[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

OVERPOTENTIAL AND CATALYTIC ACTIVITY.

BY ERIC K. RIDEAL.

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It is well known that the catalytic activity of metals in cases of heterogeneous catalysis varies both with their natures and physical states, and in a recent communication it was pointed out that a tangible explanation for the behavior of certain metals in a case of selective oxidation was to be found in W. M. Lewis's application[1] of Krüger, Marcelin and Rice's concept of activity to Harkins and Langmuir's hypothesis of surface orientation in adsorption.

It seemed possible that another application of this concept might be found in the simplest case of heterogeneous catalysis, namely the liberation of gases at electrode surfaces. The general course of an electrode reaction may be represented by the following typical example:

$$2H^+ = 2H + 2\oplus = H_2$$

making no assumption as to the possible hydration of the ions in solution. Caspari, Wilsmore, Le Blanc and others have shown that the liberation of hydrogen gas at an electrode surface is an irreversible process, or that there is always an overpotential (η volts) in excess of that demanded by the free energy relationship. Overpotentials are likewise to be found in the liberation of oxygen at anodes and in the deposition of metals and metallic hydroxides at electrode surfaces, but with the exception of the case of hydrogen where the phenomenon is well marked, little record is to be found in the literature.

Overpotential varies with the nature of the electrode, rising to high values for mercury, zinc, and lead and sinking to low values for nickel, platinum and copper.

Of the more important theories which have from time to time been advanced to explain the occurrence of overpotential, may be briefly mentioned the following:

1. The formation of unstable hydrides, a view advanced by Foerster and supported by Newbery.[2]

2. The variation in thickness of a poorly conducting gas film, a view originally suggested by Haber.[3]

3. An increased solution of hydrogen in the electrode, caused by the

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[1] *J. Chem. Soc.*, **105**, 2331 (1914); **107**, 233 (1915); **109**, 55, 67, 796 (1916); **111**, 389, 457, 1086 (1917); **113**, 471 (1918); **115**, 182 (1919); see also Lewis and Jackson, *Proc. Am. Acad.*, **41**, 397 (1906).

[2] *J. Chem. Soc.*, **109**, 1051, 1359 (1916).

[3] *Z. Elektrochem.*, **8**, 539 (1902).

relative slowness with which the electrode charged with gas can get into equilibrium with the atmosphere.[1]

4. The presence of monatomic hydrogen, a view supported by Bancroft[2] and Bennet and Thompson.[3]

5. The variation in the surface tension of large and small bubbles of gas with which the electrode is in equilibrium, an hypothesis advanced by Helmholtz[4] and Möller[5] and recently supported by MacInnes and Adler.[6]

On the adsorption theory the following view-point may be advanced. At any surface when equilibrium is established between metal and the surrounding medium, the number of molecules striking and becoming adsorbed on the surface will be equal to the number evaporating, although the actual number liberated and adsorbed per second will vary with the nature of the metal. Under these conditions the free energy equation

$$E = \frac{RT}{F} \log \frac{P}{CH}$$

will hold for all metals. On the passage of current, however, discharge of hydrogen occurs with the formation of atomic hydrogen adsorbed on the metal surface (presumably by a pair of electrons, or one valence bond). The affinity of atomic hydrogen for another atom at room temperature is so large (*ca.* 80,000 cal. per g. mol.) that immediate combination between neighboring atom pairs occurs, resulting in the formation of molecular hydrogen, which, however, is still attached to the metal by each atom, a hydrogen molecule occupying two elementary spaces on the metal surface. For very small currents, in rapidly agitated electrolytes and with metals which do not hold the molecules very firmly it will be evident that the rate of removal of the gas away from the surface by evaporation may quite easily approach the rate of supply of the gas ions, and no overpotential will result. On the other hand, if a molecule of hydrogen has to be vaporized before two empty spaces are left on the metal surface for the gas ions, it is evident that actual work has to be done by the gas ions in vaporizing the molecular hydrogen. Overpotential is thus primarily a measure of the energy necessary to *desorb* hydrogen gas from a metal surface. Two factors, however, permit of relatively large currents being passed for only a slight overpotential; one is the normal evaporation into an unsaturated electrolyte, similar to the so-called diffusion current, and the other is the tendency to the formation of bubbles.

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[1] Nernst, *Ber.*, 30, 1547 (1897).

[2] *J. Phys. Chem.*, 20, 396 (1916).

[3] *Ibid.*, 20, 296 (1916).

[4] *Theorie der Wärme*, p. 309.

[5] *Z. physik. Chem.*, 65, 226 (1909).

[6] THIS JOURNAL, 41, 194 (1919).

The hydrogen molecules attached to the metal surface are not at rest but are performing highly damped oscillations, and if the adsorbing forces are not too strong molecules can coalesce to form small bubbles, especially around small points, which, as has already been pointed out, will affect the electrode potential.

We should therefore expect bubble size to be an important factor in the η value when the energy of desorption per gram molecule is small, but for large values of the latent heat the molecules are less mobile and bubbles are not formed so easily, consequently bubble size should have but a small influence on the overpotential. Confirmation of this deduction was obtained from experiments, on the influence of temperature on overpotential which are detailed later.

The desorption theory of overpotential is also supported from another point of view. Calculation from Bohr's theory[1] of the structure of the hydrogen molecule indicates that 21,000 calories per gram molecule is required to remove an electron from one atom to the other in a hydrogen molecule, which, according to the theory alluded to above, is the critical energy increment of the activation of hydrogen gas in free space, being of course less than that necessary for the formation of atomic hydrogen, which requires another increment of energy. This critical energy increment can be equated to the electrical energy required to desorb a gram-molecule of gas from an electrode surface, or,

$$\frac{96{,}540 \times 2}{4.2} \times \eta = 21{,}000, \text{ or } \eta = 0.455 \text{ volt.}$$

It follows that metals having η values equal to or exceeding 0.455 volt, should, if used as catalysts in hydrogenation processes, show no activity since the energy necessary for desorption exceeds that necessary for the activation of hydrogen in the gaseous state in the absence of a catalytic material.

It may be noted in passing that electrolytic reduction with metals possessing η values > 0.455 volt should be able to effect the reduction of substances which are not amenable to the catalytic process, further that no metal can possess an overpotential exceeding the value for which the energy exceeds that necessary for the desorption of atomic hydrogen or

$$\frac{96{,}540 \times 2}{4.2} \times \eta = 80{,}000 \text{ or } \eta = 1.80 \text{ volts.}$$

Metals having an η value less than 0.455 volt should show catalytic activity, since the adsorbed hydrogen will not be entirely immobilized; and the catalytic activity should increase with decreasing values in the overpotential. This can be seen from the following considerations:

Imagine a hydrogen molecule oscillating between two plane surfaces

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[1] *Phil. Mag.*, **26**, 1, 476 (1913).

situated parallel and close to one another, one plane surface being perfectly reflecting, and the other adsorbent. Every time the molecule strikes the reflecting surface it will be returned to the adsorbent one. Here it will oscillate in the field of attraction until sufficient time elapses for it to acquire energy by impact from other molecules or by radiation sufficient to permit of oscillation outside the range of attraction and regain the other surface when it will be reflected *de novo*. The alteration of the energy content of one molecule with the time is analogous to the energy distribution among a number of molecules at any given instant according to Maxwell's distribution law. It is evident that if the energy required for desorption is large, or the value of η high, the rate of interchange will be small, and the converse for substances possesses a small desorption energy. There is consequently a greater opportunity for two molecules of different reacting species to become adsorbed in juxtaposition to one another and so react than in the former case. Further, the rate of desorption or evaporation of the products of the reaction, which frequently governs the reaction rate, will be more rapid if the latent heat is small.

The following figures indicate how closely the catalytic activity in hydrogenation processes is related to the overpotential:

Metals in order of decreasing catalytic activity (Sabatier).	Overpotential η volts.	
Nickel	0.03	—0.21
Cobalt	0.03	—0.01
Platinum	0.09	—0.01
Iron	0.08	....
Copper	0.36	—0.03

Palladium (η = 0.23 — 0.46 volt) has also a marked catalytic activity in certain hydrogen ion processes, while Dewar has shown that silver (η = 0.05 — 0.15 volt) occasionally exhibits extraordinary activity.

According to Sabatier, the following metals are inactive in catalytic hydrogenation processes.

Metal.	Overpotential η volts.
Tin	0.43 to 0.53
Lead	0.42 to 0.78
Mercury	0.35 to 0.64
Zinc	0.66 to 0.70

It will be noted that the figures given for the overpotentials fluctuate within somewhat wide limits; thus different samples of copper may give values within the ranges 0.03 and 0.36 volt. This fact is in perfect accord with our knowledge of the variation in catalytic activity of this metal. H. S. Taylor and the writer have shown that a sample of ordinary copper wire will only appreciably catalyze the combination of hydrogen and oxygen at a temperature of 350°, while, "active" copper produced by alternate oxidation and reduction is operative at 70° to 90°. Bright platinum η = 0.09 volt) is ineffective for the oxidation of ammonia to nitric oxide, gray platinum (η = 0.06 volt) is extremely active, while black platinum (η = 0.01 volt) is found to be much too active for this conversion, nitrogen being formed in relatively large quantities.

Experiment has shown that in the case of copper also, there is a close relationship between catalytic activity and overpotential. It appears probable that these fluctuations in catalytic activity and overpotential in the same metal may be ascribed to the same cause, a difference in the surface structure of the metal. Under the microscope these differences are noted usually as a transition from a crystalline inactive variety to a powdery amorphous, occasionally microcrystalline active variety. The crystalline form may be converted into the active variety by a process of continued catalysis or by the continuous liberation of hydrogen at its surface. Metals deposited by a high current density are more active and possess a lower overpotential than those deposited under normal conditions, an indication that the elemental, cubic space lattice of the crystal is not so active as residues or fragments of the cubes from which one or more corners may be missing. In electro deposition the metallic ions tend to build up on the active form, and the same holds true for colloidal materials undergoing cataphoretic deposition. This gives an explanation, already proposed by Bancroft, for the formation of good deposits by such addition agents, and readily interprets Möller and Pring's observations[1] that a colloidal addition agent which lowered the surface tension of the electrolyte, and according to the bubble theory, should lower the overpotential also, actually raised it. The colloidal addition agent is deposited on the active areas of the electrode, leaving the less active areas exposed to function as the electrode, which consequently acquires a higher overpotential.

Sufficient data are not available to determine whether there is any relationship between the overpotential values and the quantity of colloid retained by the deposited metal. It might, however, be anticipated that metals exhibiting a high overvoltage or possessing a high latent heat of desorption for hydrogen would possess similar values for positively charged colloids, which on deposition would consequently not return so readily to the electrolyte. Mathers and Overman[2] state that 350 g. of peptone is adsorbed per ton of lead deposited from a perchlorate electrolyt eor one g. of peptone will protect only 143 gram molecules of lead. Silver deposition certainly requires a far smaller quantity of protecting agent.

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[1] *J. Chem. Soc.*, 105, 712 (1914).

[2] *Trans. Am. Electrochem. Soc.*, 13, 441 (1909).

In previous investigations it has been assumed that the energy required for the desorption of a product could be equated to the latent heat of evaporation. The above mentioned considerations however lead us to suppose that the latent heat of desorption is not equal to the latent heat of evaporation but varies with the nature of the surface from which the film is evaporating. On the radiation theory the latent heat of desorption per gram-molecule must be given by the equation, $E = Nh$ (ν reactants — ν products), in which both metal and hydrogen must be included. The following preliminary considerations on this point are given with reserve since it is hoped to make the more xact analysis the subject of a future communication.

In the case of sublimation or even fusion, and vaporization when the melting and boiling point lie close together, according to Trouton's rule, the latent heat of change is proportional to the temperature at which that change of state takes place. The vibrational energy of the surface molecules at that temperature is approximately $3\,RT$ or the latent heat of change is proportional to the surface vibrational energy of molecules. If we assume that the energy for vaporization is supplied by radiation, the frequency of the radiation ν is given by the relationship

$$L = h\nu,$$

where L is the latent heat of sublimation and h, Planck's constant. It is generally assumed that in infra-red radiation the radiator is an atom; if we further assume that the frequency of the radiant energy and of the radiator are the same, then the frequency of the atom just before leaving the surface is ν and its kinetic energy is $^1/_2\, ma^2\nu^2$, where m is its mass and a the amplitude of vibration. The total kinetic and potential energy of the vibrating atom is therefore $ma^2\nu^2$ acquired by radiation $h\nu$, or $ma^2\nu^2 = h\nu$. It can easily be shown that this relationship is only a very approximate one, since it follows that T/ν, where ν is the vibration frequency of the surface molecule at the temperature of sublimation T should be constant.

An approximate value for this ratio for a number of elements is 2.5×10^{-10}. Exceptions are, however, very frequent, especially at very low or very high temperatures.

In the case under consideration the hydrogen molecule may be regarded as attached to neighboring metal atoms, atom to atom, and to oscillate with them but with different frequencies. The metal atoms vibrate with their natural frequency in the infra-red. The hydrogen molecule, however, although it can vibrate in the two directions parallel to the plane of the metal with its natural frequency, yet in the plane perpendicular to the metal surface has a frequency which is very different. At a certain distance from the metal surface there is a position of zero attraction for the hydrogen atoms. An atom approaching within this distance will suffer a repulsion, while an atom receding from this point will undergo attraction until it passes outside the range of molecular action.[1] Each atom on the surface possesses a kinetic energy *per se*, the magnitude of which will, however, vary from instant to instant just as the number of atoms possessing different amounts of kinetic energy distributed in a collection of atoms at any given instant according to Maxwell's law of distribution, so the energy content of one atom must vary from second to second. The atoms consequently oscillate on the metal surface by virtue of their own kinetic energy, which appears as a damped vibrational movement under the influence of the attractive and repulsive forces; every now and then one atom or molecule acquires sufficient kinetic energy to vibrate outside the attraction zone of the metal and consequently is evaporated or desorbed. Thus from the latent heat of desorption it is possible to calculate the energy required to remove an atom from the position of zero attraction to a position outside of the range of molecular attraction. If this energy be supplied by radiation, then, assuming the conditions already referred to, it is possible to calculate both the amplitude and the vibration frequency of this forced vibration.

In the case of silver the mean value of the overpotential appears to be 0.10 volt ± 0.05, giving an energy of desorption of 4,300 cal. per gram molecule or 3×10^{-13} ($\pm 1.5 \times 10^{-13}$) ergs per molecule. The average kinetic energy of a hydrogen molecule at 0° is 3.69×10^{-14} ergs. The energy of desorption is thus nearly 10 times that possessed by the molecule at that temperature. Assuming this energy to be acquired by infra-red radiation, then since $E = h\nu$

$$\nu = \frac{3 \times 10^{-13}}{6.55 \times 10^{-27}}; \text{ or } \nu = 4.6 \times 10^{13} \; (\pm = 2.3 \times 10^{13})$$

being the vibration frequency of the hydrogen molecule and consequently that of each atom. We may regard the hydrogen atom and the adsorbing silver atom as vibrating identical distances with necessarily different frequencies. On equating the kinetic energies of the two masses,

$$ma^2\nu^2 = Ma^2\nu_1^2,$$

where m is the mass of the hydrogen atom, M the mass of the silver atom, a the amplitude of each atom, and ν and ν_1 their respective frequencies. The atomic weight of silver is 108, hence its vibrational frequency is

$$\nu_1 = \frac{4.6 \times 10^{13}}{\sqrt{108}} = 4.5 \times 10^{12}.$$

Lindemann's formula gives us a value of 4.36×10^{12}.

The mass of a hydrogen atom is $1.634 \; 10^{-24}$ g., its energy in the adsorbed state is 1.5×10^{-13} ($\pm 0.75 \times 10^{-13}$) ergs. hence its velocity is

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[1] Langmuir, *Phys. Rev.*, 8, 149 (1916).

3×10^5 ($\pm 1.5 \times 10^5$) cm. per second. If its vibration frequency is 4.6×10^{13} ($\pm 2.3 \times 10^{13}$) the average distance of travel, or average amplitude is v/ν or 0.8×10^{-8} cm. This must, therefore, be the range of molecular attraction beyond the nearest point of approach of the atom; the total distance calculated by other methods is approximately 2×10^{-8} cm.

In the following table are given the mean overpotentials of a number of elements, the energy of desorption in cal. per gram-molecule, $-\Delta U$, the vibration frequency of the adsorbed atom of hydrogen and that of the adsorbing metal calculated therefrom. The metal frequencies calculated from Lindemann's formula are given for comparison:

Metal.	Overpotential volts.	$-\Delta U$.	$\nu \times 10^{-13}$. Hydrogen.	$\nu \times 10^{-12}$. Metal.	$\nu \times 10^{-12}$. Metal calc. (Lindemann).
Ag..........	0.10	4,300	4.6	4.5	4.36
Pt..........	0.08	3,600	4.1	3.0	4.36
Cu..........	0.13	5,800	6.13	7.6	6.7
Ni..........	0.12	5,200	5.6	7.5	8.2
Fe..........	0.08	3,660	3.96	5.3	8.3
Au..........	0.02	1,000	1.1	0.8	3.4
Pd[a]........	0.23	10,250	11.0	10.9	5.7

[a] The heat of formation of "palladium hydride" is given as 500 cal. which, if correct, would correspondingly reduce the overpotential value.

In the metals given below, active hydrogen is the desorption product and no relationships obtain between the calculated values and those obtained from Lindemann's equation.

Hg..........	0.78	34,700	38.1	27	1.24
Zn..........	0.70	31,000	34.1	43	4.36
Sn..........	0.53	23,700	26.1	23	2.24
Cd..........	0.48	21,200	23.3	22	3.0

In spite of the great latitude in the overpotential values recorded and of the assumptions made as to the material nature of the radiator as well as to its independent oscillation in one plane, there is a rough agreement between the two values for the radiation frequencies. It is interesting to calculate these values for a hypothetical solid hydrogen electrode. Eucken[1] gives the latent heat of vaporization of hydrogen as 220 cal.; the latent heat of fusion may be taken as approximately equal to that of nitrogen, giving a latent heat of sublimation of 390 cal., the kinetic energy of the hydrogen molecule after desorption, *viz.*, $3\,RT$ not being supplied by radiation. Hence to desorb hydrogen from a hydrogen electrode would require an overvoltage of only 0.009 volt and a corresponding radiation frequency of 4.30×10^{12}, a very close approximation to Lindemann's figure of 4.36×10^{12}.

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[1] *Ber. Phys. Ges.*, **18**, 4 (1916).

EXPERIMENTAL.

The Influence of Temperature on Overpotential.

In order to establish the conclusion that overpotential might be influenced by bubble size in elements possessing a small overpotential but not for those elements with a high value, experiments were conducted with electrodes of platinum, copper and zinc. MacInnes and Adler[1] showed that for overpotentials of the order of 0.001 to 0.002 volt there was a rough agreement between the observed bubble diameter and the calculated value. Owing, however, to the difficulties of measurement the error varied from 30 to 50%; it was clearly impossible so to refine their method for the very minute bubbles to be expected with high overpotential values. Accordingly attempts were made to determine the temperature coefficient of the overvoltage.

If the overvoltage is a simple function of the bubble size, then the temperature coefficient according to the relation, $96{,}540 \times 2 \times \eta = 3RT/pr\,\gamma$ is, $d\eta/dT = KT(d\gamma/dT) + K\gamma$, where $K = 3R/pr\,96{,}540 \times 2$, r being the bubble radius, p the gas pressure, and γ the surface tension.

The expression, $-T\,d\gamma/dT$, is equal to the latent heat of extension of the film, which in the case of water was found by Kelvin to be equal to half the work required to form the film, or $^1/_2\gamma$; hence $d\eta/dT = 1.5\,K\gamma$, or $1.5\,\eta/T$. Sheet metal electrodes were employed, each side 3.11 sq. cm. in area. The electrodes were coated with a relatively thick film of electrolytically deposited metal and were subjected to the cathodic liberation of hydrogen in 0.1 N sulfuric acid for 48 hours before use. The overvoltages in 0.1 N sulfuric acid, maintained at suitable temperatures in a thermostat were determined by means of an auxiliary 0.1 N calomel electrode with acid of the same strength as the junction liquid, utilizing a Leeds and Northrup type of potentiometer. The potential of a hydrogen electrode, of the type suggested by G. N. Lewis, was determined under identical conditons. The overpotential was accordingly given by the relationship, $\eta_t = E/\mathrm{M}\,t - E/\mathrm{H}\,t$. $E/\mathrm{M}\,t$ and $E/\mathrm{H}\,t$ being the observed potential differences for the metal and the hydrogen electrodes at a temperature t. Errors due to liquid junction potentials and temperature differences were thus eliminated. The following values were obtained:

Metal.	Current density. Milliamps per sq. cm.	Temperature, 23°.	33°.	43°.	53°.	63°.
			Overvoltage in millivolts.			
Platinum......	1.6	5.5	1.5	0.5	....	....
	3.2	8.3	6.0	6.0	2.0	0.5
	4.8	10.8	11.0	5.2	3.0	3.3
	8.0	11.8	11.0	11.0	8.6	7.4
	10.4	15.8	15.6	12.7	11.0	9.1
	16.0	18.1	17.7	16.0	13.5	12.9
Mean value $\partial\eta/\partial T$ millivolts per degree..		0.13	0.19	0.25	0.13	

Mean value obs....... 0.17 millivolt per degree.

Calc................... 0.053 millivolt per degree at 37°.

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[1] THIS JOURNAL, 41, 200 (1919).

		Temperature, 20.5°.	30.5.	40.5.	50.5.	60.5.	67.
Copper........	1.6	103.4	71.2	37.1	12.7	....	....
	3.2	130.4	105.6	76.4	56.4	40.5	23.8
	4.8	150.4	121.9	93.4	73.4	56.5	41.5
	8.0	165.9	142.4	107.4	90.5	72.5	62.0
	10.4	166.9	147.4	107.9	98.5	79.0	73.0
	16.0	190.0	166.4	130.4	110.0	90.4	....

Mean value $\partial\eta/\partial T$ millivolts per degree... 2.5 3.3 1.9 1.8 1.5
Mean value obs....... 2.2 milivolts per degree.
Calc................. 0.5 millivolt per degree at 37°.

		Temperature, 18°.	35.	45.	55.
Zinc..........	1.6	655.0	654.0	655.9	653.1
	3.2	658.8	656.0	654.9	653.1
	4.8	665.4	658.7	654.9	655.1
	8.0	672.7	663.7	655.9	661.1
	10.4	679.2	665.7	656.9	661.1
	16.0	680.0	672.2	658.9	663.0

Mean value $\partial\eta/\partial T$ millivolts per degree... 0.40 0.54 0.0
Mean value obs....... 0.31 millivolt per degree.
Calc................. 3.2 millivolts per degree at 37°.

It will be noted that in the case of zinc there is no relationship between the observed and calculated potential temperature decrement, the total variation over nearly 40° being only 2%. In the case of copper and platinum a definite temperature coefficient is observed which, however, is considerably greater than the calculated value, although in the case of copper its variation with the temperature is as would be expected on the basis of the bubble theory. The large value of the coefficient must in part be attributed to the greater mobility (at the higher temperatures) of the hydrogen molecules attached to the surface, permitting the formation of larger bubbles, and also to the increased diffusion rate of the dissolved hydrogen from the electrode surface permitting a greater evaporation rate, with a consequent increase in the current density before the maximum value of the overpotential is obtained. The following calculation gives an approximation to the ratios of the current densities required for the metals before the overpotential reaches a maximum. The latent heats of desorption of hydrogen from platinum, copper and zinc are, respectively, 3,600, 5,800 and 31,000 cal. per mol. The number of molecules possessing sufficient energy to leave the surface at any time is given by the relation $N_a/N = e^{\frac{-Q}{RT}}$, where N_a molecules out of N molecules are capable of evaporating.

For a temperature of 300° K. we find that one molecule in $10^{2.6}$ for platinum, one in $10^{4.2}$ for copper and one in 10^{23} for zinc are capable of evaporation. No data appear available to determine the absolute rates of evaporation under these conditions. It may be noted that as one sq. cm. of surface will adsorb 6.10^{14} molecules while a milliampere will deposit $3 \cdot 10^{15}$ molecules per second, evaporation must, therefore, be relatively rapid. In any case, although the absolute rates are unknown, the relative evaporation rates give us a measure of the relative current densities necessary to keep the surface permanently covered with hydrogen, the condition for the occurrence of the maximum overpotential effect. The figures given above indicate that small currents polarize zinc much more easily than copper or platinum.

Overpotential and Electrode Surface.

The alteration of the overpotential with the nature of the surface is well marked in the case of platinum and, according to the previous discussion, the same should hold true for all catalytically active metals. The following figures illustrate the magnitude of these changes in the cases of copper and zinc.

An electrolytic copper electrode was made the cathode in a 0.1 *N* sulfuric acid solution, hydrogen being continuously and rapidly disengaged at its surface, the overpotential being determined from time to time. It was found that there was a continuous fall in the η value and the bright crystalline appearance of the metal was replaced by a honeycomb-like amorphous layer occasionally yellowish brown in appearance. The observed values were as follows:

	Time. Hours.	Overvoltage, η [8 milliamperes per sq. cm.] v.	Appearance.
Temp. 20.5°..........	0	0.364	microcrystalline, bright
	24	0.284	reddish
	48	0.178	brownish, amorphous
	56	0.166	brownish, amorphous

It would appear possible to reduce the overpotential of copper to the lowest figure recorded, *viz.*, 0.03 volt by continued treatment. At higher temperatures this change takes place somewhat more rapidly, at least in the earlier stages.

	Time. Hours.	Overvoltage, η [8 milliamperes per sq. cm.] v.
Temp. 55°.............	0	0.341
	1	0.208
	2	0.178
	3	0.169
	5	0.161

Very spongy copper deposited by high current densities will, if opportunity be given for the occluded hydrogen to escape, rapidly acquire a relatively low overpotential.

	Time, Hours.	Overvoltage, η [8 milliamperes per sq. cm.].
Temp. 20.5°...........	0	0.325
	3	0.140
	5	0.139

In the case of zinc these differences in overvoltage are much less marked as will be noted from the following figures:

Time. Hours.	Overvoltage. 8 milliamperes per sq. cm.	Appearance.
0	0.841	bright, metallic crystalline
15	0.727	slightly dull
48	0.673	distinctly gray

Catalytic Activity and Overpotential.

A small strip of copper was alternately oxidized and reduced by hydrogen until it began to show signs of catalytic activity toward a hydrogen-oxygen mixture. The temperature at which traces of water were being formed, which frequently coincided with the appearance of changing oxide films on the metal surface, was noted, the metal being then removed and placed in the cell for the determination of its overpotential. Although as a result of a number of experiments no direct relationship between the overpotential and the temperature of apparent catalytic activity could be found, yet in all cases the overpotential fell with the temperature, or with the increase of catalytic activity, as will be noted from the following figures:

Temperature of catalysis. Degrees.	Overpotential. Volts.
300	0.362
280	8.353
260	0.328
250	0.306
230	0.238
150	0.195

It would appear, however, that the fraction of the total surface which has to be operative to reduce sensibly the overpotential is much greater than that necessary to effect an appreciable difference in catalytic activity, indicating that the metallic catalysts as ordinarily prepared are comparatively inefficient and should be capable of great improvement.

Summary.

It is suggested that overpotential is a measure of the energy required for the desorption of hydrogen from a metallic surface.

Metals with low latent heats of desorption are catalytically active, the activity increasing with decreasing overpotentials. Metals with overpotentials exceeding 0.455 volt are catalytically inert and no metal can possess an overvoltage exceeding 1.80 volts.

The calculated values of the catalytic activities of the metals are in agreement with Sabatier's qualitative observations.

A tentative suggestion for the mechanism of the process of desorption on the radiation hypothesis is advanced.

URBANA, ILLINOIS.