# Thermodynamic Properties of Liquid Carbon Tetrafluoride

**Lélio Q. Lobo***

*Departamento de Química, Universidade de Coimbra, 3000 Coimbra, Portugal*

**Lionel A. K. Staveley**

*Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England*

Available thermodynamic data on $CF_4$ have been collected and their reliability examined. They have been used to calculate the values of the following properties: (1) the enthalpy of vaporization of the liquid from the triple point (89.56 K) to 220 K; (2) the configurational internal energy of the liquid and gas at the saturation vapor pressure, and the adiabatic compressibility of the liquid over the same range; (3) the coefficient of expansion of the liquid from the triple point to 190 K; (4) the ratio $C_P/C_V$, the heat capacity at constant volume, the thermal pressure coefficient, and the isothermal compressibility of the liquid from 90 K to the normal boiling point (145.16 K).

## Introduction

We have measured in recent years the primary thermodynamic excess properties—$G^E$, $H^E$, and $V^E$—of a number of binary mixtures of liquefied gases. The experimental results have been used to test modern theories of liquid mixtures, and in particular the perturbation theory developed by Gubbins and co-workers. For such a theory to be successful it is essential that the intermolecular potential of each one of the pure components be known as accurately as possible. Powles, Gubbins, and collaborators in their study of hydrogen chloride (1) indicated the reasons that a knowledge of the configurational internal energy of the liquid as a function of temperature is useful in improving the intermolecular potential function, and stressed the need for such data. Results of this kind have recently become available for hydrogen chloride from high-pressure $P$–$V$–$T$ measurements (2).

As calculations concerning the system HCl + $CF_4$ are now in progress (3) with the object of comparing experiment and theory for this system, and since we have already measured in this (Oxford) laboratory the vapor pressure (4) and the density (5) of liquid carbon tetrafluoride over wide temperature ranges, it seemed worthwhile to calculate the internal configurational energy of $CF_4$ along the saturation line and the values of some other derived thermodynamic quantities. For this purpose one needs, of course, other information, and we shall briefly comment on the available data and on the methods actually used in the calculations.

## Calculations

The internal configurational energy of a pure liquid $U^*_l$ at temperature $T$ and the saturation pressure $P_s$ is the difference between the internal energy of the liquid and that of a perfect gas at the same temperature:

$$U^*_l(T,P_s) = U_l(T,P_s) - U_{pg}(T,P_s)$$
$$= U_l(T,P_s) - U_{pg}(T,0) \qquad (1)$$

where the subscript pg refers to the perfect gas.

When one assumes that the vapor in equilibrium with the liquid follows the virial equation of state

$$PV_g/RT = 1 + B'P + C'P^2 + \ldots \qquad (2)$$

where

$$B' = B/RT \qquad C' = (C - B^2)/(RT)^2 \qquad (3)$$

and so forth, and $B$, $C$, ... are the second, third, ... (volume) virial coefficients, $U^*_l$ is then given by the expression

$$U^*_l(T,P_s) = -\Delta H_v + RT - V_l P_s +$$
$$(B - B_1)(P_s - BP_s^2/RT) + (2C - C_1)[P_s^2/(2RT)] \qquad (4)$$

neglecting all the virial coefficients after the third. In this equation

$$B_1 = T(dB/dT) \qquad C_1 = T(dC/dT) \qquad (5)$$

$\Delta H_v$ is the enthalpy of vaporization, and $V_l$ is the molar volume of the saturated liquid.

Therefore, to carry out the calculation of $U^*_l$, one should have, at least, values of $V_l$ and of the virial coefficients $B$ and $C$ (and their temperature coefficients), and reliable values of $\Delta H_v$. One source of these is an appropriate vapor-pressure equation such as the Wagner equation

$$\ln P_s = \ln P_c + (A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^6)/T_R \qquad (6)$$

where $\tau = (1 - T_R)$, and $P_c$ and $T_R$ are the critical pressure and the reduced temperature, respectively. Ambrose (6) has demonstrated that this equation applies over a wide temperature range, and in fact the widest possible one spanning the triple point to the critical temperature. In the fitting of our experimental values of $P_s$ to eq 6 to obtain the parameters $A_i$ (4), the constraints discussed in Ambrose's paper (6) were adopted, so that values of $\Delta H_v$ derived from the Clausius–Clapeyron equation

$$dP_s/dT = \Delta H_v/[T(V_g - V_l)] \qquad (7)$$

should conform closely to experiment over a large temperature interval. An accurate calorimetric value of $\Delta H_v$ at the normal boiling point of $CF_4$ was obtained by Smith and Pace (7), and it is important to note that the value of $\Delta H_v$ at the same temperature obtained from eq 7 and the Wagner equation for $CF_4$ agrees virtually exactly with the calorimetric value.

Experimental second virial coefficients $B$ of carbon tetrafluoride given by Lange and Stein (8) (from −70 to 95 °C) and by Douslin et al. (9) (from 0 to 350 °C) were fitted by orthogonal polynomials to an expression of the type

$$B/V_c = \sum_i a_i T_R^i \qquad (8)$$

up to the fourth degree (the standard deviation being $\sigma(B) = \pm 0.1$ cm³ mol⁻¹). Its use on extrapolation to lower temperatures should give reasonably reliable values of $B$, as experience with other substances has shown (10).

As for the third virial coefficient $C$, the equation proposed by Chueh and Prausnitz (11) was used. An estimate of parameter $d$ in this expression was obtained by using experimental values of $C$ (8, 9) in a plot of $C/V_c^2$ as a function of $T_R$ and com-

Table I. Thermodynamic Properties of Liquid and Gaseous Carbon Tetrafluoride[a]

| $T$, K | $P_s$, kPa | $-B$, cm³ mol⁻¹ | $C$, cm⁶ mol⁻² | $V_l$, cm³ mol⁻¹ | $V_g$, dm³ mol⁻¹ | $\Delta H_v$, kJ mol⁻¹ | $-U^{\ddagger}_l$, kJ mol⁻¹ | $-U^{\ddagger}_g$, kJ mol⁻¹ | obsd |
|---|---|---|---|---|---|---|---|---|---|
| 89.56 | 0.109 | 718 | | 46.727 | 6830.7 | 14.260 | 13.515 | 0.000 | triple point |
| 90 | 0.120 | 714 | | 46.782 | 6235.0 | 14.200 | 13.452 | 0.000 | |
| 100 | 0.777 | 643 | | 48.023 | 1069.4 | 13.746 | 12.916 | 0.001 | |
| 110 | 3.416 | 578 | | 49.294 | 267.15 | 13.296 | 12.386 | 0.002 | |
| 120 | 11.316 | 520 | | 50.656 | 87.646 | 12.878 | 11.895 | 0.008 | |
| 130 | 30.379 | 467 | | 52.141 | 35.106 | 12.468 | 11.423 | 0.020 | |
| 140 | 69.520 | 420 | | 53.770 | 16.312 | 12.043 | 10.958 | 0.045 | |
| 145.16 | 101.360 | 398 | | 54.676 | 11.495 | 11.810 | 10.715 | 0.065 | normal boiling point |
| 150 | 140.622 | 378 | | 55.571 | 8.473 | 11.580 | 10.485 | 0.089 | |
| 160 | 258.150 | 339 | −1768 | 57.596 | 4.789 | 11.061 | 10.003 | 0.162 | |
| 170 | 438.670 | 305 | +4395 | 59.937 | 2.883 | 10.465 | 9.498 | 0.268 | |
| 180 | 700.435 | 275 | 7608 | 62.748 | 1.817 | 9.780 | 8.977 | 0.416 | |
| 190 | 1063.240 | 248 | 9139 | 66.257 | 1.183 | 8.991 | 8.438 | 0.611 | |
| 200 | 1548.702 | 224 | 9705 | 70.18 | 0.783 | 8.073 | 7.869 | 0.860 | |
| 210 | 2181.271 | 202 | 9733 | 76.10 | 0.522 | 7.015 | 7.301 | 1.167 | |
| 220 | 2990.970 | 183 | 9472 | 85.05 | 0.341 | 5.711 | 6.653 | 1.540 | |
| 227.5[b] | 3742[b] | 170 | 9175 | (140)[c] | (0.140)[c] | (0) | | | critical point |

[a] With the exception of the virial coefficients $B$ and $C$, which are independent of pressure, all of the properties listed refer to saturation conditions. [b] From ref 13. [c] From ref 14.

paring the trend shown by this plot with that for other substances (11). In this manner a figure of $d = 1.0$ was obtained for CF₄. The Chueh and Prausnitz expression was then used to estimate $C$ values down to 160 K, at which temperature the calculated values start to become negative, and therefore the method is no longer reliable. The neglect of the third virial coefficient below 160 K should not give rise to any serious error in the derived quantities since the pressures involved never exceed 0.2 MPa.

From this information the internal configurational energy of the saturated vapor $U^{\ddagger}_g$ can also be derived from the expression

$$U^{\ddagger}_g(T,P_s) = -|B_1(P_s - BP_s^2/RT) + C_1(2P_2^2/RT)| \quad (9)$$

For pressures above 2 MPa, the inclusion of terms involving the fourth virial coefficient $D$ in eq 4 and 9 did in no case change the calculated values of $U^{\ddagger}_l$ and $U^{\ddagger}_g$ by more than ~1%. $D$ was obtained from a linear extrapolation of the experimental values given by Douslin et al. (9).

The molar volumes of the liquid $V_l$ were derived from the experimental work of Terry et al. (5). A small correction was applied to their values, since these are now recognized to embody a systematic error and as a result to be 0.4% too high (10). Outside the temperature range to which their expression applies, estimates of $V_l$ were made by using the law of the rectilinear diameter with parameters given in their paper and values of $V_g$ calculated as explained above.

Since experimental results are also available for the velocity of sound, $u$, in liquid carbon tetrafluoride (12), we have calculated the mechanical coefficients for this substance. The procedure adopted was much the same as that indicated by Blagoi et al. (12). First, the velocity of sound was used to estimate the adiabatic compressibility $\kappa_S$

$$\kappa_S = V_l/(Mu^2) \quad (10)$$

where $M$ is the mass of unit amount of substance, and also the quantity $\gamma$

$$\gamma = 1 + T\alpha_p^2 u^2/C_p \simeq 1 + T\alpha_\sigma^2 u^2/C_\sigma \quad (11)$$

where the subscript $\sigma$ refers to saturation conditions. Values of the expansion coefficient $\alpha_\sigma$

$$\alpha_\sigma = (1/N_l)(\partial V_l/\partial T)_\sigma \quad (12)$$

were derived from the (corrected) expression of Terry et al., while those of the saturation heat capacity $C_\sigma$ were taken from

the accurate calorimetric work of Smith and Pace (7). From these values of $\kappa_S$ and $\gamma$, the isothermal compressibility $\kappa_T$

$$\kappa_T = -(1/V_l)(\partial V_l/\partial P)_T \quad (13)$$

could be obtained, since

$$\kappa_T = \gamma \kappa_S \quad (14)$$

$\kappa_T$ was in turn used to estimate the isobaric expansion coefficient $\alpha_p$ through the relationship

$$\alpha_P = \alpha_\sigma + \kappa_T \gamma_\sigma \quad (15)$$

where $\gamma_\sigma$ is the temperature coefficient of the vapor pressure

$$\gamma_\sigma = (\partial P/\partial T)_\sigma \quad (16)$$

taken from our own work (4). Next, the heat capacity of the liquid at constant pressure $C_P$ was estimated from the expression

$$C_P = C_\sigma + TV_l\alpha_P\gamma_\sigma \quad (17)$$

In the temperature range over which reliable values of $C_\sigma$ for CF₄ are available (90 to ~145 K), the pressures involved are always low, and therefore $C_P$ does not differ significantly from $C_\sigma$, nor $\alpha_P$ from $\alpha_\sigma$. No iteration is then necessary to refine the first set of values obtained from the calculations outlined above. Finally, the heat capacity of the liquid at constant volume $C_V$ was estimated from

$$C_P = \gamma C_V \quad (18)$$

and the thermal pressure coefficient $\gamma_V$ was obtained from

$$\gamma_V = \alpha_P/\kappa_T \quad (19)$$

**Results and Discussion**

The results of the calculations outlined above are shown in Tables I and II.

It would clearly be helpful if an assessment could be made of the reliability of at least some of the values in these tables. As far as the second virial coefficients are concerned, such an assessment should obviously be made at lower temperatures for which the correctness of the extrapolations that we have made (from experimental $B$ values in the range from ~200 to ~320 K) could perhaps be questioned. The method proposed by Curtiss and Hirschfelder (15) to estimate $B$ from a combination of the Clausius–Clapeyron and the virial equation of state (truncated after the second term) seems to be a reasonable choice for comparison. By using this, one arrives at a value

Table II. Mechanical, Adiabatic, and Thermal Coefficients of Saturated Liquid Carbon Tetrafluoride

| $T$, K | $10^3\alpha_\sigma$, K⁻¹ | $10^3\alpha_P$, K⁻¹ | $10^3\kappa_S$, MPa⁻¹ | $10^3\kappa_T$, MPa⁻¹ | $\gamma_\sigma$, kPa K⁻¹ | $\gamma_V$, MPa K⁻¹ | $\gamma$ | $C_P$, J mol⁻¹ K⁻¹ | $C_V$, J mol⁻¹ K⁻¹ |
|---|---|---|---|---|---|---|---|---|---|
| 89.56 | 2.70 | | 0.44 | | 0.0233 | | | | |
| 90 | 2.69 | 2.69 | 0.44 | 0.83 | 0.0253 | 3.24 | 1.882 | 78.0 | 41.5 |
| 100 | 2.59 | 2.59 | 0.51 | 0.93 | 0.1285 | 2.78 | 1.819 | 77.1 | 42.4 |
| 110 | 2.65 | 2.65 | 0.60 | 1.09 | 0.4525 | 2.43 | 1.824 | 77.2 | 42.3 |
| 120 | 2.80 | 2.80 | 0.71 | 1.33 | 1.225 | 2.11 | 1.871 | 77.4 | 41.4 |
| 130 | 2.98 | 2.98 | 0.85 | 1.62 | 2.736 | 1.84 | 1.906 | 78.2 | 41.0 |
| 140 | 3.18 | 3.19 | 1.05 | 2.01 | 5.291 | 1.59 | 1.913 | 79.5 | 41.5 |
| 145.16 | 3.30 | 3.32 | 1.17 | 2.25 | 7.112 | 1.48 | 1.921 | 80.3 | 41.8 |
| 150 | 3.42 | | 1.32 | | 9.171 | | | | |
| 160 | 3.76 | | 1.67 | | 14.611 | | | | |
| 170 | 4.25 | | 2.17 | | 21.797 | | | | |
| 180 | 4.97 | | 2.93 | | 30.885 | | | | |
| 190 | 5.98 | | 4.21 | | 42.034 | | | | |
| 200 | | | 6.45 | | 55.462 | | | | |
| 210 | | | 11.61 | | 71.541 | | | | |
| 220 | | | 27.40 | | 91.106 | | | | |
| 227.5 | | | | | 111.275 | | | | |

for $B$ at 89.56 K—the triple-point temperature $T_{tr}$ of CF₄—which is only 3% in excess of that obtained from eq 8. Moreover, at the normal boiling-point temperature ($T_b$ = 145.16 K) the deviation between the values of $B$ arrived at by the two methods is even less (4): 0.5%. It is well-known that the method of Curtiss and Hirschfelder relies on the accuracy of the vapor-pressure equation since the $B$ coefficients derived in this manner strongly depend on d$P$/d$T$. The agreement obtained in the present case can thus perhaps be simultaneously regarded as supporting our vapor-pressure equation, and hence giving confidence in the calculated $\gamma_\sigma$ values.

The expression of Chueh and Prausnitz with $d$ = 1.0 reproduces the experimental values of $C$ at both -70 and 0 °C within the experimental uncertainty quoted by Lange and Stein (8). The values of $V_g$, the molar volume of the gaseous phase, listed in Table I should therefore be reasonably accurate.

We measured the molar volume of liquid carbon tetrafluoride (10) at the triple-point temperatures of hydrogen chloride ($T_{tr}$ = 158.95 K) and hexafluoroethane ($T_{tr}$ = 173.11 K) in a pyknometer which had been calibrated at 158.95 and 182.32 K (the triple-point temperature of nitrous oxide) by using a highly purified sample of ethane and the density results of Haynes and Hiza (16). At both temperatures our results were 0.4% lower than those obtained from the work of Terry et al. (5). A discrepancy of almost the same magnitude has been found for several substances (17). Accordingly, allowance was made for this, so that the values of $V_l$ reported in Table I (and hence those of $\alpha_\sigma$) should be of adequate quality for our main purposes.

To judge the quality of the $\Delta H_v$ values listed in Table I is perhaps difficult. Although carbon tetrafluoride is an important substance in industry, and otherwise, as far as we are aware only one measurement of sufficient accuracy appears to have been reported for its enthalpy of vaporization. This is that by Smith and Pace (7), whose reported value at the normal boiling point is $\Delta H_{v,b}$ = 11814 ± 5 J mol⁻¹. Use of the Clausius-Clapeyron equation and our vapor-pressure equation gives 11810 J mol⁻¹, which is virtually the same figure, as already mentioned. We have also tried to assess the quality of the estimated $\Delta H_v$ at the triple-point temperature of CF₄ (89.56 K) by using it in an evaluation from vapor-pressure data of the enthalpy of fusion $\Delta H_f$. Several authors (7, 18, 19) have reported experimental values of ~0.70 kJ mol⁻¹ for this quantity. Simon et al. (20) estimated the enthalpy of sublimation of carbon tetrafluoride at its own triple-point temperature as $\Delta H_{sb}$ = 14.73 kJ mol⁻¹, from their measured vapor pressure of the solid. The difference between this value and ours ($\Delta H_v$(89.56 K) = 14.26 kJ mol⁻¹) gives $\Delta H_f$ = 0.47 kJ mol⁻¹, which can be regarded as being in reasonable agreement with

the experimental value, especially if one takes into account that the $\Delta H_f$ so calculated is only ~3% of the terms from whose difference it was obtained. One further test on our reported $\Delta H_v(T_{tr})$ is by using the thermodynamic relationship

$$(\partial \Delta H_v/\partial T)_P \approx C_{P,g} - C_{P,l} \qquad (20)$$

From the experimental $\Delta H_{v,b}$ and the $C_{P,l}$ from ref 7, and by assuming the perfect-gas heat capacity for gaseous CF₄ in the range from $T_{tr}$ to $T_b$, one obtains $\Delta H_v(T_{tr})$ = 14.76 kJ mol⁻¹. This is only ~3% higher than the figure reported in Table I.

Since the quantities involved in the calculation of $U^*_l$ and $U^*_g$ all seem reasonably trustworthy, one should expect the same for the calculated values of both configurational internal energies.

In view of the particular behavior of substances in the critical region, no attempt was made to extend the calculations to the critical temperature. However, it is interesting to note that the values calculated from eq 4 and 9 for $U^*_l$ and $U^*_g$ at $T_c$ = 227.5 K are -1.75 and -1.87 kJ mol⁻¹, respectively, in good agreement with each other.

Little can be said about the remaining quantities listed in Table II. The agreement with values calculated by Biagoi et al. (12) is variable. While the differences remain within their quoted uncertainties for $C_V$ and $\gamma$, the agreement is poor for $\kappa_T$ and $\kappa_S$. Since the same values of the velocity of sound, $u$, were used in both the Russian work and in ours, the difference between the two sets of $\kappa_S$ values can only be assigned to the possible use of rather poor estimates of $V_l$ by Biagoi and co-workers, especially at the lower temperatures for which comparison with our figures could be made. (The difference between the two sets of $\kappa_S$ values at 140, 120, and 100 K is respectively 0, 20, and 40% of their reported $\kappa_S$ figures).

Finally, our listed values for the expansion coefficients may be compared with $\alpha$ = (2.59 ± 0.04) × 10⁻³ K⁻¹ for $T$ from 94 to 107 K, as extracted from the work of Croll and Scott (21).

### Literature Cited

(1) Powles, J. G.; Evans, W. A. B.; McGrath, E.; Gubbins, K. E.; Murad, S. Mol. Phys. 1979, 38, 893.
(2) Nunes da Ponte, M.; Staveley, L. A. K. J. Chem. Thermodyn., in press.
(3) Gubbins, K. E.; Lobo, L. Q.; Staveley, L. A. K., unpublished data, 1979–1980.
(4) Lobo, L. Q.; Staveley, L. A. K. Cryogenics 1979, 19, 335.
(5) Terry, M. J.; Lynch, J. T.; Bunclark, M.; Mansell, K. R.; Staveley, L. A. K. J. Chem. Thermodyn. 1969, 1, 413.
(6) Ambrose, D. Proc. NPL Conf.: Chem. Thermodyn. Data Fluids Fluid Mixtures: Their Estim., Correl. Use, 1978 1979, 193.
(7) Smith, J. H.; Pace, E. L. J. Phys. Chem. 1969, 73, 4232.
(8) Lange, H. B., Jr.; Stein, F. P. J. Chem. Eng. Data 1970, 15, 56.
(9) Douslin, D. R.; Harrison, R. H.; Moore, R. T.; McCullough, J. P. J. Chem. Phys. 1961, 35, 1357.
(10) Lobo, L. Q. Ph.D. Thesis, University of Oxford, Oxford, England, 1979.

(11) Chueh, P. L.; Prausnitz, J. M. AIChE J. 1967, 13, 898.
(12) Blagoi, Y. P.; Butko, A. E.; Mikhailenko, S. A.; Yakuba, V. V. Russ. J. Phys. Chem. (Engl. Transl.) 1968, 42, 564.
(13) Engineering Sciences Data Unit, Index 1977–78, ESDU: London, 1977, p 248.
(14) Kudchadker, A. P.; Alani, G. H.; Zwolinski, B. J. Chem. Rev. 1968, 68, 659.
(15) Curtiss, C. F.; Hirschfelder, J. O. J. Chem. Phys. 1942, 8, 491.
(16) Haynes, W. M.; Hiza, M. J. J. Chem. Thermodyn. 1977, 9, 179.
(17) Nunes da Ponte, M.; Streett, W. B.; Staveley, L. A. K. J. Chem. Thermodyn. 1978, 10, 151.

(18) Eucken, A.; Schröder, E. Z. Phys. Chem., Abt. B 1938, 41, 307.
(19) Enokido, H.; Shinoda, T.; Mashiko, Y. Bull. Chem. Soc. Jpn. 1969, 42, 3415.
(20) Simon, M.; Knobler, C. M.; Duncan, A. G. Cryogenics 1967, 7, 138.
(21) Croll, I. M.; Scott, R. L. J. Phys. Chem. 1958, 62, 954.

# Measurement of the Electrical Conductivites of Molten NaNO₃-KNO₃-NaNO₂ and Molten LiF-NaF-KF by Displacing the Positions of Electrodes

Yohji Uchiyama*[†] and Kazutaka Kawamura

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan

In order to obtain the true electrical conductance of solution in the ac bridge method, it is necessary to eliminate both the frequency effect resulting from circuitry and that of the metal/salt interfacial impedance. In this study we devised the apparatus of electrical conductances so that the interfacial impedance could be neglected by subtracting the measured resistances between two positions of electrodes which were moved through a capillary cell by using a micrometer. With this method it has been found that the same solution resistance could be obtained at any frequency without extrapolating infinitely the measured resistance against the reciprocal of frequency. The experiments were carried out for molten NaNO₃, KNO₃, heat transfer salt (HTS) (a mixture of molten NaNO₃-KNO₃-NaNO₂, 7:44:49 mol %), and FLINAK (a mixture of molten LiF-NaF-KF ternary eutectic, 46.5:11.5:42.0 mol %).

Figure 1. Experimental assembly for electrical conductivity.

## Introduction

For the measurement of electrical conductivity of molten salts, two different types of conductance cells have been used: the capillary cell and the immersion cell. In general, molten salts except covalent compound like the mercuric halides have higher specific conductivities than those of aqueous electrolytes. When one takes into account that the resistance value of the immersion cell ($1 \sim 10 \ \Omega$) is low as compared with that of the capillary cell ($500 \sim 1500 \ \Omega$), polarization effects at the surface of the electrodes of the immersion cell will make accurate measurement of resistance values practically impossible. For accurate measurement of resistance, the ac conductance bridge techniques with high cell constants are readily applicable as compared with the immersion cell.

The measured resistance in the ac bridge technique also contains the frequency effects resulting from circuitry and the electrode impedance resulting from polarization effects at the electrodes, which depend on the frequency of the applied alternating voltage. If the former effects are neglected, one can consider that the measured resistance, $R_m$, and the resistance associated with the electrode/solution interface, $R_z$, depend on the frequency of the applied current.

$$R_m = R_s + R_z \qquad (1)$$

$R_z$ must be either corrected or eliminated experimentally so that $R_m$ represents the true resistance of the solution.

In the measurements of molten salts, a value of $R_m$ is generally extrapolated to infinite frequency with $f^{-1/2}$ or $f^{-1}$, where $R_z$ is assumed to be zero. However, it has been reported that, in molten nitrates (1) and chlorides and fluorides (2), $R_m$ is nonlinear in $f^{-1/2}$ or $f^{-1}$, with resistance approaching a nearly constant value at high frequencies. Although the effects of the metal/salt interfacial impedance have been studied by some investigators (3, 4), the phenomena at the interface are too complicated to clarify. This polarization effect appears to lead to the error of specific conductivity of molten salts, especially fluoride melts which exhibit high ionic conductivity. The purpose of the present work is to eliminate the polarization impedance.

We devised an apparatus of electrical conductivities so that two electrodes could be moved through a capillary cell by using a micrometer. The difference of measured resistances between two arbitrarily chose electrode positions shows the true solution resistance of a melt, $R_s$, since the polarization impedance could be considered to have the same value at any position and be neglected by subtracting.

In order to check this method, the specific conductivities of a 1.0 demal KCl solution and of molten NaNO₃ and KNO₃ were measured. Then, those of heat transfer salt and FLINAK were measured since they are stable over a relatively wide range of temperatures and, to our knowledge, there are no available data for FLINAK. With this method we found that the same solution resistance, $R_s$, could be obtained at any frequency and that it was not necessary to extrapolate the measured resistance with respect to frequency.

## Experimental Section

Figure 1 shows a schematic outline of the bridge circuit ap-

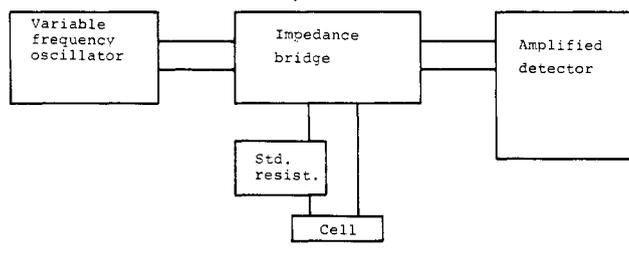[†] Present address: Central Research Institute of Electrical Power Industry, Otemachi Building, 1-6-1 Ohtemachi, Chiyoda-hu, Tokyo 100, Japan.