715. *The Catalytic Hydrogenation of Unsaturated Hydrocarbons. Part IV.*[1] *The Kinetics of the Hydrogenation of Acetylene over Supported and Unsupported Iron, Cobalt, and Copper, and over some Nickel–Cobalt and Nickel–Copper Alloys.*

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At constant acetylene pressure, the rate of hydrogenation of acetylene over pumice-supported and unsupported iron and cobalt catalysts is proportional to the hydrogen pressure, and no evidence of a " two-rate " effect (of the type described for nickel in Part III [1]) has been found. Both types of copper catalyst do show this effect, but in contradistinction to nickel the activation energy E_A of the process operating at low hydrogen pressures is greater (*ca.* 20 kcal. mole^{-1}) than that (E_B) for the additional process at high hydrogen pressures (*ca.* 4 kcal. mole^{-1}). Values of E_A for iron, cobalt, and nickel are all close to 8·6 kcal. mole^{-1}, and the activity differences, which are substantial, therefore reside in the pre-exponential terms.

Mixed nickel–copper and nickel–cobalt oxides prepared from co-precipitated basic carbonates have been reduced to homogeneous alloy powders at 500°. In the nickel–cobalt system, the " two-rate " effect persists through to the composition 20Ni : 80Co, and E_A increases markedly with increasing cobalt concentration in the range 0—40% of cobalt. With nickel–copper, E_A is similarly raised by increasing copper concentration. Activity patterns are notably temperature-sensitive, and indicate that at high temperatures the *d*-band hole concentration determines the activity, but at low temperatures the situation is more complex. The results are discussed in terms of current concepts.

PART III [1] described an investigation of the kinetics of hydrogenation of acetylene over various types of nickel catalyst, and the same general rate expression

$$-\mathrm{d}p/\mathrm{d}t = k_A P_{H_2} + k_B(P_{H_2} - P_{H_2}^0) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

fitted all the results. We can describe the phenomenon of a rate cxpression containing two rate constants as a " two-rate effect." Our first object was to extend the study of this reaction to metals lying near nickel in the Periodic Table, to see which others if any, showed this effect.

Sheridan's work [2] showed that iron and cobalt behaved similarly to, but were less active than, nickel. The reaction over copper is of course complicated by formation of cuprene, which Sheridan was able to overcome by using an excess of hydrogen. He was, however, unable to make reliable kinetic measurements over cobalt and copper owing to the deactivation of his catalysts. References to earlier work are given in Sheridan's paper.

A further object of this work was to investigate the kinetics of hydrogenation of acetylene over some alloy powders. Homogeneous binary alloys of metals occupying adjacent positions in the Periodic Table offer an excellent means of studying the relationship between the activity and the electronic constitution of the catalyst, since they often exhibit marked changes in both while the lattice dimensions scarcely alter. While the catalytic properties of the nickel–copper system have been quite widely studied, the literature reveals few such studies of the nickel–cobalt system.[3] The results for iron, cobalt, nickel,[1,4] and copper, together with the results on the nickel–copper and nickel–cobalt alloys, form a broad basis

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[1] Part III, Bond and Mann, *J.*, 1958, 4738.

[2] Sheridan, *J.*, 1945, 470.

[3] Long, Frazer, and Ott, *J. Amer. Chem. Soc.*, 1934, **56**, 1101; Rienäcker and Unger, *Z. anorg. Chem.*, 1953, **274**, 47.

[4] Bond, *J.*, 1958, 2705 (Part I).

for evaluating the significance of the electronic factor in the hydrogation of acetylene, and cast further light on possible reaction mechanisms.

EXPERIMENTAL

The apparatus and procedure were essentially as described in Parts I[4] and III,[1] save that for some later experiments the reaction vessel was modified to allow the reduction of the catalyst in a hydrogen stream *in situ*.

Metal Catalysts.—Pumice-supported iron, cobalt, and copper catalysts containing about 10% of metal by weight were prepared by the standard method, starting from the nitrates; they are designated Fe–p, etc. The pumice-supported ferric and cobalt nitrate were each calcined in an oxygen stream for 10 hr. at 350° and reduced, in an external system, in a hydrogen stream for 20 hr. at 400°. The corresponding figures for the copper catalyst are: 6 hr. at 250° and 10 hr. at 300°.

These metals were also prepared as powders (Fe–I etc.) by reduction of the oxides derived from the basic carbonates, under conditions identical with those used in preparing nickel powder in this manner.[1] An iron powder (Fe–II) was also prepared by calcination of ferric nitrate (12 hr. at 350°) followed by reduction in a hydrogen stream (24 hr. at 400°). This and other catalysts not reduced in the reaction vessel were pretreated *in situ* in a static hydrogen atmosphere at the previously used reduction temperature for the following times: Fe–p, 20 hr.; Fe–II, 10 hr.; Co–p, 2 hr.; Cu–p, 14 hr.

Alloy Catalysts.—Homogeneous nickel–cobalt and nickel–copper alloy powders were prepared by Best and Russell's method;[5] the mixed basic carbonates, precipitated from solutions containing the appropriate quantities of the nitrates, were decomposed to the oxides, which were then reduced *in situ* in a hydrogen stream for 24 hr. at 500°.

The surface areas of the alloy and the metal powders were determined by low-temperature krypton adsorption in the laboratories of the Research Department, Imperial Chemical Industries Limited, Billingham Division; the *X*-ray spectra of the alloys and of the cobalt powder were also determined there.

RESULTS

The designation of pressure–time curves is as in Parts I and III. In all cases where type IIA curves were obtained, the Arrhenius parameters derived from the α- and the β- parts of the curves were closely similar, and only the α-values are therefore quoted. Other quantities are as defined in Part III. Pre-exponential factorsf or both supported and unsupported catalysts are expressed as (g. of metal)$^{-1}$, and as m.$^{-2}$ where the surface area is known. Hydrogen was admitted first to the reaction vessel unless otherwise stated, and rate constants were evaluated from series of experiments in which the hydrogen pressure was varied through at least 200 mm. within the range 30—360 mm.

TABLE 1. *Results for iron, cobalt, and copper catalysts.*

Catalyst	Fe–p	Fe–I	Fe–II	Co–p	Co–I	Cu–p	Cu–p	Cu–p	Cu–I
$P_{C_2H_2}$ *	30	30	30	30	30	17	32	62	30
Metal (g.)	0·20	0·30	0·31	0·20	0·24	0·20	0·20	0·20	0·25
Temp. range	145—225°	108—162°	208—254°	107—157°	111—156°	150—195°	150—195°	150—195°	121—175°
E_A †	7·1	8·7	15·1	4·1	9·0	19·2	16·9	21·0	21·0
E_B †	—	—	—	—	—	5·0	5·0	—	3·2
ΔE_B †	—	—	—	—	—	−14·6	−13·3	—	−17·8
$\log_{10} A_A$ ‡	1·76	2·62	4·63	1·30	3·66	8·26	7·21	7·75	9·63
$\log_{10} A_B$ ‡	—	—	—	—	—	1·06	1·09	—	1·80
$\log_{10} \Delta A_B$ ‡	—	—	—	—	—	−6·38	−7·26	—	−9·72
Surface area §	—	4·68	—	—	1·44	—	—	—	1·01
$\log_{10} A_A$ ‖	—	1·95	—	—	3·50	—	—	—	9·63
$\log_{10} A_B$ ‖	—	—	—	—	—	—	—	—	1·80

* Initial pressure (mm.). † kcal. mole^{-1}. ‡ min.$^{-1}$ (g. of metal)$^{-1}$. § m.^{2} g.$^{-1}$. ‖ min.$^{-1}$ m.$^{-2}$.

Iron, Cobalt, and Copper Catalysts.—The principal results are shown in Table 1. With iron and cobalt catalysts, type IIA curves were obtained irrespective of the hydrogen : acetylene ratio and of the order of admission of reactants: there was no indication of an inflexion in the

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[5] Best and Russell, *J. Amer. Chem. Soc.*, 1954, **76**, 838; see also Hall and Alexander, *J. Phys. Chem.*, 1957, **61**, 1564.

rate *versus* hydrogen pressure plots up to at least 300 mm. of hydrogen, and the results are therefore fully described by the rate expression

$$-\mathrm{d}p/\mathrm{d}t = k_{\mathrm{A}}P_{\mathrm{H}_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

When hydrogen was admitted first to the cobalt–pumice catalyst, $-\Delta p_{\alpha}$ increased quite markedly with hydrogen pressure for hydrogen : acetylene ratios less than about three, but for higher ratios it remained constant at about two-thirds of the initial acetylene pressure. It was however independent of hydrogen pressure when acetylene was added first.

Of the iron powders, that (Fe–I) prepared by reduction of the oxide *in situ* was active in a much lower temperature range than that (Fe–II) reduced in an external system; the same was found for nickel,[1] and the same explanation may apply. With cobalt–pumice, an activation energy of 4·3 kcal. mole^{-1} and a value of $\log_{10} A_{\mathrm{A}}$ of 1·20 min.$^{-1}$ g.$^{-1}$ were obtained when acetylene was admitted first.

Copper-pumice as catalyst. At and below 167° the dependence of rate on hydrogen pressure was of the form

$$-\mathrm{d}p/\mathrm{d}t = R_{\mathrm{D}} + k_{\mathrm{A}}P_{\mathrm{H}_2} + k_{\mathrm{B}}(P_{\mathrm{H}_2} - P_{\mathrm{H}_2}{}^{0}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

when the initial acetylene pressure was not greater than 32 mm.; above 167° the third term of the rate expression was not detectable because of the rapid way in which $k_{\mathrm{B}}/k_{\mathrm{A}}$ fell with rising temperature (see Table 1 for values of ΔE_{B}). Table 2 gives values of the parameters in equation (3) at 150° and 167·5°; failure to observe the " two-rate " effect with 62 mm. of acetylene at either of these temperatures was presumably due to the use of insufficiently high hydrogen pressures. It has been supposed that the R_{D} term represents a catalytic decomposition or polymerisation which for a fixed acetylene pressure and temperature proceeds at a rate independent of the hydrogen pressure. From Table 2, together with results obtained at 182·5 and 195° values of E_{A}, E_{B}, etc. have been calculated (see Table 1): E_{A} has a mean value of 19·0 ± 1·4 kcal. mole^{-1} which is probably independent of acetylene pressure. That the processes whose rate constants are k_{A} and k_{B} are hydrogenations substantially free from decomposition or polymerisation is shown by the very satisfactory nature of the Arrhenius plots. Values of E_{D} show no regular trend with changing acetylene pressure, and lie between 22·5 and 25·0 kcal. mole^{-1}.

TABLE 2. *Dependence of parameters in equation* (3) *on temperature and acetylene pressure.*

Temp.	$P_{\mathrm{C}_2\mathrm{H}_2}$ (mm.)	R_{D} (mm. min.$^{-1}$)	$P_{\mathrm{H}_2}{}^{0}$ (mm.^{2})	$10^2 k_{\mathrm{A}}$ (min.$^{-1}$)	$10^2 k_{\mathrm{B}}$ (min.$^{-1}$)
150·0°	17	0·38	102	0·38	0·48
,,	32	0·44	147	0·66	0·46
,,	62	0·46	212	1·06	—
167·5	17	0·50	75	0·86	0·60
,,	32	0·55	90	1·25	0·55
,,	62	1·05	200	1·70	—

Consideration of the results in Table 2 and of other measurements at higher temperatures shows that at every temperature both R_{D} and k_{A} depend on a fractional positive power x of the acetylene pressure; values of x (which are uncertain by ±0·05) are as follows.

Temp.	150°	167·5°	182·5°	195°
x for k_{A} dependence	0·28	0·26	0·53	0·80
x for R_{D} dependence	0·17	0·52	0·72	0·77

Positive orders in acetylene were also found for certain nickel catalysts.[1] The increase in order in acetylene for k_{A} with increasing temperature denotes desorption of the acetylene, and the " two-rate " effect only seems to appear when the adsorption of acetylene is fairly strong. k_{B} is almost independent of acetylene pressure at 150° and 167°.

Copper powder as catalyst. Similar results were obtained; the " two-rate " effect was observed at 121° and 135° (but not at higher temperatures), $P_{\mathrm{H}_2}{}^{0}$ being respectively 95 and 78 mm. A decomposition was again found, and R_{D} appeared to increase linearly from 0·3 to 0·9 mm. min.$^{-1}$ between 121° and 175°.

A very satisfactory " compensation effect " exists between all the activation energies and log A terms quoted thus far: the equation is $\log_{10} A_{\mathrm{i}} = 0{\cdot}55E_{\mathrm{i}} - 1{\cdot}5$.

The corresponding equation for nickel catalysts [1] was $\log_{10} A_{\mathrm{i}} = 0{\cdot}48E_{\mathrm{i}} + 0{\cdot}40$.

Nickel–Copper and Nickel–Cobalt Alloys.—Physical characteristics. Table 3 gives the observed lattice parameters (a_0) in Å and the compositions to which these values correspond, obtained by comparison with Coles's results[6] for the nickel–copper system and with Taylor's[7] for the nickel–cobalt system: surface areas are also quoted. The accuracy of the lattice parameter measurements varied because of the variable degree of crystallinity of the powders. All the nickel–cobalt alloys had the face-centred cubic structure; pure cobalt was also examined and found to be mainly in this form, although a little of the theoretically more stable close-packed hexagonal form was also present. No alloy contained detectable free metal (<2%). The only alloy not showing the expected composition within the accuracy of the measurements was that designed to contain 60% of copper and 40% of nickel. Hall and Alexander[7a] have recently investigated by *X*-ray spectroscopy nickel–copper alloys prepared by the method used here, but reduced at only 350°, and have concluded from the degree of line-broadening that inhomogeneity within a crystallite in no case exceeds 3%. Surface areas of copper and cobalt powders are in Table 1.

TABLE 3. *Lattice parameters, composition, and surface areas of alloys.*

Nickel–copper

Copper, nominal (%)	0	20	40	60	80
Lattice parameter (Å)	3·5235 ± 0·0005	3·5405 ± 0·0005	3·555 ± 0·001	3·567 ± 0·001	3·5910 ± 0·0005
Copper observed (%)	0	21·0 ± 0·5	39·0 ± 1·0	52·5 ± 1·0	79·0 ± 0·5
Surface area (m.^{2} g.$^{-1}$)	0·41	0·79	0·76	0·54	0·49

Nickel–cobalt

Cobalt, nominal (%)	20	40	60	80
Lattice parameter (Å)	3·526 ± 0·001	3·531 ± 0·001	3·5355 ± 0·001	3·5395 ± 0·001
Cobalt observed (%)	17 ± 5	36 ± 5	58 ± 5	77 ± 5
Surface area (m.^{2} g.$^{-1}$)	0·52	1·28	0·98	1·30

Kinetic characteristics. Series of experiments were performed with about 0·25 g. of each alloy; the rate expression (1) applied throughout, and in each case the parameters of this expression were determined in the usual manner at five temperatures covering a range of 20—40°. The principal results are shown in Table 4. Pressure–time curves were generally of type I above $P_{H_2}{}^0$ and of type III below it; no decomposition of acetylene (*i.e.*, no R_D term) was ever detected. Two samples of nickel–copper alloy containing nominally 40% of nickel were prepared from mixed oxides drawn from the same batch, to check the reproducibility of measurements. Values of $P_{H_2}{}^0$ tended to fall with decreasing temperature, but generally very irregularly, and there was evidence that other variables (*e.g.*, the age of the catalyst) were operative. $P_{H_2}{}^0$ values lay between 70 and 175 mm. for nickel–copper alloys and between 70 and 190 mm. for nickel–cobalt alloys. The initial acetylene pressure was 30 mm. in all cases.

TABLE 4. *Kinetic characteristics of nickel alloy catalysts.*

	Nickel–copper						Nickel–cobalt			
Nickel * ...	100	80	60	40	40	20	80	60	40	20
Temp. range	73—150°	71—110°	83—110°	92—119°	99—122°	123—148°	114—137°	105—124°	74—108°	123—165°
E_A †	8·2	15·1	20·1	21·3	20·2	25·2	19·2	21·0	12·5	16·0
E_B †	15·1	16·4	17·1	8·9	7·8	18·2	13·7	18·2	12·0	6·2
ΔE_B †	7·3	1·7	−3·0	−13·2	−12·8	−7·1	−5·5	−2·5	−1·0	−10·8
$\log_{10} A_A$ ‡ ...	5·0	8·1	11·0	11·4	10·6	12·5	9·6	10·8	6·4	7·3
$\log_{10} A_B$ ‡ ...	8·3	9·6	9·2	4·2	3·4	8·8	6·6	9·5	5·6	1·7
$\log_{10} \Delta A_B$ ‡	4·3	1·0	−1·7	−7·6	−7·1	−3·9	−3·0	−1·3	−1·6	−6·0
$\log_{10} A_A$ ‖ ...	5·4	8·2	11·1	11·8	—	12·8	9·8	10·7	6·5	7·2
$\log_{10} A_B$ ‖ ...	8·7	9·7	9·3	4·6	—	9·1	6·8	9·4	5·7	1·6

The results for nickel are taken from Part III; those for copper and cobalt are to be found in Table 1.

The surface area of the catalyst used in the repeat measurement (col. 5) was not determined: in estimating the activities for Fig. 1, the area has been assumed to be 0·76 m.^{2} g.$^{-1}$.

* Nominal percentage. † ‡ ‖ See Table 1.

In both series, changes in activation energies and in the corresponding specific log A terms

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[6] Coles, *J. Inst. Metals*, 1956, **84**, 346.

[7] Taylor, *ibid.*, 1950, **77**, 585.

[7a] Hall and Alexander, *J. Phys. Chem.*, 1957, **61**, 242.

run parallel in a striking manner. " Compensation effects " therefore result, log A_i being simply proportional to E_i; the proportionality constants are 0·56 in the nickel–copper series and 0·50 in the nickel–cobalt series. The value for nickel catalysts was 0·48 and for the other pure metals 0·55; the differences between all these values are within experimental error.

With increasing copper content, E_A rises from 8 to 25 kcal. mole^{-1} at 80% of copper, and thereafter falls slightly; E_B and ΔE_B respectively rise slightly and fall but at above 60% of copper they behave irregularly. Experiments with a second sample of 60% copper alloy showed that activation energies (and particularly ΔE_B) were quite closely reproducible, so that the apparently irregular behaviour is probably not adventitious. With increasing cobalt content, E_A at first rises steeply, reaching a maximum at 40% of cobalt, but thereafter it changes erratically; neither E_B nor ΔE_B changes smoothly with composition.

The occurrence of compensation effects obscures possible effects of composition on activity except insofar as this is revealed by the temperature range for satisfactory operation. From the results in Tables 1 and 4, values of k_A and k_B have been computed for all catalysts at characteristic temperatures of 50°, 100°, 150°, and 200°, and in Fig. 1 these values are plotted against composition. The availability of results covering a continuous series of solid solutions from cobalt through nickel to copper provides a broad basis for considering how the electronic factor operates in the hydrogenation of acetylene.

DISCUSSION

The " Two-Rate " Effect.—The " two-rate " effect has not been found with any type of iron or cobalt catalyst under conditions where it appears with nickel and copper catalysts, although in the nickel–cobalt alloy series the effect persists through to the alloy containing only 20% of nickel. We conclude provisionally that the mechanism suggested [4] for the reaction over nickel below $P_{H_2}{}^0$ holds over a much wider range of conditions with iron and cobalt. The second mechanism is believed [8] to be caused by molecular hydrogen's initiating a kinetically independent mechanism, and we now attempt an interpretation of the results on this model.

Although the rate of the second process always increases with temperature, its activation energy E_B varies widely; it is high for nickel (15 kcal. mole^{-1}), low for copper (3 kcal. mole^{-1}), and presumably zero for iron and cobalt. In the alloy series, values of E_B lie in the range 16 ± 2 kcal. mole^{-1} from 40% of cobalt to 80% of copper inclusive, apart from the unexplained (but reproducible) low values for the 60% copper alloy. If the true activation energy of the second process were constant until at least the *d*-band is filled, the rapid fall in E_B at the cobalt-rich end of the nickel–cobalt series would reflect an increase in the heat of adsorption of molecular hydrogen, and we may expect that there will be a maximum permissible value for this quantity which if exceeded would cause a spontaneous transition of adsorbed hydrogen from the molecular to the atomic form. However this type of explanation can scarcely be applied to interpret the behaviour of copper for whose low E_B value there is no immediate explanation. A second type of hydrogen chemisorption which may be molecular in form has been observed on nickel films [9] but not on copper films [10] at room temperature; molecularly adsorbed hydrogen is probably only stable on iron catalysts at low temperatures.[11] We conclude that the present results accord reasonably with what might be expected on the basis of the previously proposed mechanism.

Relative Activities of the Pure Metals.—Changes in the constitution of the catalyst for a chosen reaction may affect its activation energy, its pre-exponential factor, or both simultaneously: experimental investigation of these relations gives information on the effect of the parameters of the catalyst on the energetics of the reaction path, and on the basic activity of the unit catalytic site. In the present case, E_A has a low and approximately constant value for iron, cobalt, and nickel powders (8·6 ± 0·4 kcal. mole^{-1}) so that

[8] Bond, *J.*, 1958, 4288 (Part II).
[9] Mignolet, *Rec. Trav. chim.*, 1955, **74**, 701; Sachtler, *Bull. Soc. chim. belges*, 1958, **67**, 369.
[10] Bloyaert, D'Or, and Mignolet, *J. Chim. phys.*, 1957, **54**, 53.
[11] Kummer and Emmett, *J. Phys. Chem.*, 1952, **56**, 258.

activity differences between these three metals reside chiefly in log A: for copper powder, E_A is 21 kcal. mole^{-1}, but log A is not large enough to compensate, and copper therefore has the lowest activity of the pure metals. The same is also true of the supported metals, although here E_A for the *d*-metals covers a wider range (*ca.* 4—10 kcal. mole^{-1}); E_A for copper is high (*ca.* 19 kcal. mole^{-1}), and copper is again the least active metal. The agreement between the Arrhenius parameters for supported and unsupported metals is satisfactory for iron and copper but poor for cobalt. The less active iron powder (Fe–II) has a much higher activation energy than the more active one (Fe–I).

Of more practical interest is the comparison of the activities of the metals at a chosen temperature: Table 5 gives the values of k_A and of k_B (both $\times\ 10^2$) at 100° for supported and unsupported metals. The activity *order* based on k_A is in both cases Ni > Co > Fe > Cu, but for k_B Ni > Cu. It is significant that the actual values of k_A and k_B per g. of metal differ by no more than a factor of three except in the case of k_B for copper: the absolute activities of the metals per unit weight are therefore generally about the same regardless of whether they are supported on pumice or not. Correction to unit surface area (line 3 of Table 5) does not change the activity order, but increases the disparity between the most and least active metals.

TABLE 5. *Values of* k_A *and* k_B *at* 100°.

	k_A				k_B	
	Fe	Co	Ni	Cu	Ni	Cu
10^2k (min.$^{-1}$ g.$^{-1}$) for supported metals ...	0·40	3·4	47	0·21	21	1·1
10^2k (min.$^{-1}$ g.$^{-1}$) for unsupported metals	1·3	2·8	24	0·18	28	8·4
10^2k (min.$^{-1}$ m.$^{-2}$) for unsupported metals	0·28	1·9	60	0·18	66	8·3

While the relative activities of the *d*-metal powders is approximately independent of temperature, the activity of copper relative to that of these metals increases with rising temperature because of its higher activation energy, and at some high temperature copper will for this reason be more active than the other metals.

It now remains to decide with what parameter of the *d*-metals we may seek to correlate their differences in activity. It is fruitless to relate them to variations in metallic radius or percentage of *d*-bond character, both of which are essentially the same for all three metals. However log A decreases smoothly as the concentration of *d*-band holes $[h_d]$ (as given either by saturation moments or by direct measurement [12]) increases, and we conclude that for the hydrogenation of acetylene the electronic constitution of the metal determines its activity through its influence on the pre-exponential term rather than on the activation energy. Iron and nickel films are about equally effective for hydrogenating ethylene,[13] while for the conversion of styrene into ethylbenzene a supported iron catalyst is much less active than supported nickel.[14]

Relative Activities in the Alloy Series.—The foregoing considerations point the direction in which the results for the alloy series are to be interpreted, but rather more detailed interpretation is made possible by the finding that the activity patterns are markedly temperature-dependent (see Fig. 1). The results for the pure metals were adequately discussed in terms of the changing concentration of *d*-band holes, but theoretical considerations have shown [15] that it is not only the energy of the Fermi surface but also the density of the electron levels $n(E)$ at this point which determines catalytic activity.

It is convenient now to consider separately our results for the two alloy series.

Nickel–Copper Alloys.—As the concentration of copper is increased, the number of *d*-band holes per atom decreases linearly and is presumed to become zero at about 60% of copper; through this range of composition the density of electron levels $n(E)$ remains almost constant, falling rapidly only when the percentage of copper exceeds 60%.[14] Coles

[12] Weiss and de Marco, *Rev. Mod. Phys.*, 1958, **30**, 59.

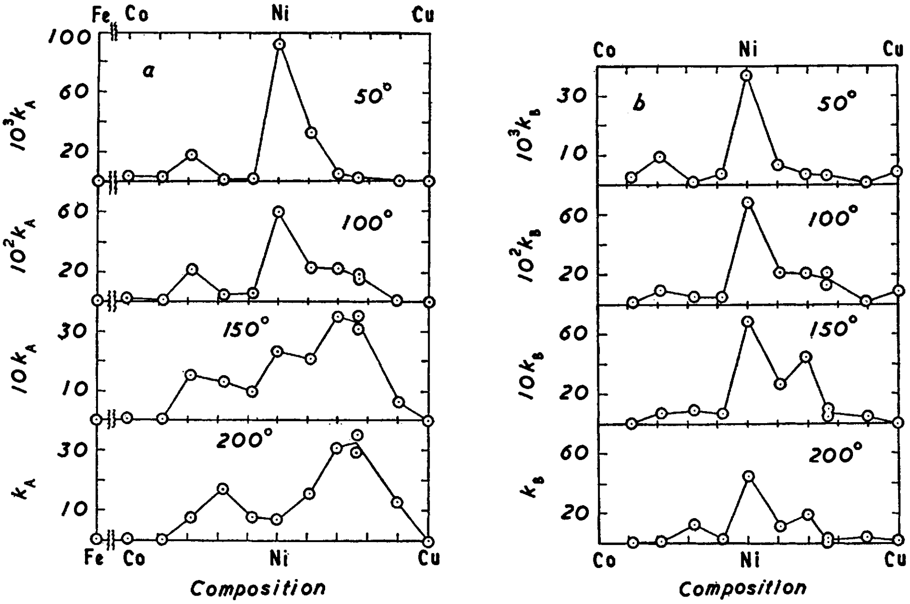
[13] Kemball, *J.*, 1956, 735.

[14] Dowden and Reynolds, *Discuss. Faraday Soc.*, 1950, **8**, 184.

[15] Dowden, *J.*, 1950, 242.

has however recently pointed out the substantial differences between the nickel–copper and the palladium–silver system, and has suggested that d-band holes still exist in the copper-rich end of the nickel–copper system;[16] a recent determination of the number of d-electrons in copper gives 9·8 ± 0·3.[12] The existence of a small concentration of d-band holes in copper, but not in silver or gold, would interpret the large differences between these metals in a wide variety of catalytic reactions.

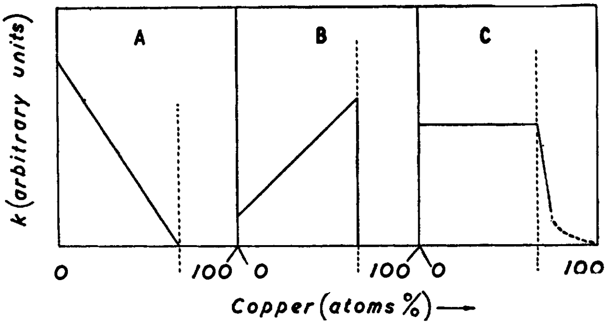
FIG. 1. *Activity patterns for nickel–copper and nickel–cobalt alloys at various temperatures.*



(a) k_A as a function of composition.

(b) k_B as a function of composition.

FIG. 2. *Idealized possible forms for the dependence of activity on composition for nickel–copper alloys.*



We may visualize three possible forms of activity patterns, represented in an idealized manner in Fig. 2. In case A, there is a progressive *decrease* in activity as $[h_d]$ falls until it becomes zero at about 60% of copper; hydrogenation of styrene on nickel–copper alloys[14] conforms to this pattern. In case B, the activity *increases* progressively as $[h_d]$ falls until a sudden decrease marks the filling of the d-band; this is the pattern expected if there is a continuous decrease in strengths of adsorption as the d-band is filled, and Best and Russell's[5]

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[16] Coles, *Proc. Phys. Soc.*, 1952, **65**, *B*, 221.

results on the hydrogenation of ethylene on nickel–copper powders suggest this pattern. Case C shows the effect expected if $n(E)$ determines the activity or if the activity is independent of $[h_d]$ as long as $[h_d] > 0$: Rienäcker and Bommer's results [17] for the hydrogenation of ethylene on nickel–copper foils at 500° conform approximately to this pattern.

We have found that E_A increases sharply with increasing copper content (Table 1) but is almost constant (20—25 kcal. mole^{-1}) between 40 and 100% of copper: there is therefore no sign of any marked change in E_A where the *d*-band is filled. However the low values of E_B at 60% of copper may be caused by an effect of *d*-band filling. Owing to the operation of a partial compensation effect, it is more instructive to discuss activity patterns (Fig. 1) than log *A* terms. At 100° both k_A and k_B are about constant over the range 20—60% of copper (respectively 18—20 × 10^{-2} and 20—21 × 10^{-2} min.$^{-1}$ m.$^{-2}$), values for nickel being each about three times greater; between 60 and 80% of copper both values fall tenfold, and there is a further fall between 80 and 100% of copper. There is thus a substantial fall in activity near the point where the *d*-band is presumably filled, probably caused by the change in the gradient of $n(E)$. The patterns are therefore intermediate between cases A and C. We can now describe the effect of temperature on the activity patterns in terms of our three idealized cases. At 50°, the patterns are still intermediate between cases A and C, but the contribution of A has increased; for k_A it is intermediate between B and C at 150° and predominantly represented by B at 200°. For k_B at these temperatures the pattern is complex and presumably is composed of elements of each of the three cases.

The agreement (especially at low temperatures) between the activity patterns based on k_A and k_B is significant. It implies that the electronic factor manifests itself equally in both mechanisms, perhaps through the energy required to break a carbon–metal bond in converting chemisorbed acetylene into an adsorbed vinyl radical.

We summarise our conclusions with reference to activity patterns based on k_A by the following generalisations: at low temperatures, the activity decreases with decreasing $[h_d]$; at intermediate temperatures, it is independent of $[h_d]$ or is determined by $n(E)$; at high temperatures, it increases with decreasing $[h_d]$ in the expected manner.

Nickel–cobalt alloys. There is again agreement between the activity patterns based on k_A and k_B (Fig. 1). If we accept the view that the low-temperature activity pattern for nickel–copper is determined by $[h_d]$, then activity in the nickel–cobalt series should increase with cobalt content. But this is not so: hence the fall in activity with increasing cobalt content must be ascribed to a falling value of $n(E)$.[14] However at high temperatures there is a reasonably smooth increase of activity with falling $[h_d]$, in agreement with the results for the nickel–copper series. The activity maximum at 60% of cobalt appears to be genuine, but no acceptable explanation has yet been found for it: it is probably only coincidental that it occurs near the composition (*ca.* 54% of cobalt) where there is exactly one *d*-band hole per atom. The maximum becomes progressively less marked with rising temperature.

With increasing cobalt content, E_A at first rises steeply and subsequently falls more slowly (Table 1). This is not easy to understand, since no electronic parameter shows a maximum between nickel and cobalt: it may simply be that the activation energy is affected by the inhomogeneity of the catalyst, just as the electrical resistance of alloys is always greater than that of its constituents.

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[17] Rienäcker and Bommer, *Z. anorg. Chem.*, 1939, **242**, 302.