The mixture is shaken vigorously for at least ten hours. For 5 kg. of mercury a 5-liter heavy-walled bottle connected with an air condenser (the heat of the reaction is small) was used. The contents of the bottle were transferred to a separatory funnel with the aid of water, the lowest layer consisting of mercury withdrawn, and then the gray precipitate (oil emulsified with mercury), the water and oil remaining in the funnel. The precipitate was steam distilled and the resulting oil united with the portion in the separatory funnel. After washing with dilute sodium hydroxide, water, and drying with calcium chloride, the oil was fractionally distilled under diminished pressure, b. p. 85° at 11 mm.

CONTRIBUTION FROM THE
I. CHEMISCHES LABORATORIUM DER
UNIVERSITÄT IN WIEN (VIENNA, AUSTRIA)

RECEIVED APRIL 6, 1935

COMMUNICATIONS TO THE EDITOR

LOCATION OF ACTIVITY IN MIXED CATALYSTS

Sir:

We have investigated the case where each component of a mixed catalyst promotes its proper reaction, acting on a single substance; from the standpoint of the multiplet theory this is effected as a result of specific orientation. The catalysts used were of the Zelinsky and Kommarewsky type [*Ber.*, **57,** 668 (1924)], Ni:Al_2O_3 = 1:1, prepared in different conditions of precipitation from nitrates, sulfates and chlorides. The parallel dehydrogenation and dehydration of isoamyl alcohol, together with carbon monoxide elimination from valeraldehyde formed, were kinetically studied in an apparatus described previously [Balandin, *Z. physik. Chem.*, **B19,** 453 (1932)]. A complete analysis of the gases evolved was made. The data fitted the Arrhenius equation. With different preparations of the catalyst the energies of activation Q varied in the range from 8850 to 22,400, from 17,950 to 45,100 and from 14,500 to 33,100 cal./mole for the dehydrogenation, dehydration and the aldehyde decomposition processes, respectively. The ratio of Q's for different processes with the same catalyst preparation was determined. It is most remarkable that for different preparations this ratio remains constant within experimental errors.

Catalyst No.	1	2	5	6	7	8	Av.
Q_{H_2}/Q_{H_2O}	(0.32)	0.50	0.61	0.50	0.59	0.57	0.51
Q_{H_2}/Q_{CO}	.62	.67	.64	.59	.71	.90	.69
Q_{H_2O}/Q_{CO}	1.20	1.36	1.05	1.20	1.20	1.58	1.26

The logarithmic relation between k_0 and Q in $k = k_0 \exp(-Q/RT)$, found previously [Balandin, *loc. cit.*] for catalytic dehydrogenation processes, holds true with practically the same coefficient $Q/\log k_0$ as before. The same relation is found for the dehydration process, $Q/\log k_0$ being here about 2 times larger.

The dehydration proceeds on the surface of nickel and the dehydration on that of alumina. Geometrically these surfaces are situated separately. But the energies of activation characterizing the processes are related one to another. Hence, the places where both reactions occur must geometrically be connected, and this can happen only at the nickel–alumina interfaces. Thus, one can conclude that the reaction on a mixed catalyst is located on its component interfaces.

In the systems considered there are two solid phases and one gaseous phase. Three phases can join together only by lines (or points) but not by surfaces. As the logarithmic relation shows, these active lines possess a varying activity. This property is the same as that of surfaces and crystal edges in the theory of H. S. Taylor [*J. Phys. Chem.*, **30,** 145 (1926); *Acta Ph. Ch. U. R. S. S.*, **1,** 397 (1935)]; however, these lines are not edges, since the micro-crystals but seldom join together by edges. These boundary lines resemble those of the Schwab and Pietsch topochemical theory [*Z. physik. Chem.*, **B1,** 385 (1928)], but are endowed with a varying activity in the sense of the theory of Taylor (*loc. cit.*) and Constable [*Proc. Roy. Soc.* (London), **A108,** 355 (1925)]. This new fact has to be taken into account in the theory of catalytic action.

SECTION OF CATALYSIS
THE ZELINSKY LABORATORY OF
ORGANIC CHEMISTRY
STATE UNIVERSITY, MOSCOW

A. A. BALANDIN
A. M. RUBINSTEIN

RECEIVED MARCH 29, 1935

ACTION OF DINITROCRESOL ON YEAST FERMENTATION AND OXIDATION

Sir:

The details of a study of the effect of 4,6-dinitro-*o*-cresol (DNC) on the metabolic activities of yeast will be presented in a paper now being prepared for publication. The present communication gives a summary of certain of these experiments conducted with normally fermenting yeast which bear on the mechanism of DNC action. These experiments were conducted in January, February and March, 1935, with yeast obtained from Anheuser–Busch, Inc.

(1) The rate of anaerobic carbon dioxide production by yeast in a glucose-phosphate medium (*p*H 4.45) was increased by DNC in concentrations from 10^{-6} to 10^{-4} molar. Greater concentrations of DNC caused a subnormal anaerobic carbon dioxide production. Maximum stimulation occurred at 10^{-5} to 2×10^{-5} *M* DNC with yeast in a concentration of 6 mg. per cc. In a normal system $Q_{CO_2}^{N_2}$ was, in two experiments, 74.5 and 78; after addition of 2×10^{-5} *M* DNC $Q_{CO_2}^{N_2}$ was increased to 159 and 157, respectively. Analysis showed that an amount of alcohol equimolar to the anaerobic carbon dioxide was produced in the presence of optimum concentration of DNC.

(2) The rate of oxygen consumption by buffer washed yeast was increased by DNC in concentrations from 10^{-6} to 2×10^{-5} molar. Greater concentrations of DNC caused a subnormal oxygen consumption. Maximum stimulation (50 to 100%) occurred at 10^{-5} *M* DNC. With 1 to 6 mg. of yeast per cc., oxygen consumption was stimulated by DNC in a medium containing glucose or alcohol as substrate but not in a medium containing pyruvate as substrate.

(3) The rate of reduction of cytochrome (549 mμ band) in buffer washed yeast was increased by DNC in concentrations from 10^{-6} to 2×10^{-5} *M*. Greater concentrations of DNC lengthened the reduction time. The greatest shortening of reduction time (from one hundred and five to thirty-two seconds) was effected by 10^{-5} *M* DNC.

(4) With a concentration of DNC (10^{-5} *M*), which caused the optimum rise in oxygen consumption of yeast in a glucose medium, an increased aerobic alcohol production occurred only at high glucose concentrations and for limited times. At low glucose concentrations, and over extended time periods, DNC effected no increase in amount of alcohol produced aerobically; in fact, any alcohol initially present was oxidized.

(5) Since part of the carbon dioxide produced aerobically resulted from fermentation, an amount of carbon dioxide equimolar to the alcohol produced aerobically was subtracted from the total to get the oxidative carbon dioxide. In several experiments where this was done the ratio of oxidative carbon dioxide to oxygen consumed was not significantly influenced by the presence of 10^{-5} *M* DNC.

(6) At 10^{-5} *M*, DNC increased not only the *rate* of aerobic oxygen consumption and anaerobic carbon dioxide production, but also the *total* amount of glucose oxidized or fermented as determined from the products of reaction.

(7) The amount of glucose disappearing, as determined by analysis, was greater than that accounted for by the products of oxidation and/or fermentation. DNC had no effect on the amount of glucose which disappeared.

(8) Actual count showed no increase in number of yeast cells during the period of the experiment.

(9) At optimum concentration, DNC stimulated anaerobic carbon dioxide and alcohol production to a greater degree than it stimulated oxygen consumption in a corresponding aerobic system, and caused increased anaerobic utilization of sufficient sugar to account for excess oxygen consumed and excess alcohol produced in the aerobic system.

These results are not incompatible with the view that the principal metabolic effect of DNC is to accelerate one of the anaerobic processes occurring early in the series of reactions concerned with the formation of (a) substances subsequently oxidized by the cell, and (b) products of anaerobic fermentation.

We wish to express our indebtedness to Miss A. K. Keltch for her coöperation.

LILLY RESEARCH LABORATORIES M. E. KRAHL
INDIANAPOLIS, INDIANA G. H. A. CLOWES

RECEIVED APRIL 11, 1935

THE RELATIVE RATES OF COMBINATION OF LIGHT AND HEAVY HYDROGEN WITH ETHYLENE

Sir:

Preliminary determinations of the rate of combination of heavy hydrogen with ethylene have been made. The reaction has been carried out both on a copper catalyst and homogeneously, the rate of these reactions being compared with the corresponding light hydrogen reaction. Owing to uncertainties in the purity of the deuterium and as to the complete role of exchange reactions, full publication is being deferred.

The catalytic experiments using copper indicated at 0° a ratio of rates H_2/D_2 of 1.59. Since Farkas, Farkas and Rideal [*Proc. Roy. Soc.* (London), **A146,** 630 (1934)] found no exchange at low temperatures over nickel, it is likely that no exchange occurred in this reaction over the comparatively less reactive copper catalyst. However, this point is being investigated. At higher temperatures (184 to 306°) the observed ratio fell from 1.34 to 1.04. How much of this decrease is due to exchange will be determined.

In the homogeneous reaction at 524 and 560° the ratios were 2.10 and 2.0, respectively. This seems to point to a real difference in the activation energies of the homogeneous reactions, but again further investigation (which will be shortly undertaken) is required.

These preliminary results point to the likelihood that comparative rates of hydrogenation can be obtained at 0° on the copper catalyst and at 500–550° in the homogeneous reaction, without serious interference from exchange reactions. Such measurements are now being made with deuterium of known purity.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
ROBERT N. PEASE
AHLBORN WHEELER

RECEIVED APRIL 15, 1935

THE SEPARATION OF CERTAIN RARE EARTHS

Sir:

It has been shown by Yntema [THIS JOURNAL, **52,** 2782 (1930)] and by Ball and Yntema [*ibid.*, **52,** 4264 (1930)] that europium and ytterbium may be separated from other rare earths by precipitation as sulfate after electrolytic or other reduction to the divalent state. However, because of the small amounts of these elements found in rare earth mixtures, it has still been necessary to resort to fractional crystallization over a period of a year or more before the reduction method becomes applicable.

Using several samples of pure rare earths put at his disposal through the kindness of Professor B. Smith Hopkins of the University of Illinois, the writer has attempted to facilitate the separation of europium through the use of a co-precipitant. In a mixture of terbium group earths too dilute in europium to give any direct precipitate of europous sulfate, it has been found possible to obtain a substantially complete co-precipitation with barium sulfate of all the europium present. The europium is then readily removed from the filtered barium sulfate by repeated washing with a little hot concentrated nitric acid. There seems, therefore, no reason why europium, and probably ytterbium also, cannot be removed practically quantitatively from a crude rare earth mixture in as many days as it formerly took years.

The writer has also examined a possible separation of neodymium and samarium. The mixture of anhydrous chlorides is treated with hydrogen at 700°. This results in reduction of the samarium to $SmCl_2$. Treatment of the resultant mixture with water brings about a reaction probably represented by $6SmCl_2 + 3H_2O \longrightarrow 4SmCl_3 + Sm_2O_3 + 3H_2$, the neodymium trichloride simply dissolving. Part of the samarium is precipitated but seems always to be contaminated with some neodymium. Although the separation obtained is good, as rare earth separations go, it is nevertheless only fractional, and because of its difficulty probably cannot compete with the usual double nitrate fractional crystallization.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
P. W. SELWOOD

RECEIVED APRIL 24, 1935

THE THERMAL REACTION BETWEEN CHLORINE AND FORMALDEHYDE

Sir:

Krauskopf and Rollefson [THIS JOURNAL, **56,** 2542 (1934)] have isolated formyl chloride from the photochemical interaction of chlorine and formaldehyde, and have suggested [*ibid.*, **57,** 590 (1935)] that this substance occurs as an intermediate in the corresponding thermal reaction [Spence and Wild, *Nature,* **132,** 170 (1933); *J. Chem. Soc.*, 1588 (1934)]. Furthermore, they suggest that the excess of carbon monoxide produced in our experiments over that calculated from the pressure change is due not to an induced polymerization of the formaldehyde, but to the presence of formyl chloride, which is produced without change of pressure. If the formyl chloride decomposed in the process of analysis giving HCl and CO, it is claimed that this explanation would account for our results equally well. Consideration of a number of additional experiments has enabled us to decide between the two views. Only two of the unpacked series need be quoted here, *viz.*, J1 and J12.

J1, *T* 140°.
HCHO 197.4 mm.; Cl_2 99.5 mm.

t, min.	*p*, mm.
0	296.9
12	365.9
20	376.8
60	376.7

Δ *p* max. 79.9 mm.
Found: CO 93.9 mm.

$$\frac{\text{HCHO polym.}}{\text{HCHO reacted}} = \frac{14.0}{93.9} = 0.149.$$

J12, *T* 150°.
HCHO 378.0 mm.; Cl_2 53.0 mm.

t, min.	*p*, mm.
0	431.0
8	441.0
17	442.0
27	438.5

Δ *p* max. 11.0 mm.
Found: CO 52.1 mm.

$$\frac{\text{HCHO polym.}}{\text{HCHO reacted}} = \frac{41.1}{52.1} = 0.789.$$

These experiments show how the discrepancy between the theoretical and the observed pressure change increases with the formaldehyde–chlorine ratio. According to Krauskopf and Rollefson's view, 40 mm. of formyl chloride must have been produced in J12 after eight minutes, remained unchanged at 150° for a further nineteen minutes, and must then have been completely decomposed in the process of pumping out over liquid air. However, experiments in a vessel packed with powdered glass gave similar results: *e. g.*, K5 (HCHO 206.0 mm.; Cl_2 168.8 mm.). 15.4 mm. of formaldehyde polymerized in forty-eight minutes before addition of the chlorine, while polymerization during forty-eight minutes of reaction amounted to 27.5 mm. Any formyl chloride present in this case would scarcely decompose at the cooler surface of the tubing leading to the liquid air trap, and once frozen out, the carbon monoxide would be lost to the analysis, resulting in an increase in the HCl/CO ratio. However, our ratios always remained very close to two, and the discrepancy between the amount of reaction and the pressure change must be attributed to an induced polymerization of the formaldehyde. Nevertheless, as we had already pointed out [*J. Soc. Chem. Ind.*, **54**, 83 (1935)] in agreement with Krauskopf and Rollefson, it is probable that formyl chloride occurs as an intermediate in the thermal reaction, but in our opinion, its concentration must be small.

THE UNIVERSITY
LEEDS, ENGLAND
R. SPENCE
W. WILD

RECEIVED APRIL 29, 1935

THE REACTION BETWEEN CHLORINE AND FORMALDEHYDE

Sir:

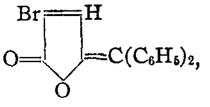
The experiments described in the note of Spence and Wild indicate that the amount of formyl chloride in the reaction mixtures was too small to be of importance in accounting for the discrepancy between theoretical and observed pressure change. It was not our intention in the previous Note [THIS JOURNAL, **57,** 590 (1935)] to account for the total discrepancy in this manner but only to account for what was left after correcting for the normal amount of polymerization. The data from experiment K5 in the packed reaction vessel (a condition very unfavorable for the existence of formyl chloride) seem to be in favor of the higher rate of polymerization in the presence of chlorine, suggested by Spence and Wild. The failure of the HCl/CO ratio to deviate appreciably from two also supports this view.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
K. B. KRAUSKOPF
G. K. ROLLEFSON

RECEIVED MAY 16, 1935

ORIENTATION IN THE FURAN SERIES. HILL'S 3,5-DIBROMO-2-FUROIC ACID

Sir:

The pivotally significant "3,5-dibromo-2-furoic acid" [Hill and Sanger, *Proc. Am. Acad. Arts. Sci.*, **21**, 135 (1885)] is actually 4,5-dibromo-2-furoic acid. This has been demonstrated as follows: (1) The β-bromo-2-furoic acid, obtained by replacing an α-bromine in the dibromofuroic acid by hydrogen, gives 2,4-furandicarboxylic acid on hydrolysis of the nitrilo-acid secured by heating with potassium cyanide and cuprous cyanide [Rosenmund and Struck, *Ber.*, **52B**, 1749 (1919)]. (2) The dibromofuran, obtained from decarboxylation of the dibromofuroic acid, gives (by a corresponding treatment) 2,3-furandicarboxylic acid. (3) The ethyl ester of the dibromofuroic acid gives with phenylmagnesium bromide the bromocrotolactone,  which with 5% sodium hydroxide yields α,α-diphenylacetone.

By a series of inter-relating reactions it now appears that Hill's structures for 3-sulfo-5-bromo-2-furoic acid, 3-sulfo-5-chloro-2-furoic, and 3,5-dichloro-2-furoic acid warrant revision.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
IOWA STATE COLLEGE
AMES, IOWA
HENRY GILMAN
ROBERT J. VANDER WAL
RAYMOND A. FRANZ
ELLIS V. BROWN

RECEIVED MAY 6, 1935

REACTION IN ETHYLENE-HYDROGEN MIXTURES INDUCED BY OXYGEN

Sir:

It has been found that small amounts of oxygen in ethylene–hydrogen mixtures cause greatly increased *initial* reaction rates in the homogeneous reaction at 538°. Reaction was carried out at constant volume. Pressure drops during the first, second and third minutes (ΔP_1, ΔP_2, ΔP_3) appear in the accompanying table.

TABLE I

REACTION IN ETHYLENE–HYDROGEN MIXTURES INDUCED BY OXYGEN

Run	Initial press., mm. H_2	C_2H_4	N_2	O_2	ΔP_1	ΔP_2 mm./min.	ΔP_3
1	576	192	...	...	4.5	4	4.5
2	572	191	...	5.8	63	10	4.5
3	191	573	...	5.8	29	6	4.5
4	...	770	...	5.8	18	6	4.5
5	...	382	382	5.8	5	3	2.5

The initial acceleration is much greater in hydrogen-rich mixtures (*cf.* No. 2 with No. 3 and No. 4). The effect could be due to accelerated ethylene polymerization, known to be induced by oxygen [Lenher, THIS JOURNAL, **53**, 3752 (1931)]. It seems more likely that the hydrogenation reaction itself is affected.

Further experiments are in progress.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
ROBERT N. PEASE
AHLBORN WHEELER

RECEIVED MAY 8, 1935

THE CALCULATION OF MOLAR POLARIZATION OF SOLUTES AT INFINITE DILUTION WITH HEDESTRAND'S FORMULA

Sir:

It has been suggested by Svirbely, Ablard and Warner [THIS JOURNAL, **57**, 652 (1935)] that Hedestrand's method of extrapolation should not be considered of general application if the values of α and β of the equation

$$P_\infty = A\left(M_2 - \beta\frac{M_1}{\rho_1}\right) + B\alpha \qquad (1)$$

are not constant for varying concentration or in other words if the dielectric constant and density are not linear functions of the concentration.

In the derivation of the above equation Hedestrand [*Z. physik. Chem.*, **B2**, 428 (1929)] says that for small concentrations the dielectric constant (ϵ) and the density (ρ) of the solutions are given by the equations

$$\epsilon = \epsilon_1 + \alpha N_2 \qquad \rho = \rho_1 + \beta N_2 \qquad (2)$$

and then proceeds to substitute these in the equation for the polarization of the solute. Then in the limit, $N_2 = 0$, we have $P_2 = P_\infty$, $\epsilon = \epsilon_1$, $\rho = \rho_1$, and $N_1 = 1$. The values of α and β are consequently $(\mathrm{d}\epsilon/\mathrm{d}N_2)_{N_2 = 0}$ and $(\mathrm{d}\rho/\mathrm{d}N_2)_{N_2 = 0}$, which may be seen from equation (2). Now if the dielectric constant and density of the solution are linear functions of the concentration, α and β are the slopes of these straight lines. If α and β are functions of the concentration then they are the slopes of the tangents to the dielectric constant and density curves at zero concentration.

As it is rather difficult to obtain a tangent to a curve it was suggested by Hedestrand (*loc. cit.*) that α and β obtained from equation (2) be plotted against the concentration and extrapolated to infinite dilution.

This was carried out for the compounds of Svirbely, Ablard and Warner and the results are listed below.

Compound	Svirbely, Ablard, Warner P_∞	$\mu \times 10^{18}$	Recalculated P_∞	$\mu \times 10^{18}$
d-Pinene	192	2.67	184	2.60
d-Limonene	95	1.56	96	1.57
Methyl benzoate	170	2.52	172	2.54
Ethyl benzoate	166	2.43	159	2.34

These are good checks and should serve to indicate that Hedestrand's formula can be used for substances in which the dielectric constant and density are not linear functions of the concentration.

It is interesting to note that compounds like the phenylacetylenes [Otto and Wenzke, THIS JOURNAL, **56**, 1314 (1934)] and the phenylethylenes [Otto and Wenzke, *ibid.*, **57**, 294 (1935)] have constant α and β while the dialkoxyalkanes [Otto, *ibid.*, **57**, 693 (1935)] have slowly increasing value of α. The values of α for the compounds of Svirbely, Ablard and Warner increase very rapidly and it might be as they suggest indication of varying degrees of dipole orientation such as has been shown to exist in solutions of alcohols.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, IND.
M. M. OTTO

RECEIVED MAY 11, 1935