states, on the other hand, that the only deuterioethanes evolved are $A_1$ and $A_2$. It follows, since ethane is formed by two consecutive additions of H(a)'s to C$_2$H$_4$ (a) according to scheme (9.3), that practically only light C$_2$H$_4$ (a) is subject to two consecutive additions, endorsing the statement of eq (13.2.E) and, in conjunction with the latter, confirming the conclusion of 13.1.1.

### 13.2 Estimate of $k(I_b)$

It has been concluded in 9.2.3. that the rate-determining step below the optimum is I$_b$. The quantity $\Delta' H(I_b)$ is thus determinable from observations of $V_s$ below the optimum identifying $V_s$ with $k(I_b)$ of eq (12.9.Ib); the value $\Delta' H(I_b) = 4.7$ kcal/mole \hspace{1cm} (13.3) is adopted; this is the mean of the two observations, $\Delta' H(I_b) = 4.60$ kcal/mole \cite{64} and $\Delta' H(I_b) = 4.80$ kcal/mole \cite{26}.

### 13.3. Estimate of $k(II)$ and $k(III)$

There are three methods of determining $k(III)$ through $\Delta' H(III)$. One is quite similar to that of determining $\Delta' H(I_b)$ in 13.2 on the basis of the conclusion in 9.2.3; this method has not, however, been adopted, since the appropriate observations above the optimum are not sufficiently reliable.

The second method consists in comparing a theoretical relation between $T_x$ and $P_E$ with the observed relation (4.3); its result, described in 13.3.2, is used for checking that of the third method adopted here, which determines $k(II)$ and $k(III)$ coherently from the experimental results of eq (13.2), as described in 13.3.1.

#### 13.3.1. The experimental results of eq (13.2)

The fraction $x_{E_{(a)}} = \sum_{n=1}^{4} nX_{E_{(a)}}/4$ may be ignored as compared with the above value of $x_{H_{(a)}}$, since the fractions $X_{E_{(a)}>E_{(a)}}$ are extremely small according to eq (13.4.E(a)). We have thus from eqs (12.23.a) and (13.4.H)

$$v_-(II) = 3 \frac{1-x_{H_{(a)}}}{x_{H_{(a)}}} v_+(I_b),$$  \hspace{1cm} (13.7.a)$$
hence by eq (13.6)

$$v_-(II) = 8.36 \ v_+(I_b).$$  \hspace{1cm} (13.7.b)$$
We have, on the other hand, from eq (12.21.E) for $n = 1$

$$-X_{E_{(a)}v_-(I_a)} + \frac{2}{3} x_{E_{(a)}v_-(II)} = 0;$$  \hspace{1cm} (13.8)$$
the first term of eq (12.21.E) vanishes because of eq (13.4.E), since $x_{E} = \sum_{n=1}^{4} nX_{E_{(a)}}/4$; eq (13.8) is arrived at by ignoring all terms containing the factors $X_{E_{(a)}}$ and $X_{E_{(a)}}$, which are small according to eqs (13.4.E(a)) and (12.21.x), except for the term $-X_{E_{(a)}v_-(I_a)}$, on account of the practically infinite magnitude of $v_-(I_a)$, as concluded in 13.1.

$V_E$ is given by eqs (13.8) and (12.31.E) as

$$V_E = (2/3)x_{H_{(a)}v_-(II)},$$

hence by eqs (13.2.E) and (13.6)

$$V_s = \frac{2}{3 \times 2.33} x_{H_{(a)}v_-(II)} = 0.0755 \ v_-(II)$$  \hspace{1cm} (13.9)$$
or, substituting $v_-(II)$ from eq (13.7.b) into eq (13.9),

$$V_s = 0.632 \ v_+(I_b).$$

Noting that $v_+(I_b)$ equals $k(I_b)$ by eq (12.16.Ib), we have from the first and third members of eq (12.19) and the above equation

$$\gamma(H) = 0.607.$$  \hspace{1cm} (13.10.H)
Writing eq (12.18) with special reference to step II as $V_s = (v_v(\text{II})/v_v(\text{II} - 1))v_v(\text{II})$ or, to eq (12.16.II), as $V_s = (\gamma(C_2H_3)/\gamma(C_2H_3 - 1)v_v(\text{II}))$, we evaluate $\gamma(C_2H_3)$ using eqs (13.9), (13.10.H) and (13.1) as

$$\gamma(C_2H_3) = 0.564. \quad (13.10.A)$$

Equations (13.1) and (13.10) give, by eq (12.19), the ratio between $k(s)$'s at 90 °C as

$$k(I_b) : k(II) : k(III) = (1 - \gamma(H))^2 : (\gamma(H) - \gamma(C_2H_3)) : (\gamma(H)\gamma(C_2H_3))^{-1}$$

$$= 1 : 14.7 : 1.84. \quad (13.11)$$

The quantities $\Delta^2 H(II)$ and $\Delta^2 H(III)$ are now determined according to eqs (13.3), (12.5), (12.9) and (13.11), noting that $P_E = 10 \text{ mm Hg}$ and $P_H = 20 \text{ mm Hg}$ in the experiment [117] in question, as

$$\Delta^2 H(II) = -12.6 \text{ kcal/mole,} \quad (13.12.II)$$

$$\Delta^2 H(III) = -18.3 \text{ kcal/mole.} \quad (13.12.III)$$

13.3.2. The rate-determining step is switched over from step I to II, when the temperature rises past the optimum, according to 9.2.3. An equation for the optimum temperature, $T_X$, is thus obtained by equating $k(I_b)$ to $k(III)$ at $T = T_X$ in accordance with eqs (12.9) as

$$\Delta^2 H(I_b) - \Delta^2 H(III) = 2.3 \ \frac{RT_X \log_{10} q_E}{P_E},$$

which gives, on comparison with the observation of eq (4.3),

$$\Delta^2 H(I_b) - \Delta^2 H(III) = 24.2 \text{ kcal/mole.} \quad (13.13.H)$$

and

$$\log_{10} q_E = 14.5. \quad (13.13.Q)$$

We have, from eqs (13.3) and (13.13.H),

$$\Delta^2 H(III) = -19.5 \text{ kcal/mole,}$$

which agrees tolerably well with the value of (13.13.III), confirming it thus, while the value of eq (13.13.Q) is in excellent agreement with the theoretical value $\log_{10} q_E = 14.596$ of eq (12.5.E).

13.4. Rates Based on the Estimated $k(s)$'s

We have from eqs (12.9.I_b), (12.5.H) and (13.3)

$$\log_{10} k(I_b) = \log_{10} \rho \left( \frac{P_H}{1.057 \times 10^{10}} \right) \left( \frac{1027}{T} \right) \quad (13.14.I_b)$$

and similarly from eqs (12.9), (12.5) and (13.12) for steps II and III

$$\log_{10} k(II) = \log_{10} \rho \left( \frac{P_H}{1.057 \times 10^{10}} \right)^{1/2} \left( \frac{P_E}{3.939 \times 10^{14}} + \frac{2751}{T} \right) \quad (13.14.II)$$

and

$$\log_{10} k(III) = \log_{10} \rho \left( \frac{P_H}{1.057 \times 10^{10}} \right) \left( \frac{P_E}{3.939 \times 10^{14}} + \frac{4008}{T} \right) \quad (13.14.III)$$

The rates $k(s)$ determine $V_s$, $\gamma(H)$ and $\gamma(C_2H_3)$ by eq (12.19) with reference to the values of $\gamma(C_2H_3)$ given in 12.5 and $\gamma(C_2H_4)$ of eq (13.1). These values of $k(s)$'s and of $\gamma(C_2H_4)$, $\gamma(H)$, $\gamma(C_2H_3)$ and $\gamma(C_2H_2)$ determine $v_v(s)$'s and $v_-(s)$'s by eqs (12.16) as shown in figure 27.

The rates $V_s$, $V_{ex}$, $V_{ex}$, $V_p$ and $V_q$ are hence developed in terms of $v_v(s)$'s and $v_-(s)$'s by eqs (12.18), (12.26), (12.27), and (12.30); $x_{H(a)}$, as required for the calculation of $V_q$, for $x_g = 0$, $x_H = 1/2$ and $u = 0$, is determined by an equation

$$x_{H(a)} = \frac{x_E V_v(II) + 3x_H V_(I_b)}{V_v(II) + 3V_(I_b)} \quad (13.15)$$

obtained from eq (12.24.H) for infinite $v_v(\text{Ia}) = k(I_a)$. The results are shown in figure 28, side by side with $k(s)$.

We see from figure 27 that $v_v(\text{II}) = v_v(\text{II})$ throughout, i.e., step II is practically in equilibrium. The rates $v_v(\text{I_b})$ and $v_v(\text{III})$ coincide at lower temperatures but diverge above the optimum which is located around the intersection of $k(\text{I_b})$ and $k(\text{III})$ in figure 28; $v_v(\text{I_b})$ coincides above the optimum with $v_v(\text{I})$ indicating an equilibrium of $\text{I_b}$, while $v_v(\text{III})$ gives practically the steady rate of hydrogenation governed by step III in accordance with 12.5.1 (iii) and figure 28, $v_v(\text{III})$ being vanishingly small as seen in figure 27.

The following is inferred from the above numerical results.

13.4.1. Figure 27 shows that at or below 200 °C, $v_v(\text{III})$ is smaller than $v_v(\text{I})$ by a factor of at least $10^6$. Such a small rate, $v_v(\text{III})$ is hardly traceable, insofar as methods reviewed here are concerned. This accounts for the results obtained by Matsuzaki and Nakajima [120] in 5.2.7 that ethane was not perceptibly involved in the catalyzed hydrogenation.

13.4.2. Figure 27 shows that step III is far from being in equilibrium over the temperature range where $\text{I_b}$ determined the rate, according to 9.2.3.