

ion bombardment and found indications that the same is the case with copper-nickel alloys.

Two additional observations support this interpretation. After the first ion bombardment, relatively little heating was required to deactivate the alloy catalysts. With increasing numbers of ion bombardment and heating, an increased amount of heating was required to achieve the same effect. This suggests that, due to diffusion to the surface and preferential removal by ion bombardment, copper was depleted from the atomic layers close to the surface. Therefore more heating was necessary to transfer copper atoms to the surface from lower lying layers. The second observation was made with the 21.4% copper-nickel alloy. With increasing numbers of cycles of heating and ion bombardment, the activity of this sample gradually approached that of pure nickel.

The results of the studies on the relative activities are in qualitative agreement with the applicable ones of Best and Russell⁴ and Hall and Emmett.⁵ When making comparisons, one should keep in mind that the catalysts in those earlier investigations were structurally quite different. They were highly porous, having surface areas of the order of several square meters. In the present work all catalysts had small, accurately defined surface areas. Moreover, the experimental conditions, and the vacuum conditions in particular, were more stringent in the present work.

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[CONTRIBUTION FROM THE BARUS PHYSICS LABORATORY, BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND]

Compensation Effect and Pressure Dependence for Ethylene Hydrogenation in Contact with Nickel

By JOHANNES TUUL AND H. E. FARNSWORTH

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During a study of the catalytic hydrogenation of ethylene in contact with nickel, a compensation effect was observed. A systematic investigation of this effect was conducted by subjecting the surface of the catalyst to various heat treatments and bombardments with positive argon ions. A linear relationship was found to hold between the logarithm of the frequency factor and the activation energy. Experiments were also carried out to determine the influence of the pressure of the reactants. The absolute rate constant and activation energy were found to be only slightly dependent on the pressure of ethylene in the range from 0.02 to 21.7 mm. The optimum temperature for the reaction was determined. An approximate relationship between the optimum temperature and ethylene pressure has been deduced.

During some activation-energy studies,¹ it was noted that the value of the rate constant did not vary as much as would be expected from the variation of the activation energy. This observation led to the study of the compensation effect in the hydrogenation of ethylene over nickel. The experimental technique has been described already.¹

The compensation effect, which sometimes has been called the "theta rule," was first reported by Constable² in 1925. Studying the decomposition of methanol over copper, Constable observed a positive correlation between the constant B of the Arrhenius equation, $k = B \exp(-E/RT)$, and the activation energy E . He obtained a straight line when he plotted the logarithm of B vs. E . Cremer³ found similar relationships in her studies of the same reaction over rare earth oxides and together with Schwab⁴ attempted to give a theoretical explanation of the phenomenon. Thus far the same substrate had been used over different catalysts. The experiments of Balandin⁵ and Cremer^{6,7} with different substrates proved that the compensation effect was not limited to one

substrate only. In addition to Cremer and Schwab, Polanyi,⁸ Constable,² Balandin⁵ and Eckell⁹ have considered the theoretical aspects of the phenomenon.

Balandin chose as his starting point the Arrhenius equation, $k = B \exp(-E/RT)$, and the empirical formula $\ln B = aE + B$, which expresses the compensation effect. Taking the logarithm of the Arrhenius equation, and substituting for $\ln B$, he obtained

$$\ln k = \ln B - E/RT = aE + b - E/RT = b - E(1/RT - a)$$

or

$$k = e^b e^{-E(1/RT - a)}$$

If $a > 1/RT$, $-E(1/RT - a)$ is a positive quantity, and hence an increase in E is accompanied by an increase in k , i.e., a catalyst with a higher activation energy is a more active catalyst. Eckell's⁹ considerations follow those of Balandin closely.

Constable has considered a continuous distribution of active sites with different activation energies. His treatment leads to an approximate equation for the frequency factor B

$$\ln B = E_{\text{min}} + \text{constant}$$

(1) J. Tuul and H. E. Farnsworth, *J. Am. Chem. Soc.*, **83**, 2247 (1961).

(2) F. H. Constable, *Proc. Roy. Soc. (London)*, **A108**, 355 (1925).

(3) E. Cremer, *Z. physik. Chem.*, **A144**, 231 (1929).

(4) E. Cremer and G.-M. Schwab, *ibid.*, **A144**, 243 (1929).

(5) A. A. Balandin, *ibid.*, **B19**, 451 (1932).

(6) E. Cremer, *Z. Elektrochem.*, **53**, 269 (1949).

(7) E. Cremer, *J. chim. phys.*, **47**, 439 (1950).

(8) E. Cremer and M. Polanyi, *Z. physik. Chem.*, **B19**, 443 (1932).

(9) J. Eckell, *Z. Elektrochem.*, **39**, 855 (1933).

which indicates that the calculated activation energy is approximately equal to that of the most active centers. According to this, if a treatment of the catalyst causes a change in E_{\min} , the frequency factor B changes with it.

Cremer and Polanyi⁸ have examined the possibility of explaining the phenomenon with a "tunnel effect." Their considerations have been based on the quantum mechanical treatment of contact catalysis by Born and Weisskopf.¹⁰ According to Cremer,¹¹ no clearly established example of compensation effect in heterogeneous catalysis is known that could be explained with a "tunnel effect," but such a case is known in homogeneous catalysis.

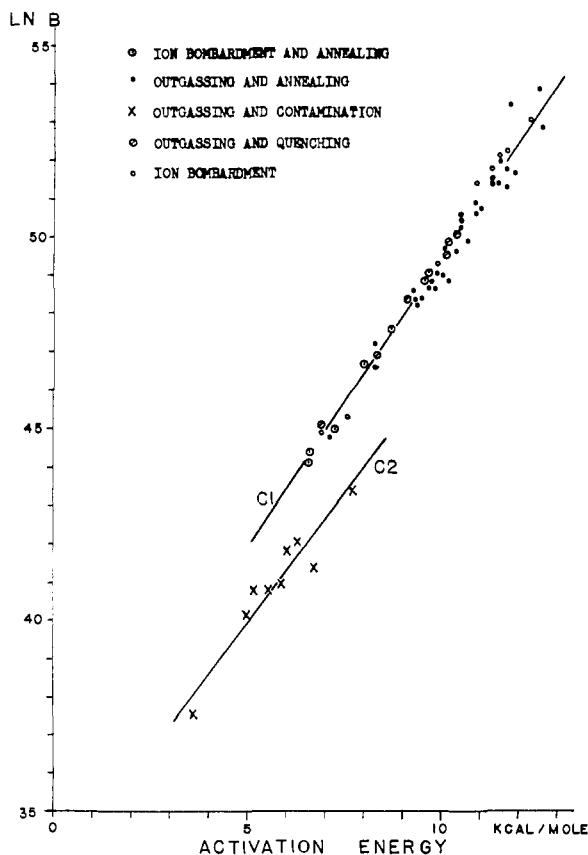


Fig. 1.—Log of the frequency factor, B , as a function of activation energy, E .

The results of about sixty determinations of the activation energy and the rate constant, both at 55° , are presented diagrammatically in Fig. 1. The relative rate constants in min.^{-1} have been converted into absolute ones in $\text{molecules cm.}^{-2} \text{sec.}^{-1}$ by multiplying them by $pV/60AkT$, where p = ethylene pressure, V = volume of the reaction vessel, A = surface area of the catalyst, k = Boltzmann constant and T = absolute temperature (c.g.s. units). The absolute frequency factors then have been obtained from $k = B \exp(-E/RT)$. In Fig. 1 $\ln B$ has been plotted vs. activation energy E for the first experiment after

(10) M. Born and V. Weisskopf, *Z. physik. Chem.*, **B12**, 206 (1931).

(11) E. Cremer, *Advances in Catalysis*, **7**, 75 (1955).

each treatment. All points, with the exception of nine, lie close to the straight line C1 whose slope is 1.59. C2, the slope of which is 1.32, was obtained with intentionally-contaminated surfaces. The activation energies as well as frequency factors are lower for the contaminated surfaces. Comparing C1 with C2, one sees that the contamination treatment has a larger effect on the frequency factor than on the activation energy.

Recently Eley and Rossington¹² have studied the compensation effect in parahydrogen conversion over copper, silver and gold. Assuming a temperature dependent activation energy $E(T)$ and frequency factor $B(T)$, they have derived the formula for the apparent activation energy

$$E = RT \ln B_0 + [E(T) - RT \ln B(T)]$$

where B_0 is the observed frequency factor. If the term in the brackets is a constant, the observed activation energy should be a linear function of the logarithm of the frequency factor. Plotting E vs. $\ln B_0$, they found that for the three metals (Cu, Ag, Au) the slope of the straight line depends on the condition of the catalyst rather than its composition. Thus, they have obtained one common straight line for wires, another for films and a third for foils of all three metals. The agreement of the slopes with the theoretical value RT was best for wires, whereas for the films and foils the experimental value was about one-half of the theoretical one. However, the best agreement with the theoretical value was found for tungsten wires.

Results similar to those found by the writers have been published by Sosnovsky¹³ in 1959. She found a compensation effect in the decomposition of formic acid over silver single crystals, activating the crystals by means of ion bombardment in the range of energies from 15 to 3000 eV. The observed activation energy varied from 12 to 35 kcal./mole, being lowest for the (111), and highest for the (100) crystal face. The slope of $\ln B$ vs. E was about the same for the (111) and (110) but larger for the (100) crystal face.

Influence of the Pressure of the Reactants.—Another goal of this work was the study of ethylene hydrogenation at lower pressures than those which had been used previously in this Laboratory.¹⁴ Most previous studies had been limited to a rather narrow range of pressures.

As had been found previously,¹ the sputtered film was many times more active than the catalyst. In order to determine whether the reaction did proceed with a measurable velocity at low pressures, four experiments were carried out with the sputtered film and the sample both at room temperature, 23° . The pressure of ethylene in these experiments ranged from 1 mm. to 0.12 mm. The reactions proceeded at a high rate at all of these pressures.

A number of experiments were carried out at gradually lower pressures, with the catalyst at

(12) D. D. Eley and Rossington, "Chemisorption," W. E. Garner, ed., Academic Press, Inc., New York, N. Y., 1957.

(13) H. M. C. Sosnovsky, *J. Phys. Chem. Solids*, **10**, 304 (1959).

(14) H. E. Farnsworth and R. F. Woodcock, *Advances in Catalysis*, **9**, 123 (1957); *Ind. Eng. Chem.*, **49**, 258 (1957).

elevated temperatures. The rate constants and activation energies were determined for out-gassed and annealed, and ion bombarded surfaces. With decreasing pressure of ethylene a shorter time interval was required to complete a reaction at a certain temperature. This would be expected if the absolute rate of the reaction is independent of the ethylene pressure or increases with decreasing ethylene pressure. The data were analyzed on the basis of the same first-order rate law which was used at higher pressures. No decrease in the absolute rate constant was found with decreasing pressure of the reactants; on the contrary, there was a considerable increase in the absolute rate constant.

At temperatures above 175° the rate of the reaction became immeasurably low. When the temperature was reduced to 90 or 60°, the rate constant was still approximately zero. Thereby it was proved that at temperatures in excess of 175° a permanent poisoning of the catalyst had occurred. Experiments were carried out to determine the cause of such poisoning. First, the catalyst was kept at 195° *in vacuo* for about half an hour. Before the reactants were admitted, the sample was cooled to the temperature at which the reactions were carried out. A slight poisoning was noticed, due to the increased pressure of the residual gas at the elevated temperature. A similar decrease in its activity was caused by standing 15 minutes in hydrogen at 195°. This also may be ascribed to the effect of the ambient rather than hydrogen. A decrease in the activity by a factor of about fifteen was caused by standing for 15 minutes in ethylene at 195°. But even then the poisoning was not as complete as it was when the temperature was raised quickly to 195° in the middle of a reaction run. This suggests that ethane (or ethylene, hydrogen and ethane combined) causes the more complete poisoning of the catalyst.

It is plausible that above 175° the surface of the catalyst rapidly becomes covered with adsorbed fragments of ethylene or ethane molecules. This is in qualitative agreement with the work of Selwood.¹⁵ Using magnetic susceptibility measurements, Selwood has interpreted some of his results as indicating fractionation of ethylene on adsorption on nickel. Unfortunately, Selwood's experiments were carried out only at room temperature and at 100°. The present work indicates that rather crucial changes take place above 175°. However, Selwood's results point in the right direction, *viz.*, to a much higher degree of fragmentation at 100° than at room temperature.

Hydrogen usually was admitted first into the reaction chamber. When ethylene was admitted before the hydrogen at room temperature, the rate was only one third to one half of its normal value. Experiments were carried out with the sample at the temperature of Dry Ice to test the precautionary measures employed for eliminating other sources of activity than the sample. In one such experiment the sample was warmed to 35° after 2 hr. at -78°. The reaction started imme-

diately, and the rate constant was found to be unaffected by this treatment.

Experiments were continued until the lower pressure was reached at which the equipment was still capable of yielding meaningful results. Measurement of the pressure of the reactants finally became the limiting factor. The lowest pressure of ethylene used in an experiment was 0.02 mm. This is about the lowest pressure ever used in such experiments. Only zur Strassen¹⁶ has published data taken in that pressure range.

A few experiments were carried out at ethylene pressures in excess of six mm. The highest pressure of ethylene in an experiment was 21.7 mm. Thus, this work is unique in encompassing a pressure range from 0.02 mm. up to about one thousand times this value. In all cases an excess of hydrogen was used. This has been taken into account when calculating the rate constants. The absolute rate constant and activation energy did not vary much over the whole range of pressures. There was a tendency toward smaller values with increasing ethylene pressure for both of these quantities, which may be due to the above mentioned contaminating effect of ethylene.

The optimum temperature for the reaction was determined in the two to four mm. pressure range of ethylene. For this a determination of the rate constant at several different temperatures was required. The curve of the rate constant *vs.* reaction temperature had a rather flat maximum at about 120° for this pressure range. At low pressures the reaction times were too short to obtain a sufficient number of values of the rate constant. As evidenced by Fig. 1, there was a considerable spread in the results even for the same kind of surface treatment. Therefore, to obtain accurate results for the temperature dependence of the rate constant, all points for one curve were taken after the same surface treatment. Consequently, this had to be accomplished within the total time for the reaction to reach its completion.

These results provide an interesting comparison with some previous data. In his early studies of ethylene hydrogenation, Rideal¹⁷ observed that above 140° the sign of the temperature coefficient of the rate was reversed. Similar observations subsequently were made by zur Strassen,¹⁶ Melville,¹⁸ Tucholski and Rideal¹⁹ and Toyama.²⁰ Unfortunately, at that time the relationship between this phenomenon and the pressure of the reactants was apparently not known. The authors did not always clearly state at what pressure the optimum temperature was determined. However, the writers have been able to find or estimate the following approximate data. The temperature obtained from Melville's data is rather uncertain since it is a result of extrapolation. All the quoted data have been obtained in work with equimolar mixtures of ethylene and hydrogen or with an excess of hydrogen.

(16) H. zur Strassen, *Z. phys. Chem.*, **A169**, 81 (1934).

(17) E. K. Rideal, *J. Chem. Soc.*, **121**, 309 (1922).

(18) H. W. Melville, *ibid.*, 797 (1934).

(19) T. Tucholski and E. K. Rideal, *ibid.*, 1701 (1935).

(20) O. Toyama, *Rev. Phys. Chem. Japan*, **12**, 115 (1938).

(15) P. W. Selwood, *J. Am. Chem. Soc.*, **79**, 3346 (1957).

From Toyama's work two different values have been deduced. This is because he used two different methods. In one series of experiments he kept the pressure of hydrogen constant by compensating for the hydrogen used in the process of the reaction. He did this by admitting small amounts of hydrogen into the reaction vessel through a capillary. In the other series of experiments he kept the pressure of ethylene constant in the same manner. Although the addition of the reactants was made through a capillary, it is possible that a certain amount of mixing of gases in the reaction vessel and the storage volume could occur. This would have introduced an uncertainty as to the actual pressures of the reactants in the reaction vessel.

TABLE I

REPORTED OPTIMUM TEMPERATURES FOR ETHYLENE HYDROGENATION

Observer	Initial ethylene pressure, mm.	Temp. for maximum rate, °C.
Rideal	30	137.5
zur Strassen	0.03	60
Melville	50	170
Tucholski and Rideal	3	130
Toyama	48	140
Toyama	51	165
The writers	3	120

When the optimum temperature T_0 for ethylene hydrogenation in contact with nickel is plotted *vs.* the logarithm of ethylene pressure, the approximate relationship found is

$$T_0 = 30 \log p + 105^\circ$$

where p is the ethylene pressure in mm. and T_0 is measured in °C. The two points due to Toyama's two methods fall on either side of the straight line. The fit with the data is rather good except for the point obtained from Melville's work. Toyama did not observe any promoting effect of hydrogen. He obtained the same results when he admitted ethylene before hydrogen into the reaction vessel

as when admitting hydrogen first. This is at variance with the results of the present work, as well as with some other observations.^{21,22}

There is still no general agreement about the mechanism of the catalytic hydrogenation of ethylene. All investigators agree, however, that at least one of the reactants is chemisorbed. The other may be chemisorbed also or impinging from the gas phase or from a van der Waals layer. The equilibrium coverage of the catalyst surface at each temperature is determined by the pressures of the reactants. The rate of the reaction is influenced by the surface coverage. Thus, the pressure-dependent optimum temperature may be a result of the interplays between the factors mentioned.

As stated earlier, there was a considerable spread in the results even after similar treatments of the catalyst. In some cases the rate constant varied inversely with the ethylene pressure. This led the writers to suspect that the reaction might not obey the commonly accepted rate law. The primary data, obtained in the pressure range from a few mm. down to about 10^{-1} mm. of ethylene, were treated by assuming the reaction to be first order in hydrogen and minus first order in ethylene. The consistency in the results thus obtained was as good or better than when using the commonly accepted rate law. However, it is conceivable that the reaction is of fractional order in one or both of the reactants. A more definite conclusion in that respect would require another series of systematic experiments in which the pressure of one reactant is kept constant while the pressure of the other is varied. This matter was not a primary goal of the present work. As has been stated previously, an excess of hydrogen was used in all experiments. This implies that the pressure of hydrogen was varied along with the pressure of ethylene. Our data suggest that below a few mm., the reaction is nearly first order in hydrogen and between zero and minus first order in ethylene.

Acknowledgment.—This work was assisted by Office of Ordnance Research, U. S. Army.

(21) A. T. Gwathmey and R. E. Cunningham, *Advances in Catalysis*, **10**, 57 (1958).

(22) G. C. A. Schuit and L. L. van Reijen, *ibid.*, **10**, 242 (1958).