

NOTES.

An Alternating-current Cell. By ERNEST SYDNEY HEDGES.

ONE example of a cell furnishing an alternating current is known (Kistiakowsky, *Z. Elektrochem.*, 1909, **15**, 268). It was produced by immersing two iron electrodes in a solution containing 5% of potassium dichromate and *N*-sulphuric acid, and the effect was to

furnish an *E.M.F.* alternating between + 0.4 volt and - 0.4 volt. This was accomplished by a very rigorous preparation of the iron, and, as is usually the case with the periodic passivity of iron, the behaviour depended largely on the individual piece of iron, most specimens not producing the effect.

The author has constructed a readily reproducible alternating-current cell by the application of a periodic reaction discovered by Hedges and Myers (J., 1925, 127, 1023). In the first experiments a small plate of rolled copper and another of annealed copper were immersed in a solution consisting of 25 c.c. of nitric acid (*d* 1.42), 10 c.c. of hydrochloric acid (*d* 1.16), and 70 c.c. of water. This combination gave a periodic unidirectional current varying between 30 milliamperes and zero. Although no current was produced in the negative direction in this case, the experiment is a striking illustration of the periodic properties imparted to metals through cold-working.

An alternating current is produced by using two electrodes of rolled copper in the solution specified above. As a rule, the positive and negative currents are asymmetrical, for the probability is that the electrodes will be neither quite in phase nor quite out of phase. The maximum difference in *E.M.F.* obtainable from this cell is 0.14 volt. The frequency is about one cycle per minute. Often the periods are not produced during the first $\frac{1}{2}$ hour or so, particularly if a slight excess of nitric acid is used. The copper should be subjected to at least 50% reduction in thickness by cold-rolling. Samples kept for several months still retained this periodic property.—BEDFORD COLLEGE (UNIVERSITY OF LONDON), REGENT'S PARK, N.W.1. [Received, May 27th, 1926.]

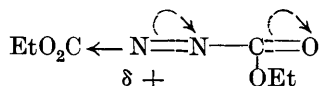
The Hydrolysis of Acetyl-o-benzylideneaminophenol. By FRANK BELL and JOSEPH KENYON.

o-BENZYLIDENEAMINOPHENOL (12 g.) was dissolved in acetic anhydride (12 c.c.), and the excess of the latter removed by distillation. The residual *acetyl-o-benzylideneaminophenol* separated from benzene-light petroleum as a white, microcrystalline powder, m. p. 93–96° (Found: C, 75.2; H, 5.5; N, 6.2. $C_{15}H_{23}O_2N$ requires C, 75.3; H, 5.4; N, 5.9%). It suffered loss of both acetic acid and benzaldehyde on being warmed with dilute acid; but when it was boiled with water, benzaldehyde alone was evolved and *N*-acetyl-*o*-aminophenol, m. p. 202°, was obtained—an interesting illustration of the ease with which an acyl group migrates from oxygen to nitrogen.—BATTERSEA POLYTECHNIC, S.W.11. [Received, February 23rd, 1926.]

The Reversibility of Triazan Formation. By KENNETH ERNEST COOPER and EDITH HILDA INGOLD.

THE reaction between aniline and azodicarboxylic ester, $\text{Ph}\cdot\text{NH}(\text{H}) + \text{CO}_2\text{Et}\cdot\text{N}:\text{N}\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{Ph}\cdot\text{NH}\cdot\text{N}(\text{CO}_2\text{Et})\cdot\text{N}(\text{H})(\text{CO}_2\text{Et})$ —an example of the fundamental additive reaction of which, according to the correlation principle (E. H. Ingold, *Chem. and Ind.*, 1923, **42**, 1246; compare this vol., p. 1868), diazoamino-tautomerism is a derived form—is detectably reversible under the conditions in which the direct change may be effected. In the quantitative study, however, difficulties were encountered due to the tendency of the azo-ester to oxidise the aniline when the latter was present in considerable concentration.

The great reactivity of azodicarboxylic ester in additive reactions has been proved by Diels and others in numerous papers, and may be compared with the remarkable reactivity of fumaric ester in the Michael reaction, and similar additive processes. In each case, the electron-affinity of the carbethoxyl groups (compare this vol., p. 1868) may be assumed to be the cause of the reactivity observed :



Ethyl 1-phenyltriazan-2 : 3-dicarboxylate was obtained by keeping a mixture of aniline (11 g.) and ethyl azodicarboxylate (prepared by oxidising the hydrazinedicarboxylate) (20 g.) at 0° for 24 hours. The product was rubbed with ice-cold 50% acetic acid. As soon as crystals formed, they were collected and drained free from acetic acid as rapidly as possible, the filtrate being used for the further extraction of the product. The crystalline triazan was dissolved in boiling carbon disulphide saturated with methyl alcohol; the solution, on evaporation at 0°, gave crystals which, on recrystallisation from methyl alcohol, yielded the pure compound (Found : C, 53·7; H, 6·8. Calc. : C, 53·9; H, 6·4%).

A 0·05*M*-solution (40 c.c.) of the triazan in benzene, or a mixture of 20 c.c. of 0·1*M*-aniline and 20 c.c. of 0·1*M*-ethyl azodicarboxylate in the same solvent, was kept for a definite time at a known temperature in a closed vessel. Preliminary investigation had shown that ethyl azodicarboxylate does not react with benzene under any of the conditions employed in these experiments, although interaction takes place in the presence of concentrated sulphuric acid (Stollé and Leffler, *Ber.*, 1924, **57**, 1062). After being cooled rapidly (if an elevated temperature had been employed), the mixture was extracted with 50 c.c. of *N*-sulphuric acid, and 40 c.c. of the acid

solution were cooled to 0° in an atmosphere of carbon dioxide and titrated with 0.05 *N*-sodium nitrite, with cadmium-starch-iodide paper as indicator; 25 minutes were allowed after each addition of nitrite, the titration process having previously been carefully standardised with artificial solutions of aniline. At 26°, the quantity of aniline produced rose during 3 weeks to an amount corresponding with about 6.0% of triazan decomposed. The reaction was more rapid in both directions at 95°, and combination was more rapid in more concentrated solution, as the following data show. The indicated proportion of triazan decomposed at equilibrium is, however, certainly too low, as the products of decomposition acted on one another to an appreciable extent, giving substances amongst which emeraldine and ethyl hydrazinedicarboxylate were definitely identified.

Temperature 95°. Concentration M/20. Aniline + azo-ester.

Time (hrs.)	3	8	13.5	20	48
Aniline remaining (%)	89	75	60	54	10

Temperature 95°. Concentration M/20. Triazan.

Time (hrs.)	1	17	24	30
Aniline formed (%)	3	5	6	6

Temperature 95°. Concentration M/10. Aniline + azo-ester.

Time (hrs.)	1	2	19
Aniline remaining (%)	93	86	35

Azodicarboxymethylamide, $\text{NHMe}\cdot\text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NHMe}$, prepared by adding a 33% solution of methylamine in methyl alcohol to ethyl azodicarboxylate previously diluted with five times its volume of ether, separated from methyl alcohol as a bright yellow, microcrystalline powder, or from ethyl acetate as stellate bunches of yellow needles, m. p. 170° (decomp.) (Found: N, 39.2. $\text{C}_4\text{H}_8\text{O}_2\text{N}_4$ requires N, 38.9%). It is readily soluble in water, methyl or ethyl alcohol, ethyl acetate, or 50% acetic acid, sparingly soluble in chloroform, and insoluble in glacial acetic acid, benzene, or ligroin.

Hydrazinedicarboxymethylamide, $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$.—The azo-amide did not appear to react with aniline in the cold, but on being heated with aniline at 115–120° for 3 hours it became reduced to the hydrazo-amide with the simultaneous formation of dyes of the type of aniline-black. The same hydrazo-amide was formed when hydrogen sulphide was passed into a warm aqueous solution of the azo-amide until the bright yellow colour had disappeared. The hydrazo-amide, precipitated together with sulphur, was extracted with hot glacial acetic acid, and crystallised from the same solvent as a colourless, microcrystalline powder, m. p.

247° (Found: N, 38.7; *M*, in phenol, 147. $C_4H_{10}O_2N_4$ requires N, 38.4%; *M*, 146).

Azodicarboxamide also is partly reduced to hydrazinedicarboxamide (m. p. 243—244°) when heated with aniline at 150° for 4 hours.

We wish to record our thanks to the Chemical Society for a grant which has defrayed part of the expense of this work.—THE UNIVERSITY, LEEDS. [Received, March 15th, 1926.]

The Solubility of Lead Iodide in Solutions of Sodium Chloride at 25°.

By LESLIE JAMES BURRAGE.

THESE experiments (for analytical details and methods, see p. 1703) were the outcome of a paper by Glasstone (*J.*, 1921, **119**, 1997), who used sodium chloride instead of the potassium iodide commonly employed to keep lead iodide in solution during the estimation of lead by a direct volumetric method.

The figures (conc. in g. per 100 g. of solution) in the table are the average of those obtained after 24 and 48 hours' shaking; the difference between them is 0.1—0.5%. The solid phase is lead iodide in all cases.

PbI ₂	0.758	0.778	0.859	0.951	1.10	1.41	1.64	1.79
NaCl	—	0.29	0.59	1.16	2.34	5.86	11.70	29.80

Further increase in the concentration of sodium chloride causes a change in the solid phase, which now contains chlorine. The nature of this change has not, however, been ascertained. In any case, it results in the three-component system becoming one of four components.

Hertz claims (*Amer. Chem. J.*, 1892, **14**, 107) that the complex salt, PbICl, obtained by Field (*Chem. News*, 1893, **67**, 157) from solutions of lead chloride and potassium iodide is an isomorphous mixture of lead chloride and iodide.—KING'S COLLEGE, UNIVERSITY OF LONDON. [Received, April 23rd, 1926.]

Action of Nitrous Acid on p-Iododimethylaniline. By MARGARET FERRIER AITKEN and THOMAS HAROLD READE.

WHEN sodium nitrite is added to a cold solution of *p*-iododimethylaniline in 4*N*-sulphuric acid, *p*-nitrodimethylaniline, iodine, and 4-iodo-2-nitrodimethylaniline are rapidly produced. Nitric acid of the same concentration is without action, and even pure nitric acid causes very little nitration.

In alkaline solution, no displacement of iodine was detected when an alcoholic solution of the base was heated under reflux for

6 hours with potassium hydroxide, sodium ethoxide, or potassium phthalimide, respectively. Displacement was not detected in a 4*N*-sulphuric acid solution which had been kept for weeks at laboratory temperature. The simultaneous formation of a nitroso-amine did not occur. In this respect, as also in the production of free halogen, *p*-iododimethylaniline differs from *p*-chloro- or *p*-bromo-dimethylaniline (compare Wurster and Scheibe, *Ber.*, 1879, **12**, 1816; Heidelberg, *Ber.*, 1887, **20**, 149; Koch, *ibid.*, p. 2460; Pinnow, *Ber.*, 1898, **31**, 2984).

The bromonitrodimethylaniline, m. p. 67·5°, isolated by Koch is readily obtained also by bromination of 2-nitrodimethylaniline in glacial acetic acid at 60°, and is probably 4-bromo-2-nitrodimethylaniline. The orientation given for the iodonitrodimethylaniline, m. p. 60—60·5°, is probable because its hydrochloride is precipitated immediately when ethereal solutions of iodine monochloride and 2-nitrodimethylaniline are mixed at 15°.

Iododimethylaniline of m. p. 79·5° (Weber, *Ber.*, 1877, **10**, 765; Reade and Sim, *J.*, 1924, **125**, 158) has also been formed from *p*-nitrosodimethylaniline by reduction, diazotisation, and introduction of iodine, to prove that it is the para-compound.

p-Iododimethylaniline (1/10 mol.) in 80 c.c. of 4*N*-sulphuric acid was slowly run into silver nitrite (1/10 mol.) in $\frac{1}{2}$ l. of water at 18° (alternatively into aqueous sodium nitrite, when iodine separated). After 1 hour's shaking, digestion of the precipitate with hot alcohol, filtration, and concentration, 6—7 g. of greenish-brown crystals were obtained. These were separated by fractional crystallisation from absolute alcohol into *p*-nitrodimethylaniline, melting, alone or mixed with an authentic specimen, at 163°, and a more soluble, less abundant fraction, consisting of orange needles of 4-iodo-2-nitrodimethylaniline, m. p. 60·5° (Found: C, 33·0; H, 1·9; N, 11·0; I, 43·5. $C_8H_9O_2N_2I$ requires C, 32·9; H, 3·1; N, 9·6; I, 43·5%).

o-Nitrodimethylaniline sulphate, prepared by Weissenberger's method (*Monatsh.*, 1912, **33**, 821) and crystallised from alcohol, melted at 168° (Weissenberger gives m. p. 126—127°). When a dried ethereal solution of the base obtained from 9·3 g. of the sulphate was treated with 5·4 g. of iodine monochloride at 15°, 4-iodo-2-nitrodimethylaniline hydrochloride was rapidly precipitated. The corresponding base crystallised from absolute alcohol in orange needles, m. p. 60—60·5°, alone or mixed with the specimen described above.

The authors thank the United Alkali Company for a gift of *o*-chloronitrobenzene.—UNIVERSITY OF ABERDEEN. [Received, April 26th, 1926.]

The Alleged Decomposition of Aqueous Ammonium Nitrite Solutions by Light. By MARSHALL HOLMES.

WHEN a 2.5*N*-solution of ammonium nitrite (smelling of ammonia, but free from nitrate) was insolated in a quartz flask by means of a 110-volt Cooper-Hewitt quartz-mercury lamp at a distance of 8—16 cm., no loss of nitrite could be detected even after 6 hours, titration with *N*/10-potassium permanganate being the analytical method employed. If the insolation was continued up to 100 hours, slight losses were detected, but these were due entirely to thermal decomposition, since similar "dark" control solutions suffered the same loss within the limits of experimental error.

In the foregoing experiments the temperature of the solution had been kept at $22^{\circ} \pm 1^{\circ}$ by the circulation of tap water round the reaction vessel. As this method of cooling led to slight and variable absorption of ultra-violet light by the water, another apparatus was devised wherein such absorption was eliminated. After 9 hours at $20^{\circ} \pm 0.1^{\circ}$ at a distance of 15 cm., titrations showed almost the same decomposition as in the "dark" solution :

Original solution required	21.70 c.c.
Solution after 9 hours' insolation required	21.16 c.c.
" " " " in dark " 	21.19 c.c.

It is therefore concluded that Berthelot and Gaudechon (*Compt. rend.*, 1911, **152**, 522) were in error in stating that nitrogen was evolved as a result of insolating ammonium nitrite. As they gave but scanty details of their experimental procedure, however, it is impossible to determine the cause of disagreement, but it is probable that, as no mention is made of control experiments in the dark, they omitted this precaution and were, in fact, observing a purely thermal reaction. In the same paper, they record temperatures of 35—50° as being reached when studying other photo-reactions.

The author is indebted to Professor Allmand for suggesting this work, and to the Department of Scientific and Industrial Research for a grant which enabled him to carry it out.—KING'S COLLEGE, UNIVERSITY OF LONDON. [*Received, April 28th, 1926.*]

The Temperature of Maximum Density of Alcohol-Water Mixtures.
By JOHN P. MCHUTCHISON.

ACCORDING to Despretz (*Ann. Chim. Phys.*, 1839, **70**, 49; 1840, **73**, 296) the lowering of the temperature of maximum density of water caused by the addition of a soluble salt is directly proportional to the concentration of the solute (Despretz's law). It

appears, however (see Coppet, *ibid.*, 1903, 28, 12; Wright, J., 1919, 115, 119), that feebly ionised or non-ionisable substances do not obey Despretz's law, and even that ethyl alcohol in certain concentrations causes an elevation of the temperature of maximum density.

The behaviour of five alcohols has now been investigated with Wright's apparatus (*loc. cit.*), and the following results have been obtained :

TABLE.

Temperatures of Maximum Density of Alcohol-Water Mixtures.

Alcohol.	2M.	M.	M/2.	M/4.	M/8.	M/16.
Methyl	1.90°	3.65°	3.95°	4.00°	4.00°	—
Ethyl	0.15	3.70	4.25	4.20	4.15	—
<i>n</i> -Propyl	—	1.50	3.30	3.80	4.15	4.10°
<i>iso</i> Propyl	—	2.65	3.70	4.00	4.00	—
<i>n</i> -Butyl	—	—	—	3.10	3.90	3.90

(Temperature of maximum density of pure water as determined by the apparatus employed, 4.00°.)

It is clear (1) that in none of these cases is there proportionality between the lowering of the maximum-density temperature and the alcohol concentration, and (2) that, besides ethyl alcohol, *n*-propyl alcohol alone gives rise to an elevation of the temperature of maximum density.—GLASGOW UNIVERSITY. [Received, May 14th, 1926.]
