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Dependence of Activity and Activation Energy on Surface Treatment of Nickel and Copper-Nickel Catalysts

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An omegatron rf. mass spectrometer was used in a study of the catalytic hydrogenation of ethylene at low pressures. Experiments were carried out in an ultra-high vacuum system where the pressure of the ambient varied between 2 and 6×10^{-9} mm. Four different copper-nickel alloys, as well as pure nickel and pure copper, were used as catalysts. The specimens were made in the form of 0.3 mm. sheets of solid material, each having a total surface area of approximately 2.5 cm.² They were cleaned and activated by various heat treatments up to 900° and by bombardment with positive argon ions. The influence of these treatments on the activation energy was examined. The activation energy for all ion bombarded catalysts was about 11 kcal./mole and was lower after the other treatments. Catalysts subjected to small amounts of gaseous contamination displayed a very low activation energy. The relative activities of the catalysts of various compositions were measured.

Introduction

According to the theory of Dowden,^{1,2} the catalytic activity of the transition metals is due to holes in the d-band. When a transition metal which has holes in the d-band (*e.g.* nickel) is alloyed with another which can donate electrons (*e.g.* copper), then at a certain composition the holes in the d-band are filled. According to Dowden's theory the catalytic activity should drop to a negligible value at the same composition. Reynolds,³ who studied the hydrogenation of styrene and benzene over copper-nickel alloys, found that the catalytic activity of the alloy decreased very rapidly when the content of copper was increased over 50%. At about the same composition, the magnetic susceptibility dropped to a very low value.

However, more recent investigations of Best and Russell⁴ and Hall and Emmett⁵ have rendered results in disagreement with the theory of Dowden. Both these investigations dealt with the hydrogenation of ethylene over copper-nickel catalysts. Best and Russell used copper, nickel and two alloys as catalysts. Both alloys (one containing 63% copper, the other 90% copper) were found to be more active than pure nickel, whereas according to the theory they should have been rather inactive. Hall and Emmett used copper, nickel and several alloys as catalysts. They found that in general the activity of the catalyst increased with increasing content of nickel. However, with a certain treatment of the catalysts, two alloys were slightly more active than the pure nickel catalyst. Thus, neither of these two investigations under consideration have confirmed the theoretical prediction that the activity of copper nickel catalysts should drop to a very low value at the critical composition of 60% Cu:40% Ni. The catalysts of Hall and Emmett, as well as those of Best and Russell, were manufactured by coprecipitating the basic carbonates of copper and nickel, then sintering and reducing in hydrogen. These catalysts were highly porous with the surface areas being as high as 10,000 cm.²/gram.

The findings of Gwathmey, *et al.*,⁶⁻⁹ also indi-

cate that Dowden's theory is not a complete answer to the problem of the catalytic activity of transition metals. In some cases they have found greater differences between the catalytic activities of different crystal faces of the same metal than between two metals with different electronic configurations.

In this Laboratory Farnsworth and Woodcock^{10,11} have studied the hydrogenation of ethylene over nickel and platinum catalysts. They activated their catalysts by various heat treatments and by ion bombardment. It was found that the activity of the ion bombarded catalysts was much higher than that of the outgassed catalysts.

Many different values of activation energy have been reported in the past for the catalytic hydrogenation of ethylene in contact with nickel.¹²⁻¹⁸ The reported values range from 1.8 to 10.7 kcal./mole. The highest value, reported by Beeck,¹⁸ has been considered to be the most reliable. However, within the last two years, two new values were published by Schuit and van Reijen¹⁹ and by Hall and Emmett.⁵ The former reported a value of 8.4 kcal./mole and the latter a value half as large, or 4.2. The different published values of activation energy present a challenge: one would like to find the reason for such a wide variation.

The present work was carried out with this objective in mind. The activation energy of ethylene hydrogenation was measured on catalytic surfaces which had been subjected to various treatments. Five different surface treatments were used (with minor variations within each of the five groups). These were: (1) outgassing and radiation quenching (rapid cooling primarily by radiation); (2) outgassing and annealing; (3)

(7) A. T. Gwathmey and H. Leidheiser, *J. Am. Chem. Soc.*, **70**, 1200, 1206 (1948).

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

(9) R. E. Cunningham and A. T. Gwathmey, *ibid.*, **9**, 25 (1957).

(10) H. E. Farnsworth and R. F. Woodcock, *ibid.*, **9**, 123 (1957).

(11) H. E. Farnsworth and R. F. Woodcock, *Ind. Eng. Chem.*, **49**, 258 (1957).

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

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

(14) O. Toyama, *Rev. Phys. Chem. (Japan)*, **11**, 153 (1937).

(15) C. Schuster, *Trans. Faraday Soc.*, **28**, 406 (1932).

(16) H. W. Melville, *J. Chem. Soc.*, 797 (1934).

(17) G.-M. Schwab and H. Zorn, *Z. physik. Chem.*, **B32**, 169 (1936).

(18) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

(19) G. C. A. Schuit and L. L. van Reijen, *Advances in Catalysis*, **10**, 242 (1958).

(1) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).
 (2) D. A. Dowden, *Ind. Eng. Chem.*, **44**, 977 (1952).
 (3) P. W. Reynolds, *J. Chem. Soc.*, 265 (1950).
 (4) R. J. Best and W. W. Russell, *J. Am. Chem. Soc.*, **76**, 838 (1954).
 (5) W. K. Hall and P. H. Emmett, *J. Phys. Chem.*, **63**, 1102 (1959).
 (6) A. T. Gwathmey and A. F. Benton, *J. Chem. Phys.*, **8**, 569 (1940).

bombardment with positive argon ions; (4) argon ion bombardment with subsequent annealing; (5) subjecting a clean catalyst to controlled amounts of contamination. This research was carried out in a high-vacuum system where the residual pressure normally was 2 to 6×10^{-9} mm.

Experimental

The progress of the reaction was observed with an omegatron rf. mass spectrometer. The sensitivity and resolution of the omegatron were fully satisfactory for the purpose. The instrument performed very well at a total pressure of between 10^{-9} and 10^{-6} mm. Its resolution, defined as $M/\Delta M$ where M is the mass number, was about 100 at the half-value of the mass 28 (M28) peak under normal operating conditions. Under these conditions an ionizing electron beam of ten microamp. and an rf. voltage of 0.2 were used. The uniform magnetic field of 4000 gauss was produced by an electromagnet. The M28 peak was chosen as a reference since it is the strongest peak in the mass spectrum of the reactant ethylene as well as in the reaction product, ethane.

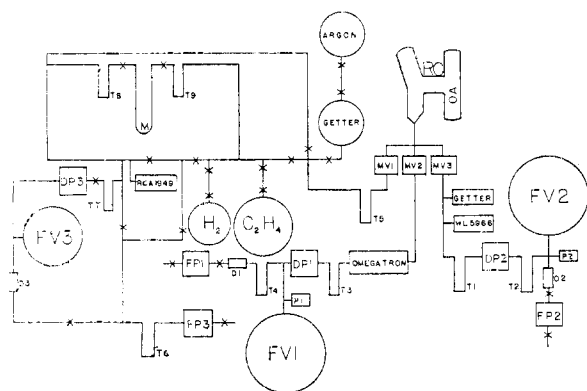


Fig. 1.—Block diagram of the vacuum and gas-handling apparatus.

The main features of the vacuum apparatus are shown schematically in Fig. 1. The vacuum apparatus consisted of three separate vacuum systems, each having its own diffusion pump and mechanical backing pump. These vacuum systems could be connected with each other through stopcocks or metal valves. The mass spectrometer diffusion pump, DP1, and the reaction-chamber diffusion pump, DP2, were three-stage oil diffusion pumps. In the former Dow Corning DC 703 silicone oil was used, in the latter Octoil S. The third diffusion pump, DP3, was a one-stage pump in which DC 703 silicone oil was used. It was operated on the gas handling system. Due to the complicated system of tubing, the gas handling system could not be outgassed, except for some parts which could be heated with a gas flame. Therefore, the one-stage oil diffusion pump was adequate for its evacuation. The best vacuum achieved in the gas handling system, measured with an RCA type 1949 ionization gauge, was 10^{-7} mm., whereas usually it varied between 10^{-7} and 10^{-6} mm.

The reaction chamber was a vessel of approximately 300 cc. volume, consisting of Pyrex tubing, approximately $1\frac{1}{4}$ inches in diameter, in general appearance resembling the shape of a letter "H." During a reaction run it was completely closed off from the rest of the vacuum system by means of three metal valves. Through the first of them, MV1, the reaction chamber could be connected with the gas-handling system. This was done while admitting the reactants or when evacuating it after an experiment with the mechanical pump or the one-stage diffusion pump. The second metal valve, MV2, connected the reaction chamber with the mass spectrometer and was used mainly as an adjustable leak for continuous sampling of gases to the mass spectrometer during a reaction run. The third valve, MV3, connected the reaction chamber with its three-stage

diffusion pump for achievement of the ultimate vacuum. A Bayard-Alpert type ionization gauge, the Westinghouse WL5966, was located on that pumping line. Since the ionization gauge with its metal electrodes might influence the catalytic reactions under study, it was so located that during the reaction, when metal valve MV3 was closed, it was isolated from the reaction chamber. The same applied also to the molybdenum getter, which was incorporated in the pumping line to facilitate the achievement of high vacuum in a short time after an outbaking. The three metal valves were Granville-Phillips type C ultra-high vacuum valves. They were mounted on a steel plate of $\frac{1}{4}$ inch thickness on which an electrically-heated oven was built for baking the valves.

The electronic equipment included a constant emission circuit for the omegatron mass spectrometer. It supplied the heating current for the filament, as well as all d.c. potentials with the exception of the trapping voltage, which was taken from batteries. The rf. oscillator was a Hewlett-Packard Model 650A. For amplification of the ion current from the omegatron, a Vibrating Reed Electrometer, Model 30, manufactured by the Applied Physics Corporation, was used. A Varian Associates Model G-10 graphic recorder was connected to it. A simple mechanical construction was made so that the recorder drove the rf. oscillator, thus giving a continuous scanning of the mass spectrum. In order to improve the performance of the electronic equipment, a Sorensen a.c. Voltage Regulator, Model 500S, was used. The two outlets of the regulator were reserved for the rf. oscillator and the Vibrating Reed Electrometer.

The reaction chamber and the omegatron were baked out at about 300° in two periods, each of 6 to 10 hr. duration. Between these two periods the filaments were outgassed and the cold traps warmed to room temperature for a few minutes to remove condensed water vapor from cold traps. The metal valves were baked for the same time and temperature as for the reaction chamber.

All gases were admitted through cold traps to prevent condensable vapors from stopcock grease from entering the reaction chamber or the omegatron. The reactants, hydrogen and ethylene, were stored in one- and two-liter flasks, respectively. They could be admitted to the reaction chamber in small quantities by means of a slug system. Pressures of the reactants were measured with an oil manometer employing Octoil S. For ion bombardment of the sample, a one-liter flask of spectroscopically-pure argon was sealed onto the gas handling system. From that flask a small amount of argon was admitted to another one-liter volume and stored there until its use for ion bombardment purposes. That latter volume contained two molybdenum filaments. After it had been thoroughly evacuated and before admitting the argon, a molybdenum film was deposited on the inside of that container by flashing one of the filaments, so that possible traces of all active gases in the argon should have been removed.

The samples were made in the form of thin rectangular plates. The dimensions of each sample are given below. Close to one short edge of the sample a hole was drilled about 1 mm. in diameter, and one side of the hole was filed into the shape of a letter "V." This was done to achieve better mechanical stability of the sample during its heat treatments. In one arm of the reaction chamber (RC in Fig. 1) there was a hook of thin tungsten wire, from which the sample hung during the experiments. A cylindrical, electrically heated oven could be placed over that arm for studies above room temperature. Temperatures up to 400° could be obtained with this oven. In the opposite arm of the RC, called the outgassing arm (OA), there was an identical hook from which the sample hung during its treatment. The transportation of the sample from one position to the other was accomplished by means of a small carriage of Pyrex glass containing a nickel slug, which was manipulated with magnets from the outside.

For outgassing purposes the sample was hung from the hook in OA and an induction coil wound around it. With that coil and an induction heater, the sample could be heated to about 1000° . Temperatures above 750° were measured with an optical pyrometer and corrected for emissivity and losses in the glass walls of RC. The corrected readings were used to construct a curve of sample temperature vs. heating power. Another point on that curve at 358° , the Curie point, far below the range of the pyrometer, could be de-

terminated for the nickel specimen. At that temperature the sample ceased to react on its hook when a strong magnet was moved near it outside of the reaction chamber. The shape of the curve of sample temperature *vs.* heating power for the nickel catalyst was helpful in constructing similar curves for Cu-Ni alloy catalysts since for those the curves between the pyrometer range and room temperature had to be interpolated.

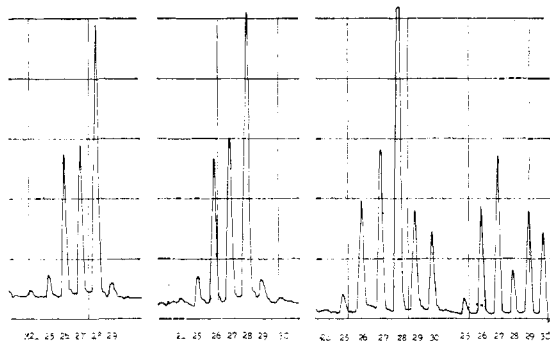


Fig. 2.—Recorder trace of the important range of the mass spectrum.

The procedure in a typical experiment is described. The sample was outgassed at temperatures up to 900° for a predetermined length of time or until the pressure in the RC had dropped below 2×10^{-8} mm. while the sample was at its highest temperature. According to the desired treatment, the sample was then quenched, *i.e.*, cooled rapidly by turning off the heating power or annealed by gradually reducing the heating power; the duration of the annealing was usually 1 hr. When the effects of ion bombardment were studied, the outgassing was followed by bombardment with argon ions using an applied voltage of 500 to 600 volts. In a number of experiments an annealing of the sample was carried out after the ion bombardment. When the treatment of the sample had been completed, the OA of the RC was immersed in a Dry Ice and acetone bath to suppress the activity of the sputtered film. Blank runs were made with the catalyst in the cold chamber to determine that the cooling of the film suppressed its activity. The reaction chamber was isolated by closing MV3. With the exception of a few special experiments, hydrogen was admitted into the reaction chamber first and its pressure was measured. After the gas-handling system had been evacuated, ethylene was admitted into the measuring volume and its pressure measured with the oil manometer M. By opening MV1 about $1/4$ turn for about 1 sec. or less, ethylene was injected into RC. Knowing the ratio of the measuring volume to the volume of RC, the pressure of ethylene in RC was calculated. There was reason to assume that no hydrogen escaped during the injection of ethylene. Ethylene pressure in the measuring volume was always several times higher than hydrogen pressure in the RC. The small leak and short injection time conceivably accomplished the unidirectional flow into the RC. Experiments with variation of the injection time up to three times the normal value indicated that, within the experimental error, there was no dependence of the results on the injection times used. The instant of time when ethylene was injected was marked as zero on the recorder chart. The time for scanning of the important range of the mass spectrum was about 2 minutes. Then the oscillator was returned manually into starting position of the desired range. Occasionally the spectrum from mass 6 to about mass 60 was scanned. The constant speed (40" per hour) of the recorder chart gave a linear time scale.

An ordinary determination of the activation energy consisted of determining three rate constants at three different temperatures, which were measured with a mercury thermometer. In order to calculate a rate constant with a reasonable accuracy, an observation time of at least an hour was required. Only two points could be obtained in some cases where the reaction was fast. With very slow reactions more than 2 hr. were required for determination of each rate constant. Preparations for an activation energy

experiment usually lasted 3 to 4 hr., the experiment itself required 4 to 5 hr., and the work for restoring a good vacuum after the experiment required two additional hours. A number of rate-constant determinations were carried out for comparison with the results of previous work in this Laboratory. But the bulk of the present work was made up of more than 100 determinations of the activation energy under various conditions.

Preparation of Reactants.—Spectroscopically pure hydrogen from Linde Air Products Co. was used. It was supplied in one-liter flasks with a break-off tip. The ethylene was taken from a tank and purified. For this purpose a cartridge, filled with nickelous carbonate, was incorporated in an auxiliary vacuum system employing a two-stage oil diffusion pump. The nickelous carbonate powder was kept at 250° under high vacuum for 24 hr. to remove desorbable gases, after which it was reduced with hydrogen at 250°. The system was evacuated while the resulting porous nickel was still at 250°. Ethylene was condensed in a bulb and fractionally distilled, thus removing the contaminants with higher and lower boiling points. Only the middle third of it was passed over the porous nickel at 150° into a previously evacuated storage volume. Mass spectrographic analysis did not reveal any detectable amounts of hydrogen, methane or ethane in the purified ethylene (*cf.* Fig. 2).

Activity Studies.—The first catalyst was made of polycrystalline 1001 electrolytic nickel. It was 0.35 mm. thick, and each side of it had a surface area of 136 mm.² After the sample had been polished with #4/0 metallographic emery paper, it was etched in a '70-20F-10' solution, *i.e.*, a mixture of 70% glacial acetic, 20% fuming nitric and 10% concentrated hydrochloric acid.

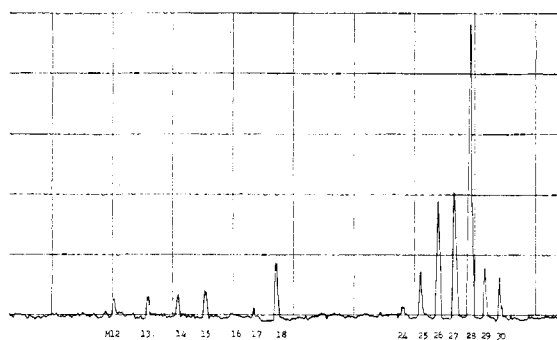


Fig. 3.—Recorder trace of a major portion of the mass spectrum.

In the first experiments the catalyst was cleaned by outgassing alone. As has been described above, hydrogen usually was admitted before ethylene. A mass 30 peak was found in the beginning of the experiment after the admission of ethylene as soon as the analysis could be started. The delay time could be made as small as one minute. Yet the M30 peak, which was about 20-25% of the M26 peak, indicated the presence of ethane. The source of this reaction was traced to the metal valve, between the reaction chamber and the mass spectrometer, by suppressing the activity when the valve was cooled with Dry Ice. After about twenty reaction runs this spurious activity of the metal valve disappeared.

In Figs. 2 and 3 some recorder traces have been reproduced. Figure 2 shows the scanning of the important range of the mass spectrum on three different occasions. To the left, the spectrum of ethylene with peaks from M24 through M29 is

seen. Next follows the spectrum of a mixture of ethylene with a small amount of ethane, formed by the reaction. To the right is the spectrum of ethane, recorded twice. In the first of these, the whole spectrum has been taken with the same sensitivity. Since the M28 peak is much stronger than the others, its upper half has been cut off by the recorder. In the second, the M28 peak was taken with only one-tenth the sensitivity as for the rest of the peaks so that its real intensity is obtained by multiplying by a factor of ten. In Fig. 3 a major portion of the spectrum is recorded, showing not only the peaks of the ethylene-ethane mixture, but also some peaks due to residual gases in the omegatron. Peaks for each mass from 12 through 18 and from 24 through 30 are readily seen.

The spectra of Figs. 2 and 3 have been recorded with 10^{10} ohm input resistance of the vibrating reed electrometer and the most sensitive range (full scale deflection is 1 millivolt). From this it can be seen that the background noise is lower than $\pm 2 \times 10^{-15}$ ampere. The recording in Fig. 3 is made with values of the electron beam intensity and rf. voltage such that all peaks can be accommodated without changing the sensitivity of the apparatus. Due to the low value of the beam intensity (8 microamperes) and rf. voltage (30 millivolts), the resolution of the instrument is excellent, but its sensitivity is relatively low. The resolution at half-value of the M28 peak is about 240.

On the basis of the results²⁰ reported by zur Strassen,¹⁸ Farkas, Farkas and Rideal,²¹ Toyama,¹⁴ Beeck¹⁵ and Twigg and Rideal,²² the primary data were analysed assuming the reaction to be first order in hydrogen and zero order in ethylene.

As evidenced by Figs. 2 and 3, the M30 peak is due exclusively to ethane. The percentage of ethylene that has reacted with hydrogen, thus forming the ethane, is calculated from the ratio of the M30 to the M26 peak. The M26 peak has been chosen, firstly, because it is of approximately the same height in the case of ethylene as in the case of ethane and secondly, because in the case of 100% ethane, its intensity is approximately the same as that of the M30 peak. The results of the activity studies are in satisfactory agreement with those of Woodcock, with the exception of the ion bombarded catalyst. The discrepancies most probably depend on small differences in catalyst composition and on different vacuum conditions which were better in the present work.

The catalytic activity of the sputtered film at room temperature was found to be roughly an order of magnitude higher than that of the sample. Use was made of this fact to carry the reaction to completion in a short time because of the following conditions. The output of the omegatron was dependent on its operating conditions, the optimum being chosen for each experiment. Since even the relative strength of the peaks was affected to a certain extent, each reaction was allowed to

go to completion in order to obtain the ratio M30/M26 for ethane in each experiment. To save time in the case of many slow reactions, the Dry Ice and acetone bath was removed from OA as soon as sufficient data had been obtained for determination of the rate constants. The sputtered film was allowed to warm up to room temperature or, by warming gently with a torch, kept at a somewhat higher temperature. The reaction then went to completion in a short time.

Activation Energy Studies.—Almost as many different values of the activation energy have been reported for the hydrogenation of ethylene as there have been different scientists determining it. The available data are compiled below in Table I, together with the names of the observers and literature references. As can be seen from Table I, there is a large spread in the observed activation energy, the highest value, reported by Beeck, being about six times larger than the lowest one. Due to the method of its derivation, Beeck's value usually has been considered to be the most reliable one.

TABLE I

PUBLISHED ACTIVATION ENERGY VALUES FOR THE HYDROGENATION OF ETHYLENE OVER NICKEL CATALYSTS

Observer and lit. reference	Reported activation energy, kcal./mole
Rideal ¹²	1.8
Toyama ¹⁴	6.0
Schuster ¹⁵	3.6
zur Strassen ¹⁸	4.6
Melville ¹⁶	5.2
Schwab and Zorn ¹⁷	8.3
Beeck ¹⁵	10.7
Hall and Emmett ⁵	4.2
Schuit and van Reijen ¹⁹	8.4

One objective of the present work was to study the dependence, if any, of the activation energy on the surface treatment of the catalyst, as well as on the experimental conditions. The activation energy is calculated from the Arrhenius equation²⁰

$$k = B \exp(-E/RT) \quad (1)$$

where k is the rate constant for the reaction, B is the frequency factor, R the universal gas constant, T the absolute temperature and E the activation energy. Taking the logarithm of both sides of this equation, we have

$$\ln k = \ln B - E/RT \quad (2)$$

Plotting $\ln k$ vs. $1/T$, a straight line is obtained with the slope $-E/R$. The same result should be obtained by differentiating equation 2

$$\frac{d \ln k}{dT} = E/RT^2$$

from which follows

$$E = RT^2 \frac{d \ln k}{dT}$$

(20) S. Arrhenius, *Z. Physik. Chem.*, **4**, 226 (1889).

(21) A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A146**, 630 (1934).

(22) G. H. Twigg and E. K. Rideal, *ibid.*, **A171**, 55 (1939).

The first method was used in the present work since it allows a simple check of the reliability of the value of E which is obtained. Whenever possible, three rate constants were determined at three different temperatures. If the logarithms of all three lay on a straight line when plotted *vs.* $1/T$, the correct value of activation energy was plausibly obtained. In case of large deviations from a straight line, the calculations were rechecked and possible causes for spurious effects were examined. The three temperatures, at which the rate constants were determined, were ordinarily 35, 55 and 85°. These temperatures were found to give conveniently measurable rate constants in most cases. Some experiments were started at 25°, but the rate often was too slow at that temperature. In case of some slow reactions, rate constants were determined also at 100° and above. All values of activation energy to be quoted below have been calculated at 55° to render them comparable.

About eighty determinations of the activation energy were made with the pure nickel catalyst under various circumstances, with four surface treatments: (1) bombarding with argon ions; (2) outgassing and annealing; (3) outgassing and quenching; (4) ion bombardment and subsequent annealing at various temperatures. Argon-ion bombardment usually was carried out at energies between 500 and 600 eV. In a few experiments the ionization was accomplished with an electron beam, but usually a self-maintained discharge was used, in order to dispense with the requirement for a hot filament. In the beginning, the discharge was initiated with a Tesla coil, but there was a possibility that this might drive off contaminating gases from the glass walls of the reaction chamber. It was found that the discharge could be initiated by raising the negative potential on the catalyst to 800–1000 volts, after which the voltage was lowered to about 550. The ion bombardment was usually of five minutes duration at a current density of about 80 microamp. per cm.² of the catalyst surface.

A series of experiments was carried out to study the contaminating effects of the reactants and the residual gases in the reaction vessel. The effect of the reactants was studied by making several consecutive reaction runs without any treatment of the catalyst between runs; the activity decreased with each such experiment. It has been suggested^{18,23} that a hydrogenation catalyst is gradually covered with acetylenic residues. Hall and Emmett⁵ have proposed that these residues may cause an increase in the activation energy. This was not confirmed by the present work. In the quoted temperature range the activity decreased considerably with successive reactions whereas the activation energy remained almost the same or decreased slightly. As an example, the results of a series of four experiments after an ion bombardment are quoted, the pressure of ethylene having varied between 1.2 and 1.5 mm.

When similar experiments were carried out after outgassing and annealing the sample, the rate of the reaction was very low at 35° in the second ex-

Experiment	1	2	3	4
Corr. rate	0.0035	0.0023	0.0015	0.00065
const. at	35°	55°	55°	85°
Activation energy				
kcal./mole	10.9	9.7	10.5	10.2

periment after treatment. A sharp rise in the rate occurred around 55°. If the activation energy had been calculated on the basis of the rate constants at 35 and 55°, a very high value would have been obtained, whereas the rates at 55 and 85° rendered a normal value of the activation energy.

Owing to the following considerations, the latter value then was taken to be the correct one. Two consecutive reaction runs could be completed during one day. On the next morning, *i.e.*, 13–14 hr. later, the reaction chamber was evacuated, and fresh reactants were admitted. In the second-day experiments, a certain improvement in the activity of the catalyst was observed. The relative recovery was most remarkable at 35°, since, as stated above, the rate at that temperature in the second experiment of the previous day had been abnormally low. These findings indicate a certain type of poisoning which inhibits the reaction at lower temperatures and is partially reversible at room temperature. Jenkins and Rideal^{23,24} have presented evidence that up to 80% of the surface of the nickel catalyst may become covered with acetylenic residues. Assuming this to be the case, some of the acetylenic residues may have been hydrogenated during the overnight standing, and after desorption of the product more of the active surface became available for the hydrogenation during the second-day experiment. Ethane had no poisoning effect at room temperature as has been reported already by Toyama.^{25,26}

Another series of experiments was carried out to determine the effects of gaseous contaminants in the reaction chamber on the activity and the activation energy. Controlled amounts of contamination were produced by heating part of the reaction chamber with a small electrical oven. Pressures ranging from 3×10^{-8} to 3.6×10^{-7} mm. were obtained in the reaction chamber by keeping this oven at temperatures from 200 to 350°. To increase the contaminating effect in some experiments, the reaction chamber was separated from its diffusion pump by closing the metal valve MV3. In these cases the amount of exposure was estimated from the pressure burst when MV3 was opened. (An exposure is defined as $\int p dt$, where p is the pressure in mm., and t is the time in min.) The exposures ranged from 1×10^{-6} to 7×10^{-6} mm. min. The activation energies found with contaminated surfaces were smaller than those obtained with clean surfaces. The contaminating influence proved to be a combined effect of exposure and temperature, an exposure at higher temperature causing a larger effect than an equal exposure at a lower temperature. The lowest activation energy found in these investi-

(24) G. I. Jenkins and E. K. Rideal, *ibid.*, 2940 (1955).

(25) O. Toyama, *Proc. Imp. Acad. (Tokyo)*, 11, 319 (1935).

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

(23) G. I. Jenkins and E. K. Rideal, *J. Chem. Soc.*, 2496 (1955).

gations was 3.6 kcal./mole, which was obtained after an exposure of 4×10^{-6} mm. min. at a maximum temperature of 350°.

Using the omegatron, an attempt was made to determine which gases were responsible for the contaminating effects. The oven, which had been used in the contamination studies, was heated up to 400°. The omegatron revealed that the desorbed gas was composed mainly of carbon monoxide, ethylene, water vapor and carbon dioxide. The principal peaks of these gases were present, as well as the M12 and M16 peaks due to the decomposition of CO and CO₂. But mass peaks M39 and M41 also were present. These may be from potassium isotopes or the radicals C₃H₃ and C₃H₆. If these radicals were present, some propene, propane or higher order hydrocarbons must have been produced in the reaction chamber. However, this is improbable since during the whole study of this reaction, no clear indication of hydrocarbons heavier than ethane was found. The very weak M44 peak probably came from residual CO₂ in the omegatron.

The results of the studies on activation energy are summarized in Table II.

TABLE II

Treatment	Apparent activation energy, kcal./mole	No. of determinations
Ion bombardment	11.0 ± 0.3	11
Outgassing and annealing	10.7 ± .2	24
Outgassing and quenching	9.0 ± .6	5
Ion bombardment and annealing	7.9 ± .5	6
Contamination at elev. temp.	6.0 ± .4	10

Evidently the activation energy depends on the condition of the surface of the catalyst. The above described studies have shown in particular that the activation energy for a contaminated nickel surface is lower than for a clean surface. The highest values have been obtained for clean ion bombarded and outgassed and annealed surfaces. Taking into account the mean deviations, the two averages are actually overlapping. They coincide with Beeck's value, which has been considered as the most reliable one. On intentionally contaminated surfaces, a range of activation energies has been found, the lowest being 3.6 kcal./mole. These findings suggest that some of the previously published activation-energy data might have been obtained on surfaces which were contaminated, due to the methods of preparation or handling, prior to their use in experiments.

Studies with Copper-Nickel Alloys.—The reaction rate and the activation energy of ethylene hydrogenation also were studied using four copper-nickel alloys and pure copper as catalysts. These experiments were carried out in the same temperature range as those for the pure nickel catalysts. The contents of copper in those five samples (II to VI) were: II, 21.4%; III, 41.7%; IV, 60.5%; V, 80.0%; VI, 100%. All samples were prepared in the same manner. The material was cut in the form of thin rectangular slices, ground and polished, first with metallographic

emery papers and then with MgO powder on a plane wax surface. After that the samples were electropolished for two minutes in a hot 40% solution of orthophosphoric acid in glycerol, etched three minutes in a solution of one part HNO₃ and three parts of distilled water, and finally rinsed thoroughly with distilled water. The total surface area of each sample was between 2.5 and 3 cm.². Only sample II was ferromagnetic to such a degree that it could be lifted with a magnet.

Without any further treatment subsequent to etching, all of these samples proved to be inactive. Contrary to what had been the case with pure nickel, it was found that the alloy samples could not be activated by heat treatments which were carried out at temperatures up to 900°. At the highest temperatures some metal evaporated from the samples, thus producing a transparent metal film inside the outgassing arm of the reaction chamber. This film seemed to consist mainly of copper, and its rate of formation increased as the content of copper of the sample increased. Obviously, some phases of the study, which had been carried out with the pure nickel catalyst, could not be repeated with the alloy catalysts.

After ion bombardment, all alloy catalysts were found to be more active than pure nickel after the same treatment. The activity of pure copper was very low even after ion bombardment. Taking the activity of ion bombarded nickel as unity, the relative activities of the copper-nickel alloys were found to be approximately

Catalyst composition, % Cu	Relative activity
21.4	2
41.7	3
60.5	3
80.0	2
100	0.03

The activation energy of the reaction on the ion-bombarded copper-nickel alloys was approximately 11 kcal./mole. A compensation effect, similar to the one described in connection with the nickel catalyst, was also observed with copper-nickel alloy catalysts. The activity of copper was so low that no activation energy could be determined. That the copper sample exhibited any measurable activity at all probably was due to impurities in it.

The activity, which had been induced by ion bombardment, decreased after heat treatments at temperatures above 500° and, after sufficient heating, the alloy samples became inactive. This deactivation by heat treatment was accomplished more easily with samples of higher copper content. These observations suggest that during heat treatments copper diffuses to the surface of the alloy catalyst, and after sufficient heating covers the surface with at least a complete monolayer of copper. By ion bombardment, copper is removed preferentially from the catalyst surface. This interpretation is in accord with the observation of Gillam²⁷ who has reported that copper is removed preferentially from copper-gold alloys by

(27) E. Gillam, *J. Phys. Chem. Solids*, **11**, 55 (1959).

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

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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

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

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