

TABLE 2.

Compound	Spin s of free ion	S , J mole ⁻¹ deg ⁻¹		
		total magnetic, $R \ln(2s+1)$	$S_{\text{latt}}, 298.15^\circ\text{K}$	$S_{\text{mag}}, 298-70^\circ\text{K}$
MnCO ₃	5/2	14.9	98.0	0.5
FeCO ₃	2	13.4	82.7	7.6
CoCO ₃	3/2	11.5	77.0	5.7
NiCO ₃	1	9.1	76.2	0.2

It is noteworthy that CoCO₃ shows an anomaly in its heat capacity, with a maximum at about 270°K and an integral heat of about 100 J, so that the value of $S_{298.15^\circ\text{K}}$ for CoCO₃ contains an uncertainty of about $\pm 0.2-0.3$ J mole⁻¹ deg⁻¹. This anomaly must be attributed to the presence of sorbed water in the specimen.

SUMMARY

1. The temperature variation of the heat capacities of the isomorphous carbonates of manganese, iron, cobalt, and nickel has been investigated between 70° and 300°K, on specimens containing 0.2-0.3% of impurities.
2. Standard entropies have been calculated from the measured heat capacities.
3. In the cases of FeCO₃ and CoCO₃ the magnetic part of the entropy has been determined at temperatures above the antiferromagnetic transition point, which is associated with complete disordering of the magnetic moments of the paramagnetic ions.

1. I. N. Kalinkina, Zhur. Eksper. Teor. Fiz., **43**, 6(12), 2028 (1962).
2. C. T. Anderson, J. Amer. Chem. Soc., **56**, 340 (1934).
3. P. G. Strelkov, E. S. Itskevich, V. N. Kostyukov, G. M. Mirskaya, and B. N. Samoilov, Zhur. Fiz. Khim., **28**, 459 (1954).
4. N. Yu. Ikornikova, Kristallografiya, **6**, 745 (1961).

Received 11th May 1963

U.D.C. 541.13.

EXPERIMENTAL VERIFICATION OF INFLUENCE OF OHMIC POTENTIAL DROP IN BULK OF SOLUTION ON LIMITING ANION REDUCTION CURRENT

B. N. Rybakov, N. V. Nikolaeva-Fedorovich, and G. V. Zhutaeva.

Heyrovský was the first to show¹ that the presence of an ohmic potential drop in the solution diminishes the current in the cathodic reduction of anions. Increasing the concentration of foreign electrolyte decreases the bulk potential

TABLE.

Electrode	Rate of rotation, rev/min	$(id)'$, mA cm ⁻²	$(id)''$, mA cm ⁻²	$(id)'/ (id)''$	Electrode	Rate of rotation, rev/min	$(id)'$, mA cm ⁻²	$(id)''$, mA cm ⁻²	$(id)'/ (id)''$
Amalgamated copper	1050	0.50	0.62	0.80	Lead	1400	0.62	0.72	0.71
	2500	0.75	0.95	0.79		2800	0.80	1.05	0.76
	7700	1.15	1.75	0.70		5600	1.10	1.43	0.78
	9400	1.35	2.00	0.67		8000	1.25	1.65	0.75
Mean				0.74	Mean				0.75

drop, and hence increases the rate of reduction of the anions. It is now known² that the retardation of reduction due to the electric field of the double layer is also eliminated by addition of an electrolyte. Florianovich and Frumkin³ estimated the retarding effect due to the bulk potential drop for the case in which reduction results in the formation of anions having the same charge as the original anion. They showed that, if the thickness of the diffusion layer is constant, the ratio of the limiting anion reduction current in the absence of foreign electrolyte $(id)'$ to its value in the presence of a foreign electrolyte $(id)''$ is given by

$$\frac{(id)'}{(id)''} = \frac{(n+1)p(D_{A_1}/D_{A_2})^{1/(n+1)} - 1}{p(D_{A_1}/D_{A_2}) - 1} \quad (1)$$

where n is the charge on the anions, p is the number of particles formed in the reduction, and D_{A_1} and D_{A_2} are the diffusion coefficients of the reducible anion and the resulting anion respectively. In the case of the reduction of $S_2O_8^{2-}$ we have $n = p = 2$, while $D_{A_1}/D_{A_2} = U_{A_1}/U_{A_2} = 1.08$, where the mobilities of the anions at infinite dilution are respectively $U_{A_1} = 86.2$ and $U_{A_2} = 79.8$. Calculation based on Eqn. (1) for this reaction yields the value $(id)'/ (id)'' = 0.76$. This calculation could not be tested because the effective surface of the electrode could not be determined with sufficient accuracy.

The above calculation has now been subjected to experimental verification by the use of rotating lead disc electrodes and an amalgamated copper electrode having a constant apparent surface. The electrodes were rotated by means of a device described previously⁴. The accompanying Table gives experimental values of the limiting currents for solutions in 0.001 N $K_2S_2O_8$ $(id)'$ and 0.001 N $K_2S_2O_8 + 0.1$ N KCl $(id)''$. It is evident that the mean values of the ratio $(id)'/ (id)''$ agree well with the theoretical value of 0.76, which confirms the correctness of Florianovich and Frumkin's formula.

SUMMARY

Good agreement is shown between ratios, determined from experimental results and calculated theoretically, of the limiting current for reduction of the anion $S_2O_8^{2-}$ in the absence of foreign electrolyte to the limiting current in the presence of such an electrolyte.

1. J. Heyrovský, "Polyarograficheski Metod, Teoriya i Prakticheskoe Primenenie" (The Polarographic Method, Theory and Practical Application), ONTI, Leningrad, 1937, p. 28.

2. A. N. Frumkin and N. V. Nikolaeva-Fedorovich, "Progress in Polarography", Vol.1, 1962, p.223.
3. G. M. Florianovich and A. N. Frumkin, Zhur. Fiz. Khim., **29**, 1827, 1846 (1955).
4. M. P. Belyanchikov, Yu. V. Plěskov, and V. G. Pominov, Zhur. Fiz. Khim., **34**, 1638 (1960) [Russ. J. Phys. Chem., 782 (1960)].

Lomonosov Moscow State
University

Received 13th May 1963

U. D. C. 541.13

DIELECTRIC PROPERTIES OF BENZOPHENONE IN THE LIQUID STATE

A. V. Komandin and A. D. Smirnova

The present paper reports measurements of the dielectric constant and tangent of the loss angle for liquid benzophenone at temperatures between 95° and -55°C and at frequencies of the external electric field of 50 and 800 kc/s and 20 Mc/s. The results have been used to calculate the free energy, enthalpy, and entropy of activation of the dielectric relaxation processes. The preparation, purification, and constants of the benzophenone have been described and reported in previous papers¹. The dielectric properties were measured by a resonance method using a Q-meter of type KV-1, as described previously². The accuracy of the measurements was $\pm 1\%$ in the case of the dielectric constant, $\pm 5-10\%$ for the tangent of the loss angle, and ± 0.1 deg in the case of temperature.

Table 1 gives results for the temperature dependence of the dielectric properties of benzophenone at frequencies of 5.0×10^4 , 8.0×10^5 , and 2.0×10^7 c/s. Table 2 gives thermodynamic functions for the dielectric relaxation processes in benzophenone. The calculation and notation of all the quantities have been given previously². The experimental relation between $\log \tau$ and $1/T$ for benzophenone is represented by the linear equation $\log \tau = -31.78 + 6212/T$. Calculated and experimental values of $\log \tau$ differ by $\pm 1\%$. The linear equation for the enthalpy is $\Delta H^\ddagger = 28.426 - 0.0019877T$ kcal mole⁻¹. Curves 1-3 on the accompanying diagram illustrate the temperature variation of the dielectric constant of benzophenone at frequencies of 50 and 800 kc/s and 20 Mc/s respectively.

DISCUSSION

Table 1 and the diagram show that, at all the frequencies studied, the temperature variation of the dielectric constant of liquid benzophenone obeys the general rules which we observed with the compounds studied earlier: as the temperature falls, the dielectric constant rises, reaches a maximum, and then drops rapidly to the low values characteristic of deformation polarisation. The point of inflection on this curve corresponds to the maximum value of $\epsilon''_{\max}$ and determines the temperature T_x at which the relaxation time was calculated. The tangent of the dielectric loss angle has a maximum near T_x , as follows from Debye's theory. At a frequency of 50 kc/s, however, a subsequent

TABLE 1. Temperature dependence of dielectric properties of benzophenone.

$t, ^\circ\text{C}$	ϵ'	$\tan \delta$	ϵ''	$t, ^\circ\text{C}$	ϵ'	$\tan \delta$	ϵ''
5.0×10^4 c/s, $T_x = 237^\circ\text{K}$							
95.1	10.32	0.155	1.60	-33.0	14.35	0.093	1.34
80.4	10.60	0.120	1.27	-34.1	12.65	0.165	2.09
61.7	11.32	0.090	1.02	-34.9	11.94	0.178	2.12
50.2	11.72	0.063	0.74	-36.1	11.22	0.211	2.37
42.2	12.00	0.050	0.60	-38.2	7.86	0.208	1.64
18.3	13.12	0.023	0.30	-39.2	6.29	0.179	1.13
-2.0	14.21	0.009	0.13	-43.1	4.13	0.086	0.36
-13.0	14.60	0.005	0.07	-47.5	3.50	0.028	0.10
-24.0	14.80	0.015	0.22	-51.0	3.50	0.007	0.02
-28.3	14.75	0.029	0.43	-53.7	3.50	0.007	0.02
8.0×10^5 c/s, $T_x = 246^\circ\text{K}$							
83.3	10.57	0.014	0.15	-27.4	11.38	0.177	2.02
77.0	10.75	0.012	0.13	-30.1	7.53	0.196	1.48
66.0	11.10	0.011	0.12	-32.0	6.75	0.169	1.14
48.3	11.78	0.009	0.11	-32.4	5.75	0.158	0.91
21.1	12.90	0.006	0.08	-34.2	5.51	0.134	0.74
0	14.02	0.007	0.10	-35.2	4.65	0.122	0.57
-8.8	14.35	0.012	0.17	-36.5	4.07	0.101	0.41
-12.1	14.40	0.016	0.23	-37.0	4.02	0.092	0.37
-16.4	14.25	0.027	0.38	-39.0	3.74	0.052	0.20
-19.9	14.10	0.052	0.73	-42.0	3.65	0.031	0.11
-23.5	13.58	0.106	1.45	-46.0	3.60	0.017	0.06
-24.8	13.30	0.122	1.63	-48.0	3.50	0.013	0.05
-25.6	12.73	0.136	1.73	-50.0	2.45	0.011	0.04
-26.4	12.17	0.161	1.96	-54.5	3.45	0.010	0.03
2.0×10^7 c/s, $T_x = 263^\circ\text{K}$							
81.8	10.65	0.019	0.20	-8.5	12.33	0.183	2.25
67.7	11.10	0.020	0.22	-12.9	9.75	0.227	2.22
61.0	11.35	0.020	0.22	-15.4	8.21	0.247	2.03
38.7	12.15	0.023	0.28	-17.2	6.53	0.263	1.72
28.8	12.61	0.026	0.33	-21.9	5.37	0.203	1.09
15.2	13.25	0.036	0.48	-36.4	3.80	0.044	0.19
10.2	13.55	0.043	0.59	-40.9	3.50	0.038	0.13
3.5	13.80	0.067	0.92	-42.5	3.50	0.033	0.12
0	14.06	0.082	1.15	-46.9	3.50	0.030	0.11
-4.4	13.69	0.117	1.61	-50.8	3.50	0.028	0.10

TABLE 2. Thermodynamic functions of dielectric relaxation processes in liquid benzophenone

$$\begin{aligned}
 (\Delta H^\ddagger &= 28.426 - 0.0019877T \text{ kcal mole}^{-1}; \\
 \lambda_e^{579^\circ\text{K}} &= 14.18 \text{ kcal mole}^{-1}; \lambda_e^{316^\circ\text{K}} = \\
 &= 4.34 \text{ kcal mole}^{-1}; \log \tau = -31.78 + \\
 &+ 6212/T; \Delta S_e^{579^\circ\text{K}} = 24.51 \text{ e.u.}; \Delta S_e^{316^\circ\text{K}} = \\
 &= 13.7 \text{ e.u.})
 \end{aligned}$$

$f, \text{c/s}$	$T_x, ^\circ\text{K}$	τ, s	$\Delta F^\ddagger, \text{kcal mole}^{-1}$	$\Delta H^\ddagger, \text{kcal mole}^{-1}$	$\Delta S^\ddagger, \text{e.u.}$
$5.0 \cdot 10^4$	237	$3.18 \cdot 10^{-8}$	7.80	27.96	85.0
$8.0 \cdot 10^5$	246	$2.00 \cdot 10^{-7}$	6.77	27.94	86.0
$1.72 \cdot 10^6$	251	$9.25 \cdot 10^{-8}$	6.53	27.93	85.2
$2.0 \cdot 10^7$	263	$7.95 \cdot 10^{-9}$	5.58	27.90	85.0

