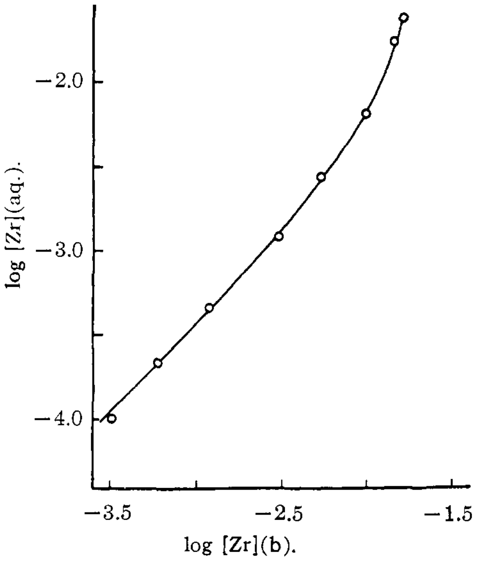

Fig. 2.—Change in equilibrium aqueous and organic Zr molarity with changing Zr concentration; initial TBP concentration in TBP-benzene, 0.131 *M*, initial aqueous HCl concentration, 6.628 *M*.

varies with initial metal concentration in the following manner

$$\left(\frac{\partial \log D}{\partial \log C_m}\right)_{[H],[L]} = \frac{(m - \bar{m})(1 + D)}{(m + \bar{m}D)} \qquad (14)$$

where C_m is the total metal ion concentration, m represents the "polymerization number, "*i.e.*, the average number of metal atoms per molecular species in the organic phase and $\bar{m}$ the "polymerization number" in the aqueous phase.

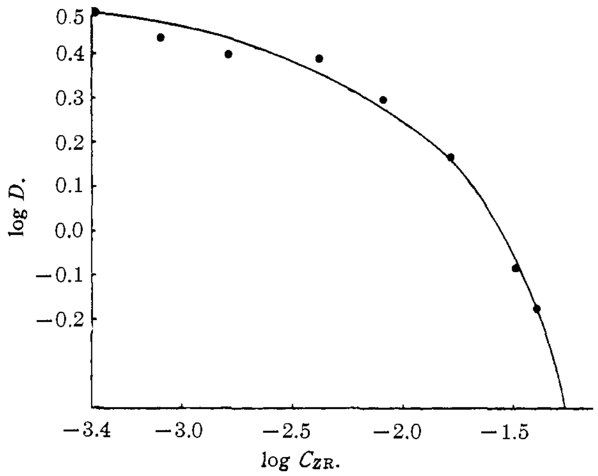

Fig. 3.—Change in distribution ratio D with changing initial Zr concentration; conditions as in Fig. 2.

In this study a plot of log D *versus* log C_{Zr} was constructed as shown in Fig. 3. In the lower zirconium concentrations the slope of the curve is very close to zero, indicating little difference in extent of polymerization between the two phases. At the higher zirconium concentrations the slope approaches a minus one value, again indicating a higher degree of polymerization in the aqueous phase than in the organic phase.

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Diffusion Coefficients for Aqueous Solutions of Sodium Chloride and Barium Chloride

BY V. VITAGLIANO AND P. A. LYONS

RECEIVED SEPTEMBER 12, 1955

In this report are presented diffusion coefficients for aqueous solutions of sodium chloride and barium chloride obtained at 25 ± 0.01° using the Gouy interferometric technique. They supplement existing data, in each case confirm the electrometric results for dilute solutions and assist in the selection of consistent self-diffusion measurements in concentrated sodium chloride solutions.

Materials and Methods—Solutions of NaCl were prepared by weighing dried C.P. salt and transferring it into calibrated volumetric flasks. $BaCl_2$ solutions were prepared from an analyzed stock solution of the C.P. salt.

Diffusion measurements were made using the Gouy interferometric technique for which detailed descriptions are available.[1,2] At the lowest concentrations experiments were performed in a Tiselius cell with channel dimensions 92 × 50 × 5 mm. and the other data were obtained using a cell with 92 × 25 × 3 mm. channels.

A few viscosity measurements were made to supplement the information in the International Critical Tables. A Cannon–Fenske viscometer was used for this purpose.

Experimental Results

In Table I are listed diffusion coefficients measured in a Gouy diffusiometer, and related information obtained for NaCl solutions. Table II contains analogous data for $BaCl_2$ solutions.

The reported diffusion coefficients were estimated using the positions of the lowest six or seven fringe minima. No unusual drifts in C_t were observed for the data reported. In previous work it has been reported that for electrolytes downward drifts in C_t occur at low concentrations.[3] Similar results were obtained in the present work, the value of C_t at $J \cong {}^1/_2 J_m$ being about 0.3 or 0.4% lower than the average of C_t obtained from the lowest seven fringes. The earlier work[3] argues strongly for the possibility that the lowest concentration Gouy data for electrolytes might be 0.1–0.2% high when the conventional computation[2] is used. This method of computation was used here, and with the excep-

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(1) L. G. Longsworth, THIS JOURNAL, **69**, 2510 (1947).

(2) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

(3) P. A. Lyons and J. F. Riley, *ibid.*, **76**, 5216 (1954).

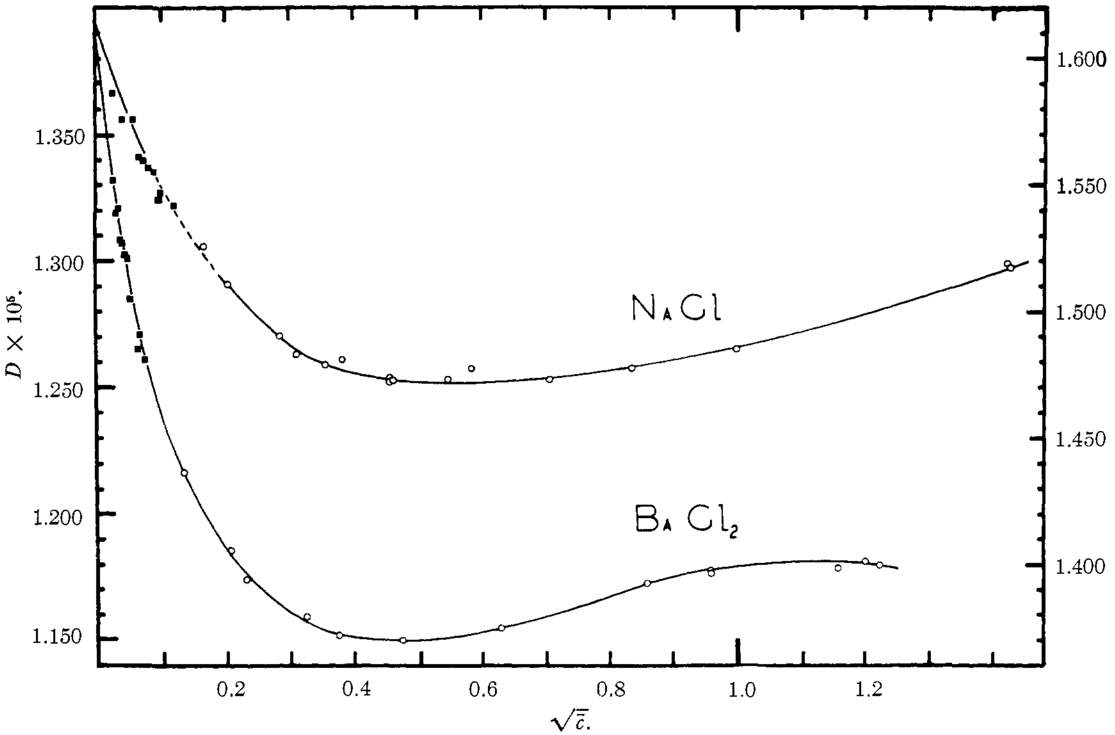

Fig. 1.—Diffusion coefficients for aqueous solutions of NaCl and $BaCl_2$ against $\sqrt{\bar{c}}$. The values of the ordinate at the left refer to $BaCl_2$; those on the right to NaCl: ■, conductometric data; O, Gouy data.

tion of such lowest concentration data (and the values for NaCl at $\bar{c}$ = 0.1419 and $\bar{c}$ = 0.3416, which are unaccountably 0.3% high) the results should have a precision of ~0.1%.

Although for these experiments Δc was not measured with extreme precision, reasonably accurate values for $\Delta n/\Delta c$ may be obtained from a smoothed plot against $\bar{c}$ of the values of $\Delta n/\Delta c$ listed in Tables I and II.

Table I

Gouy Data for NaCl Solutions at 25 ± 0.01°

$\bar{c}$[a]	Δc[b]	J_m[c]	$(\Delta n/\Delta c) \times 10^5$[d]	$D \times 10^5$[e]
0.02715	0.0656	42.44	1029	1.526
.02757	.0475	44.65	1024	1.512
.08059	.1039	48.39	1016	1.490
.09644	.1085	50.64	1019	1.483
.1267	.1345	62.54	1015	1.479
.1419	.1427	66.26	1013	1.481
.2082	.1508	69.43	1005	1.472
.2082	.1508	69.43	1005	1.474
.2130	.1529	70.39	1005	1.473
.3000	.200	91.36	9970	1.473
.3416	.1927	87.70	993.$_5$	1.477
.5004	.2076	92.06	967.$_7$	1.473
.6987	.2073	91.56	964.$_0$	1.477
1.0000	.2000	86.73	946.$_3$	1.485
2.0028	.2244	91.41	889.$_2$	1.519
2.0305	.3674	149.21	886.$_6$	1.517
3.000	.2400	94.17	856.$_4$	1.565
4.000	.200	74.60	814.$_1$	1.594
4.5261	.2604	96.58	809.$_5$	1.592
5.000	.300	108.63	790.$_3$	1.590

[a] $\bar{c}$, average concentration in g. moles/liter. [b] Δc, difference in concentration across the boundary. [c] J_m, total number of fringes in the Gouy pattern. [d] $(\Delta n/\Delta c) = (J_m/\Delta c)(\lambda/a)$, where a = length along the optic axis of the diffusion cell and λ = 5460.7 Å. [e] D, diffusion coefficient at $\bar{c}$ in cm.²/sec.

Table II

Gouy Data for $BaCl_2$ Solutions at 25 ± 0.01°

$\bar{c}$	Δc	J_m	$(\Delta n/\Delta c) \times 10^5$	$D \times 10^5$
0.01833	0.0140	39.85	3100	1.217
.04234	.0338$_6$	47.88	3086	1.186
.05334	.0349$_5$	49.34	3082	1.174
.1066	.0286$_7$	39.94	3040	1.159
.1418	.0313	43.42	3027	1.152
.2267	.136$_4$	189.88	3038	1.150
.3968	.0378$_3$	50.40	2907	1.155
.9218	.0685$_2$	88.66	2824	1.178
.9218	.0685$_2$	88.98	2835	1.177
1.3442	.0520$_5$	66.01	2767	1.178
1.4486	.070$_4$	87.28	2706	1.181
1.5034	.0462	5548	2621	1.180

Discussion

Figure 1 includes a plot against $\sqrt{\bar{c}}$ of both the Gouy data and electrometric data for NaCl solutions. It is apparent that the two sets of data are self-consistent. In the dotted section of the curve, it can in fact be shown that the predicted values of the Onsager–Fuoss theory[4] coincide, within experimental error, with the best smooth curve through the experimental points. The Onsager–Fuoss expression provides a valid representation of experimental data to $\sqrt{\bar{c}} \cong 0.18$.

In the interval of concentration from 0.05–1 molar the Gouy data for NaCl solutions are in excellent agreement with existing diaphragm cell measure-

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[4] H. S. Harned and C. L. Hildreth, This Journal, **73**, 650 (1951).

ments.[5] At higher concentrations the diaphragm cell results are somewhat lower than the optical data. In addition, the Gouy data give the familiar maximum in the plot of D vs. $\bar{c}$. This maximum has been observed for all electrolytes which are sufficiently soluble that the decrease in mobility, which accompanies increasing viscosity, may overwhelm the thermodynamic factor $(1 + c\,(\mathrm{d}\ln y_\pm/\mathrm{d}c))$ which tends to increase the value of D at high electrolyte concentration.

A considerable amount of information has accumulated on the subject of ionic self-diffusion in NaCl solutions. The most recent publication includes a complete list of pertinent references.[6] One aspect of the work has been ambiguous. A set of diaphragm cell measurements[7] gave approximately constant self-diffusion coefficients for Na^+ and Cl^- at higher concentrations than 1 molar, while other methods, including the open-ended capillary method, give decreasing values in the same region.

In Fig. 2 are plotted all the Gouy data for NaCl solutions together with a set of open-end capillary ionic self-diffusion measurements.[8]

The equations

$$D = \omega kT\left(1 + c\,\frac{\mathrm{d}\ln y_\pm}{\mathrm{d}c}\right)$$

and

$$D^* = \omega^* kT$$

apply to salt diffusion and self-diffusion, respectively, where the D's and the ω's are the appropriate diffusion coefficients and mobilities. No thermodynamic factor applies to the self-diffusion phenomenon and the self-diffusion coefficient is directly a measure of the self-diffusion mobility.[9,10] If the salt diffusion coefficient is divided by the thermodynamic factor the quotient, $D' \equiv D/(1 + c(\mathrm{d}\ln y_\pm/\mathrm{d}c))\,kT$, is by definition equal to the salt mobility, ω. In the event that the same factors similarly influence both ionic and salt mobilities the ratio D'/D^* would be expected to remain reasonably constant at different concentrations.

This qualitative assumption appears to be fairly reasonable for 1-1 electrolytes. For these solutes both the first- and second-order electrophoretic corrections for salt diffusion are very small and become essentially constant at concentrations above 1 molar.[11] In addition the experimental self-diffusion data show that the time of relaxation correction is only significant in extremely dilute solutions.[8] Finally, the analogous conductivity data support this assumption. Each of the ratios of the equivalent conductivity of salt to the ionic conductivities of cation and anion approach constancy at moderately high concentrations of 1-1 electrolytes.[12]

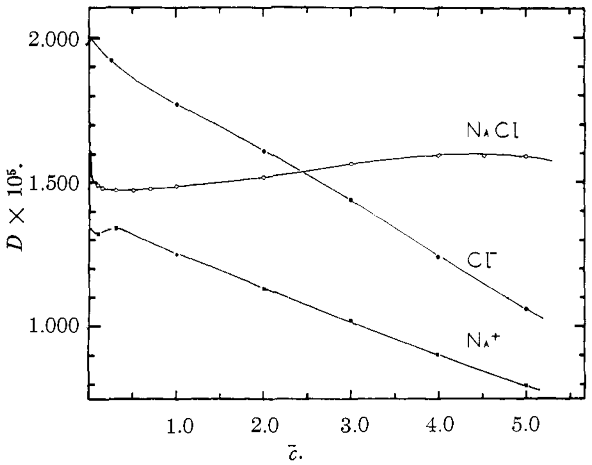

Fig. 2.—Diffusion coefficients for NaCl and ionic self-diffusion coefficients for Na^+ and Cl^- against $\bar{c}$.

The last two columns in Table III list pertinent ratios for the data plotted in Fig. 2. In solutions more concentrated than 2 molar the ratios are remarkably constant. From this necessarily qualitative argument (there is no rigorous theory for concentrated electrolyte solutions) it may be concluded that, in the range of concentrations chosen, the open-end capillary data and the free diffusion data are reasonably self-consistent and that the diaphragm results in this region are probably incorrect.

TABLE III

COMPARISON OF SELF-DIFFUSION IONIC MOBILITIES WITH SALT MOBILITY

$\bar{c}$	th.t[a]	$D \times 10^5$	$\frac{D \times 10^5}{\text{th.t}} = D'$	$D^*_{Na^+} \times 10^5$	$D^*_{Cl^-} \times 10^5$	$D'/D^*_{Na^+}$	$D'/D^*_{Cl^-}$
0	1	1.612	1.612	1.34	2.04	1.20	0.79
1	0.9986	1.485	1.487	1.25	1.77	1.19	.84
2	1.0158	1.518	1.494	1.13	1.61	1.32	.93
3	1.1704	1.565	1.337	1.02	1.44	1.31	.93
4	1.3323	1.594	1.197	0.904	1.24	1.32	.96
5	1.5912	1.590	0.9995	0.796	1.06	1.26	.94

[a] th.t $= (1 + c(\mathrm{d}\ln y_\pm/\mathrm{d}c)) = c/m(1 + m(\mathrm{d}\ln\gamma_\pm/\mathrm{d}m)(\mathrm{d}m/\mathrm{d}c))$. This quantity was obtained from the expression

$$\log \gamma_\pm = -\frac{0.5092\sqrt{\bar{c}}}{1 + 1.3045\sqrt{\bar{c}}} + 0.027384m\,[0.9102 + 0.02514m + 0.0061m^2] - \log\,[1 - 0.02703m]$$

which was derived from the relation proposed by Robinson and Stokes in "Electrolyte Solutions," p. 246. The second term in the expression is $n/\nu \log a_A = m\phi\,\frac{W_A n}{2303}$. ϕ was obtained as a function of m by least squaring the osmotic coefficient data in Robinson and Stokes' book, p. 468. Finally the expression relating molality to concentration which was used was taken from Harned and Owen "Physical Chemistry of Electrolytic Solutions," p. 557.

Fortunately this argument is bolstered by other evidence. First, recently reported self-diffusion data for Na^+ are in fair agreement with the quantities plotted in Fig. 2 from 1 to 5 molar.[6] Secondly, the ratios of the mobilities of Na^+ and Cl^- at infinite dilution to the corresponding values in concentrated solutions are internally consistent. For example, at c = 4 molar, the particular ratios in question are, $D^{*\circ}_{Na^+}/D^*_{Na^+} = 1.48$ and $D^{*\circ}_{Cl^-}/D^*_{Cl^-} = 1.64$ (the relative viscosity at this concentration is 1.552). The mobility of Cl^- is more sensitive to a change in salt concentration than is the Na^+ mo-

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(5) R. H. Stokes, THIS JOURNAL, **72**, 2243 (1950).

(6) R. Mills and A. W. Adamson, *ibid.*, **77**, 3454 (1955).

(7) J. M. Neilson, A. W. Adamson and J. W. Cobble, *ibid.*, **74**, 446 (1952).

(8) J. H. Wang and S. Miller, *ibid.*, **74**, 1611 (1952).

(9) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(10) L. J. Gosting and H. S. Harned, THIS JOURNAL, **73**, 159 (1951).

(11) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," John Wiley and Sons, Inc., New York, N. Y., p. 305.

(12) Ref. 11, p. 159.

bility. This is compatible with the view that at infinite dilution the water molecules in the immediate neighborhood of the cation are more electrostricted than those surrounding the anion. Consequently the change in environment for the cation is less drastic than for the anion when the solvent is subjected to increased electrostriction by increasing the total electrolyte concentration. Since these effects would be more apparent in dilute solutions (when most of the electrostriction occurs) it can be assumed that these differences in environmental change are, in part, responsible for the lack of constancy of the ratios of salt mobilities to ionic mobilities which are observed in the more dilute solutions. As would be anticipated, in the same concentration interval, the ratio $D'/(2D^*_{\mathrm{Na}^+}D^*_{\mathrm{Cl}^-})/(D^*_{\mathrm{Na}^+} + D^*_{\mathrm{Cl}^-})$ is nearly constant (it equals 1.12 ± 2%). At lower concentrations it approaches unity by analogy with the Nernst expression.

Also in Fig. 1, all the Gouy data are plotted for $BaCl_2$ as well as the available electrometric values. The two sets of data are entirely consistent. The not unexpected maximum in the D *vs.* $\sqrt{c}$ plot is evident for this system at $\bar{c} \cong 1.4$ molar.

The fact that the Gouy data for $BaCl_2$ so nicely substantiate the electrometric data in dilute solutions leaves still unexplained the anomalous behavior of $CaCl_2$ solutions which have been shown to depart from the Onsager–Fuoss theory much more drastically than either $MgCl_2$ or $BaCl_2$.[3,13]

Acknowledgments.—The authors are grateful for discussions with Professor H. S. Harned during this study. The work was supported in part by Atomic Energy Commission Contract AT-(30-1)-1375. One of the authors, V. V., is indebted to the Fondazione A. Beneduce, Napoli, for a foreign study fellowship.

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[13] H. S. Harned and F. M. Polestra, THIS JOURNAL, **76**, 2064 (1954).

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE PENNSYLVANIA SALT MANUFACTURING CO., RESEARCH AND DEVELOPMENT DEPARTMENT, WHITEMARSH RESEARCH LABORATORIES]

The Density of Liquid Fluorine between 67 and 103 °K.[1,2]

BY ROGER L. JARRY AND HENRY C. MILLER

RECEIVED NOVEMBER 17, 1955

The density of liquid fluorine has been measured over the temperature range 67 to 103 °K. An all metal system was used. The data obtained have been fitted to the equation. $d = 1.907 - 2.201 \times 10^{-3}T - 2.948 \times 10^{-5}T^2$, where d is the density in g./cm.^{3} at temperature T. The uncertainty in the density is estimated to be ±0.1%, and in temperature ±0.05°.

Introduction.—As part of a program at this Laboratory for the determination of the physical properties of fluorine-containing compounds, an all-metal apparatus was devised for measuring the density of liquefied gases. This apparatus was used to extend the temperature range of measurements on liquid fluorine and to prevent possible contamination by reaction with glass.

Apparatus and Experimental Procedure.—A cryostat similar to those in the various low temperature laboratories in this country was used. The nickel pycnometer was enclosed in a copper block which was suspended within a vacuum space. A small monel packless valve was used to close off the pycnometer volume (about 27 cc.). Measurement of temperature was accomplished by means of a capsule type platinum resistance thermometer, which had been compared with the National Bureau of Standards temperature scale.

The mass of fluorine introduced into the pycnometer was measured by means of calibrated volumes in an air thermostat. Pressure of the fluorine in these calibrated volumes was measured by means of a Booth–Cromer nullpoint gage[3] and a mercury manometer.

The determination of the amount of liquid fluorine held in the pycnometer was made in the following manner. To start a series of determinations the pycnometer was filled at a temperature slightly below that chosen for the first point, using an excess of about 2%. Following the condensation filling operation and after temperature equilibrium had been obtained the pycnometer valve was closed and the excess liquid allowed to expand as a gas into an evacuated volume. At the same time heat was applied to the valve and the $^1/_8$″ nickel line leading from it. This heat was maintained until the valve and line had reached a temperature well above that needed to prevent condensation in the line and valve. From this initial point each successive determination was made by allowing the liquid to expand with increasing temperature into the line above the valve, obtaining temperature equilibrium, closing the valve and allowing the excess liquid to expand into a calibrated volume. As a check on the mass balance at the end of a run, the entire remaining quantity of liquid fluorine was expanded into the volumes and measured.

Materials.—The fluorine used in this study was production material manufactured by this company and packaged in cylinders as a compressed gas. To purify the fluorine, it was condensed using liquid nitrogen and the middle portion from the revaporization used. The purity of the fluorine used in this study by comparison with analysis of a cylinder of the same lot which was not given any purification step was 99% or better. In view of the agreement with previous data (see Results and Discussion below), and within the limits of precision of the measurements, the fluorine must have been of a purity of at least 99.5%.

Results and Discussion.—The values for the density obtained from the experimental data, for two separate runs, are given in Table I. The estimated uncertainty in the density is ±0.1%. Temperature was known to ±0.05°. In the temperature equilibrium period of approximately 25 minutes, the temperature drift was no more than 0.002° per minute. This order of stability was easily maintained due to the large size of the copper block, approximately 6000 g. Since the pycnometer was calibrated at 30°, the volume was corrected using values of the coefficient of thermal ex-

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[1] Presented before the Symposium on Fluorine Chemistry, Division of Industrial and Engineering Chemistry, 128th meeting of the American Chemical Society, September, 1955.

[2] This paper represents the results of one phase of research carried out under Contract #18(600)-(761) sponsored by the Air Force Research and Development Command.

[3] S. Cromer, USAEC Declassified Report, MDDC-803.