TABLE XII. Pressures at 18°.

Volume 0,0	Compositions $x =$									
	0.0000	0.0494	0.0995	0.1990	0.3528	0.4993	0 6445	0.7963	0.8972	1.0000
30	28.90[1])	29.68	30.37	31.33	32.70	33.81	34.77	35.80	36.19	36.31
29	29.73	30.43	31.33	32.25	33.75	34.92	35 95	37.09	37.46	37.59
28	30.58	31.35	32.25	33.24	34.85	36.12	37.19	38.43	38.83	38.97
27	31.45	32.32	33.23	34.34	36.04	37.39	38.56	39.81	40.29	40.45
26	32.40	33.33	34 28	35.53	37.32	38.80	40.05	41.33	41.87	42 04
25	33.36	34.40	35.37	36.77	38.64	40.23	41 64	42.98	43.62	43.77
24	34.38	35.53	36.54	38.04	40.12	41.80	43.33	44.80	45.48	45.65
23	35.47	36 73	37 78	39.43	41.72	43.57	45.17	46.73	47.48	47.70
22	36.55	38.00	39.11	40.91	43.40	45.46	47.18	48.90	49.67	49.94
21	37.75	39.40	40.55	42.50	45.26	47.50	49 39	51.20	52 15	52.40
20	39.08	40.85	42.10	44.26	47.30	49.65	51.80	53 75	54.80	55.10
19	40.40	42.40	43.76	46.15	49.49	52.10	54.45	56.65	57.80	58.10
18	41.90	44.02	45.56	48.22	51.90	54.05	57.45	59.85	61.15	61.50
17	43.43	45.70	47 47	50.40	54.60	58.00	60.75	63.45	64.90	65.25
16	45.00	47.52	49.55	52.80	57.50	61.30	64.55	67.45	69.10	69 50
15	46.64	49.45	51.85	55.45	60 80	65.00	68.75	72.10	73.85	74.35
14	48.35	51.65	54.30	58.40	64.60	69.30	73.35	77.50	79.25	79.95
13	50.05	54.00	56.00	61.75	68.80	74.30	78.80	83.55	85.65	86.45
12	51.85	56.40	59.85	65.60	73.60	80.00	85.30	90.85	93.10	94.10
11	53.65	59.00	63.05	69.75	79 10	86.75	93.00	99.25	102.0	103.1
10	55.50	61.65	66.55	74.25	85.40	94.40	102.1	109.6	112.9	114.3

Chemistry. — „*On the velocity of electrical reaction*". By Dr. ERNST COHEN, (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. If two elements, arranged as follows.

Electrode, reversible with respect to the anion.	Saturated solution of a salt S in presence of the *stable* solid phase of the salt.	Electrode, reversible with respect to the cathion.

and

[1]) This column has been deduced from isothermal determinations of pure carbonic acid, not yet published.

Electrode, reversible with respect to the anion.	Saturated solution of the salt S in presence of the *metastable* solid phase of the salt.	Electrode, reversible with respect to the cathion.

are coupled up in opposition to each other, a transition element of the third kind [1]) is obtained.

If the salt S is zinc sulphate, the combination in question may be composed of two CLARK-cells; in the one $Zn\,SO_4 . 7\,H_2O$, in the other $Zn\,SO_4 . 6\,H_2O$ forms the solid phase provided that the temperature lies between the cryohydratic temperature of $Zn\,SO_4 . 6\,H_2O$ and the transitionpoint (39°).

2. The electromotive force E of this transition element is the measure of the maximum work which the reaction occurring in the element at the temperature T can perform.

In a later communication I shall show how E may be calculated by thermodynamics.

Experimentally, E may be directly determined or it may be calculated from the measurements of JAEGER [2]), who has measured the *E. M. F.* of CLARK-cells at different temperatures, $Zn\,SO_4 . 7\,H_2O$ (the stable phase) or $Zn\,SO_4 . 6\,H_2O$ (the metastable phase) being present as the solid phase between 0° and 39°.

In this way the following numbers are obtained:

Temperature.	*E.M.F.* of the transition element.
— 5°,0	16.2 Millivolts.
0°,0	14.9 „
+ 5°,0	13.5 „
9°,0	12.3 „
15°,0	10.3 „
25°,0	6.4 „
30°,0	4.2 „
35°,0	1.9 „
39°,0	0 „

3. The velocity with which the reaction which occurs in the

[1]) See COHEN, Zeitschrift für phys. Chemie, Bd. 25 (1898). S. 300.

[2]) WIEDEMANN's Annalen, Bd. 63 (1897), 354.

transition element proceeds at the temperature T is represented by the equation

$$K = \frac{E}{\Sigma(W)} \quad \ldots\ldots\ldots \quad (1)$$

where $\Sigma(W)$ is the sum of the internal resistances (at T^0) of the elements of which the transition element is composed, and E the electromotive force of the transition element at T^0.

I have shown [1]) that the internal resistance of a CLARK-cell at T^0 is proportional to that of the zinc sulphate solution, saturated at T^0.

Let the measured resistance of a saturated solution of

$$Zn\,SO_4 . 7\,H_2O = W_1$$

and that of a saturated solution of $Zn\,SO_4 . 6\,H_2O$ at the same temperature $= W_2$. Then

$$\Sigma(W)_{T^0} = (p_1 W_1)_{T^0} + (p_2 W_2)_{T^0} ,$$

where p_1 and p_2 are constants depending on the capacities of the CLARK-cells used and of the vessels in which the resistances of the saturated solutions were determined.

If the same vessel is used for all the measurements, the equation may be written

$$\Sigma(W)_{T_0} = p(W_1 + W_2) .$$

If we call Ω_1 and Ω_2 the specific resistances of the saturated solutions of $Zn\,SO_4 . 7\,H_2O$ and $Zn\,SO_4 . 6\,H_2O$ at T^0 and $\varkappa$ the resistance-capacity of the vessel employed in measuring W_1 and W_2, then

$$\Omega_1 = \varkappa\, W_1$$

$$\Omega_2 = \varkappa\, W_2$$

and
$$K = \frac{E}{\frac{p}{\varkappa}(\Omega_1 + \Omega_2)} .$$

Or
$$K_1' = \frac{E}{\Omega_1 + \Omega_2} .$$

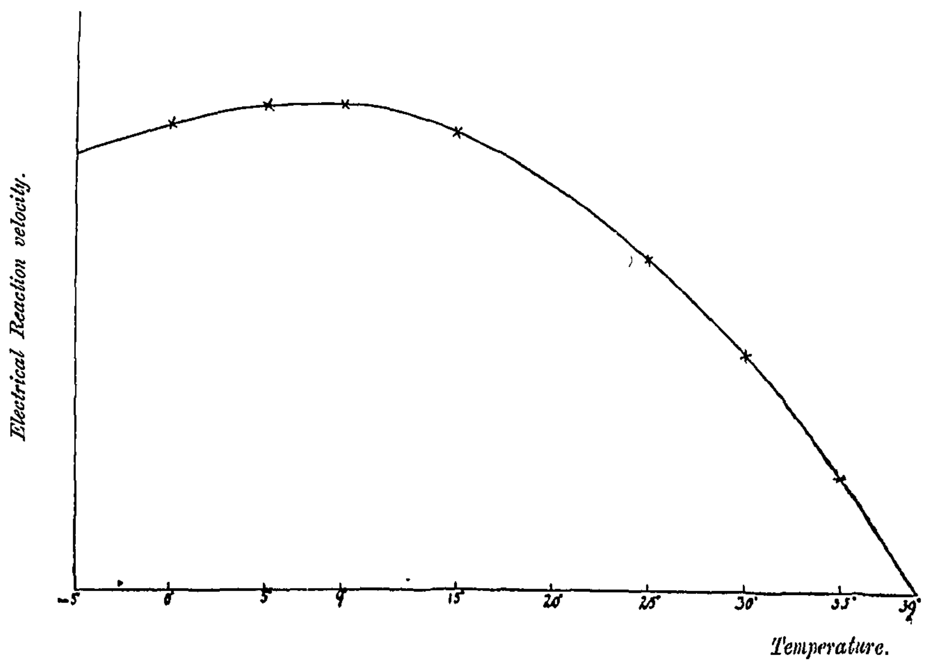
1) The paper relating to this will appear shortly in the Zeitschrift für physikalische Chemie.

The values of the *electrical reaction velocity constant*, K_1, are placed in the last column of the following table, which contains the results of the observations.

T	E (Millivolts)	W_1	W_2	$K_1 = \frac{E}{\Omega_1 + \Omega_2}$
— 5°	16.2	445.9	524.1	0,0167
0°,0	14.9	384.2	452.2	0,0178
+ 5°,0	13.5	337.0	396.3	0,0184
9°,0	12.3	305.75	360.35	0,0185
15°,0	10.3	271.60	315.50	0,0175
25°,0	6.4	236.40	274.25	0,0125
30°,0	4.2	225.10	248.85	0,0088
35°,0	1.9	218.50	228.35	0,0042
39°,0	0	215.0	215.0	0

The observations cannot be continued below — 5° because the cryohydratic temperature of $Zn\,SO_4 . 7\,H_2O$ lies at about — 6°.

Representing the values of K_1 graphically as a function of the temperature the following curve is obtained.



From this it is clearly seen that starting from 39° the *velocity of electrical reaction* rapidly increases, reaching a maximum at about 9° and then diminishing again.

It is worthy of note that the curve, which here represents the *velocity of electrical reaction* at different temperatures, possesses the same form as that representing the rate of crystallisation of many substances at temperatures below the melting-point [1]). I shall take up this subject more fully later, as also the study of the velocity of the following reactions:

$Zn + CuSO_4 = Cu + ZnSO_4$ (DANIELL-element).

$Zn + Hg_2SO_4 = Hg_2 + ZnSO_4$ (CLARK-element).

$Zn + 2AgCl = Ag_2 + ZnCl_2$ (WARREN DE LA RUE-element).

$Zn + 2HgCl = Hg_2 + ZnCl_2$ (HELMHOLTZ element).

Amsterdam, February 1899.

Chemistry. — Prof. FRANCHIMONT presents to the library of the Academy the dissertation of Mr. L. T. C. SCHEY entitled: *„On synthetically prepared neutral glyceryl-ethereal salts — triacylins — of saturated monobasic acids with an even number of C-atoms"* and elucidates it in the following words:

Since CHEVREUL's experiments in the first quarter of this century, fats, at least animal fats, are considered as mixtures of glyceryl-ethereal salts, on account of the products formed by them after treatment with solutions of bases; but it is extremely rare that a glyceryl-ether has been extracted from it in a pure form. The difficulties attached to such separations have as yet not been sufficiently overcome.

About the middle of this century some of these glyceryl-ethereal salts have been made synthetically by BERTHELOT and others, but generally they did not obtain them in a pure condition. Now Mr. SCHEY has, with a view to the acids said to have been obtained from butter, made synthetically eight glycerides, called by him, in order to prevent confusion with polyglycerinderivatives, *triacylins* and has determined

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[1]) See GERNEZ, Journal de physique (2) 4, (1885) p. 349. TAMMAN, Zeitschrift für phys. Chemie, o. a. 23, 326 (1898). VAN 'T HOFF, Vorlesungen über theor. und phys. Chemie (1898). S. 226.