FUSED-SALT SPECTROPHOTOMETRY

By D. M. GRUEN

(CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS)

Introduction

HIGH-TEMPERATURE absorption spectrophotometry has been extensively employed in studies of the physicochemical properties of fused salts.[1–11] This technique has reached a state of development in recent years which makes possible the quantitative measurement of absorption spectra of solute species in melts at temperatures up to and well above 1000°C.

The methods which have been developed for the measurement of absorption spectra at high temperatures will be discussed. Spectral results will be surveyed to illustrate the variety of solute species which can be studied and to point out features which must be taken into consideration for quantitative measurements.

The Scope of Fused-salt Spectrophotometry

Molar absorptivities of solute species in fused salts can be determined from accurate measurements of absorbance, optical path length, and solute concentrations. The technical problems involved in making such measurements at high temperatures will be discussed later. We will first consider the absorption spectra of a variety of solute species and the effects of temperature and solvent composition on the spectra.

The scope of fused-salt spectrophotometry in the present context is essentially defined by and limited to the wavelength range of available spectrophotometers, *ca.* 50,000 to *ca.* 4000 cm.$^{-1}$ or 200 mμ to 2500 mμ. Electronic transitions occurring in this region of the electromagnetic spectrum can therefore be studied.

The fused-salt solvents for the most part do not absorb light energy over most of this region. In fact many fused-salts such as molten alkali halides and nitrates are more transparent than water in the near infrared and infrared regions so that electronic transitions can be measured in

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[1] D. M. Gruen, "Fused Salts," ed. B. R. Sundheim, McGraw-Hill Book Co., New York, 1964, ch. "Spectroscopy of Transition Metal Ions in Fused Salts."

[2] G. P. Smith, "Molten Salt Chemistry," ed. M. Blander, Inter-Science Publishers, New York, 1964, ch. "Review of Electronic Absorption Spectra of Molten Salts."

[3] G. Harrington and B. R. Sundheim, *Ann. New York Acad. Sci.*, 1960, **79**, 950.

[4] J. R. Morrey, *Inorg. Chem.*, 1963, **2**, 163.

[5] J. P. Young and J. C. White, *Analyt. Chem.*, 1959, **31**, 1892.

[6] (*a*) E. Rhodes and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1959, *A*, **251**, 156; (*b*) E. Rhodes, W. E. Smith, and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1965, *A*, **285**, 263.

[7] I. V. Tananeev and B. F. Dzhurinskii, *Doklady Akad. Nauk S.S.S.R.*, 1961, **140**, 374.

[8] R. Molina, *Bull. Soc. chim. France*, 1961, 301.

[9] W. T. Carnall, *Analyt. Chem.*, 1962, **34**, 786.

[10] H. Lux and T. Niedermaier, *Z. anorg. Chem.*, 1956, **285**, 246.

[11] K. Sakai, *J. Phys. Chem.*, 1957, **61**, 1131.

fused-salt media which are masked by solvent absorption bands in aqueous solutions.

An important early investigation by Retschinsky[12] contains results on the temperature variation of the absorption edges of some 30 salts in the crystalline as well as in the molten state. Measurements on a number of salts in the molten state are reproduced in Fig. 1. The experimental

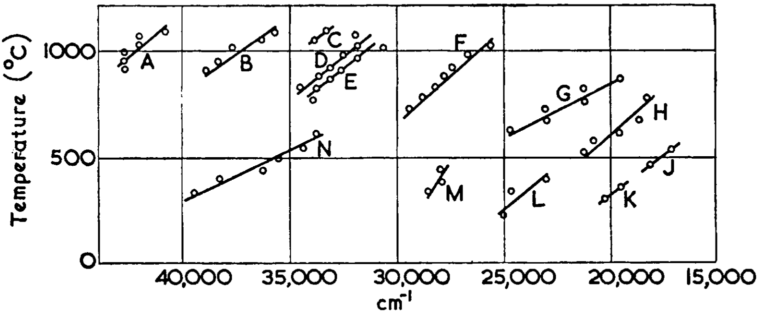

FIG. 1. *Temperature variation of the absorption edges of molten salts: A*, Li_2SO_4; *B*, Na_2SO_4; *C*, Rb_2SO_4; *D*, KCl; *E*, RbCl; *F*, NaBr; *G*, $CdCl_2$; *H*, $PbCl_2$; *J*, AgCl; *K*, $BiCl_3$; *L*, $AgNO_3$; *M*, KNO_3; *N*, $ZnCl_2$. [Adapted from T. Retschinsky, *Ann. Phys.*, 1908, **27**, 100.]

points correspond to the highest energy of light transmitted through *ca* 1 cm. of the molten salt as recorded on a photographic plate.

Depending on the salt, the edge of the fundamental absorption band shifts 1000—2000 $cm.^{-1}$ to the red for each 100° rise in temperature. The red shift was found to be essentially of the same magnitude above and below the melting point. Because of the large number of salts investigated, Retschinsky was able to correlate the energies of the absorption edges with the constitution of the salts:

1. Heavy-metal salts absorb at lower energies than salts of the alkali and alkaline-earth metals.

2. For the same metal, with the exception of silver, the energy of the absorption edge decreases in the order $SO_4^- < Cl^- < Br^- < I^- < NO_3^-$. With silver, the order $Cl^- < NO_3^-$ is reversed.

3. For the same anion, the energy of the absorption cut-off decreases with increasing atomic number of the metal in a given group of the Periodic Table.

Although Fig. 1 includes data only on chlorides, nitrates, and sulphates very similar results can be expected for fluoride melts and oxidic melts such as molten silicates and borates.

The location of the edges of the fundamental absorption bands of the fused-salt solvents are, of course, very important insofar as observation and precise measurements on electronic transitions of solute species are

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[12] T. Retschinsky, *Ann. Phys.*, 1908, **27**, 100.

concerned. For example, the intensities of inner electronic transitions occurring within the 3*d*, 4*d*, 5*d*, 4*f*, or 5*f* shells of the ions are lower than the intensities of charge-transfer bands by a factor of 10^3 to 10^4. For this reason the charge-transfer bands virtually obscure all inner electronic transitions occurring at energies greater than the edges of the charge-transfer bands. It should be pointed out that charge-transfer bands involving the transition-metal ions are usually found at somewhat lower energies than the bands due to alkali-metal ions. The charge-transfer bands of the transition-metal ions therefore set a limit on the highest energy at which inner electronic transitions can be observed. Fortunately a large number of the inner electronic transitions occur at energies lower than *ca.* 30,000 cm.$^{-1}$ where the edges of charge-transfer bands often begin to make their appearance in melts. Many electronic spectra of transition-metal ions can therefore be observed in fused-salt solutions. Furthermore, ions of heavy metals such as Tl^+, Pb^{2+}, and Bi^{2+}, metals and intermetallic compounds dissolved in fused-salts, and species, such as dissolved sulphur, selenium, and tellurium have characteristic absorption bands in wavelength regions available for measurement. The number of different solute species which have so far been studied in fused salts is relatively small and one can confidently predict that as fused-salt solution chemistry develops, many other species with electronic absorption bands will be studied.

Spectra of Transition-metal Ions

Transition-metal ions may be defined as all those ions having unfilled 3*d*, 4*d*, 5*d*, 4*f*, and 5*f* shells. This group includes ions of about half of all the elements in the Periodic Table. The absorption spectra (and the colours) of these ions in crystals and in solutions are due to transitions occurring within the unfilled inner electron shells. The Hamiltonian for the electrons of a transition-metal ion consists of two terms $H = H_F + V$ where H_F is the Hamiltonian of the free ion and V is the potential provided by its ligands. In fused-salt solutions, the ligands are, of course, derived from anions provided by the melt, *e.g.*, Cl^-, F^-, O^{2-}, NO_3^-, etc.

In the Hamiltonian of the free ion, H_F, there are two perturbing quantities, an electronic repulsion term, R, and a spin–orbit coupling term, S, whose magnitudes compared with that of ligand field potential, V, determine the spectral characteristics of the ions in solution.

Four broad classes, distinguished by different relative magnitudes of the perturbation terms, are as follows; each class is representative of a particular group (or groups) of transition-metal ions.

(1)	$S < V < R$	3*d* ions
(2)	$V > R > S$	4*d* and 5*d* ions; oxygenated 5*f* ions such as NpO_2^{2+}
(3)	$V < S < R$	4*f* ions and tripositive 5*f* ions
(4)	$V \cong S \cong R$	tetrapositive 5*f* ions

This classification scheme is, of course, an approximate one only and represents an over-simplification of the actual situation. Nonetheless, it is useful since it helps one to understand the magnitude of the effects produced on the spectra by changing the number and kinds of ligands surrounding a particular transition-metal ion. The magnitude of the spectral changes which are caused by changing the solvent, the temperature, or both vary from one group of ions to another.

Solvent and temperature effects are largest for the $3d$ and the tetrapositive $5f$ ions, smaller for the $4d$ and $5d$ ions, and of least importance for the tripositive $4f$ and $5f$ ions. The underlying reason for this ordering is the magnitude of the ligand potential V relative to the S and R terms.

The large solvent and temperature effects on $3d$ ion spectra necessitates a somewhat closer examination of their origin. The absorption spectra of the $3d$ ions are due to transitions between electronic levels whose energies and intensities are strongly influenced by the number, symmetry, and bonding of the nearest-neighbour anions.

The ground states of the free ions of the $3d$ series are: ${}^2D(d^{1,9})$; ${}^5D(d^{4,6})$; ${}^3F(d^{2,8})$; ${}^4F(d^{3,7})$; ${}^6S(d^5)$. These states are split under the action of the electric field set up by the ligands.[13]

In a cubic (octahedral or tetrahedral) field, a D-state is split into two levels designated by T_2 and E and separated by an energy 10 Dq. In the case of d^1 and d^9, these are the only levels arising from the d-configurations. In the free ion d^4 and d^6 configurations, there are upper triplet H, P, F, and G multiplets spaced in the region 22,000—28,000 cm.$^{-1}$. Transitions from the quintet ground states to these excited triplet multiplets can be expected to be of low intensity. Because of their relatively high energy, they would occur very near the intense charge transfer bands and would in all likelihood be masked by them. For these reasons, the D-state ions in chloride melts would be expected to display as the most prominent feature in their spectrum a single absorption band due to the $T_2 \rightleftharpoons E$ transition.

An F-state in an electric field of cubic symmetry is split into three energy levels designated by T_1, T_2, and A_2 where the T_1–T_2 separation is 8 Dq and the T_2–A_2 separation is 10 Dq. In addition to ${}^3F$ and ${}^4F$ ground states, there are ${}^3P$ and ${}^4P$ excited states spaced in the region 10,000—14,000 cm.$^{-1}$ in the free-ion configurations d^2, d^3, d^7, d^8. Transitions from the F-ground states to the $P(T_1)$ excited states are intense because no change in spin-multiplicity is involved. The $P(T_1)$ states are not split by a cubic crystal field. For d^2 and d^7 configurations in octahedral fields and d^3 and d^8 configurations in tetrahedral fields, the $A_2(F)$ and $T_1(P)$ states cross at $Dq \approx 1000$ cm.$^{-1}$, so that at larger Dq values the $T_1(P)$ state lies below the $A_2(F)$ state. In any event, the spectra of ions possessing F-ground states can be expected to have more than one band in the region accessible to measurement in chloride melts. One is likely to observe three bands cor-

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[13] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, 1962.

responding to transitions from the lowest *F*-state component to the upper two components and in addition a transition to the *P*-multiplet.

The ^6S ground state of the Mn^{2+} ion is not split in a crystal field and transitions to upper ^4G, ^4P, and ^4D states would be expected to occur in the region 20,000—35,000 cm.$^{-1}$.

It can be shown that the T_2—E transition energy for ions with *D*-ground states and the energy between the lowest ligand field states and the *P*-states of ions with *F*-ground states increase with increasing values of *Dq*, the crystal field splitting parameter.

The empirical observation that the successive replacement of I^- ligands by Br^-, Cl^-, and H_2O ligands shift the maxima of spin-allowed bands to progressively shorter wavelengths led to the construction of the spectrochemical series.[14,15,16] One can rationalise the ligand sequence in the spectrochemical series in terms of increasing values of *Dq* and if one considers only transitions between levels in an octahedral ligand field, one would expect their energies to increase with increasing magnitude of *Dq*. On the other hand, according to the point-charge model *Dq* tetrahedral = —4/9 *Dq* octahedral so that, a change in the number of ligands from six to four would be expected to decrease the transition energy by several thousand wavenumbers.

The intensities of spin-allowed bands are larger by a factor of 5—10 in tetrahedral as compared with octahedral fields because in a tetrahedral field the absence of a centre of inversion symmetry results in a relaxation of selection rules for $d \rightarrow d$ electronic transitions.

Solvent and Temperature Effects on 3*d* Transition-metal Ion Spectra in Fused-salt Solutions

The absorption spectra of the 3*d* ions undergo profound changes which arise from changes in the nature and composition of the fused-salt solvents.

In Table 1 are listed the absorption maxima of several transitions between ligand field levels for the ions Co^{II}, Ni^{II}, and Cr^{III} in aqueous solution, in molten $LiNO_3$–KNO_3 eutectic, in molten LiF–NaF–KF eutectic and in molten aluminium chloride. In all of these cases the 3*d* ions are in an octahedral field of six ligands. The absorption maxima are seen to shift to progressively lower energies going from aqueous solution to the aluminium chloride melt indicating that *Dq* decreases in the order $H_2O > NO_3^- > F^- > Cl^-$. The overall shift in the maxima varies from *ca.* 3000 to 5000 cm.$^{-1}$ depending on the ion and the particular transition involved. Changes of this magnitude in the energies of absorption bands can, of course, change the visually observed colours of solutions very markedly.

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[14] K. Fajans, *Naturwiss.*, 1923, **11**, 165.

[15] R. Tsuchida, *Bull. Chem. Soc. Japan*, 1938, **13**, 388, 436.

[16] W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, 1956, **7**, 107.

TABLE 1. *Octahedral spectra of* Cr^{III}, Co^{II}, *and* Ni^{II} *in fluoride, chloride, and nitrate melts and in aqueous solutions.*

	Absorption maxima								
	Water mμ	Ref.	NO_3^- mμ	Ref.	F^- mμ	Ref.	Cl^- mμ	Ref.	Transn.
Co^{II}	510	17	560	19	580	22	634	21*b*	$T_1(F) \rightarrow T_1(P)$
Ni^{II}	395	17	425	19	434	22	487	21*b*	$A_2(F) \rightarrow T_1(P)$
	720	17	775	19	850	22	927	21*b*	$A_2(F) \rightarrow T_1(F)$
Cr^{III}	425	18			448	22	545	21*b*	$A_2(F) \rightarrow T_1(F)$
	585				685	22	795	21*b*	$A_2(F) \rightarrow T_2(F)$

The change from an octahedral to a tetrahedral configuration produces both a decrease in band energy and an increase in band intensity. In going from an octahedral ligand field with a relatively high *Dq*, say nitrate, to a tetrahedral ligand field with a relatively low *Dq*, say Cl^-, very large spectral changes are encountered. The effects are illustrated in Figs. 2 and 3. In these illustrations Co^{II} and Ni^{II} spectra in aqueous $HClO_4$ and in

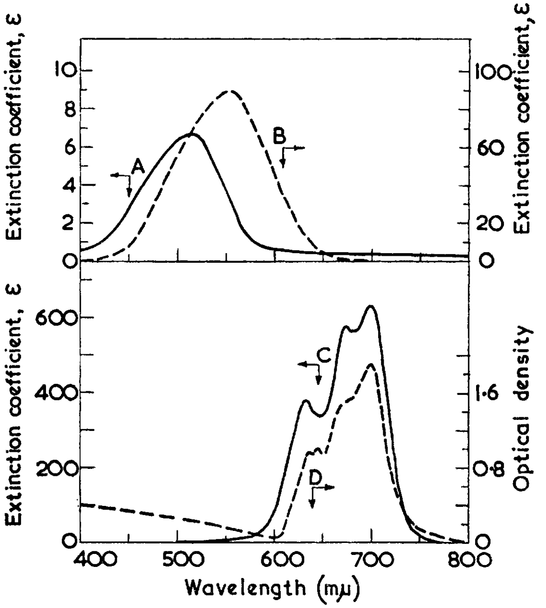

FIG. 2. *Absorption spectra of* Co^{II} *in A*, M-$HClO_4$ *at* 25°; *B*, $LiNO_3$–KNO_3 *eutectic at* 160°; *C, pyridine hydrochloride at* 160°; *D*, Cs_2ZnCl_4 *solid solution at* 25° *illustrating the effect of an octahedral–tetrahedral co-ordination number change.*

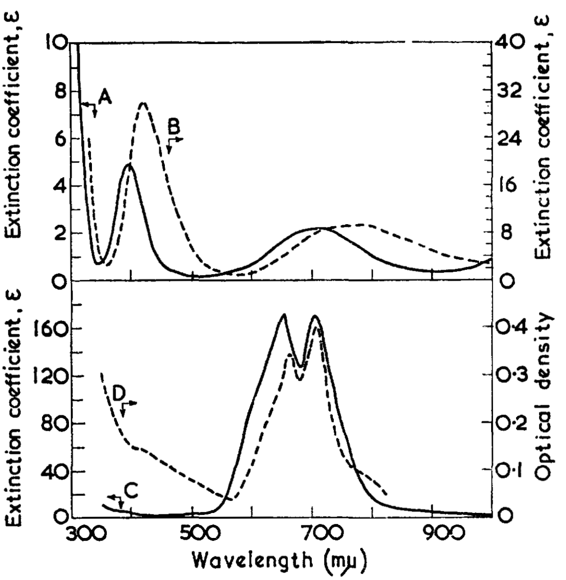

FIG. 3. *Absorption spectra of* Ni^{II} *in the same media as in Fig. 2 illustrating the effect of an octahedral–tetrahedral co-ordination number change.*

molten $LiNO_3$–KNO are compared with spectra of these two ions in molten pyridinium chloride and in crystals of Cs_2ZnCl_4. The aqueous solutions and nitrate melt spectra are "octahedral" spectra. The spectra in molten pyridinium chloride on the other hand are "tetrahedral" spectra owing to the ions $CoCl_4^{2-}$ and $NiCl_4^{2-}$. This is proved by the close similarity of the $Cs_2Zn(Co)Cl_4$ and $Cs_2Zn(Ni)Cl_4$ crystal spectra and pyridinium chloride melt spectra. Not only the band energies but the intensities of the bands are profoundly effected in going from the ionic nitrate to the ionic chloride solvent.

Co-ordination-number changes from six to four with their attendant spectral effects are observed in alkali chloride melts as a function of temperature. For example, V^{II} in LiCl–KCl eutectic undergoes the series of spectral changes shown in Fig. 4 as the temperature varies from 400°C to 800°C. The spectral changes can be interpreted as arising from an equilibrium of the sort

$$VCl_6^{4-} \rightleftharpoons VCl_4^{2-} + 2Cl^-$$

In the case of V^{II}, increasing the temperature leads to a pronounced increase in the intensity of the spectrum and a shift of the band maximum to lower energies.[17] Solutions of Co^{II} in LiCl–KCl eutectic on the other hand display a decreasing transition intensity with increasing temperature over the same temperature interval. In this ionic melt Co^{II} is four-co-

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[17] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, 1962, **66**, 57.

ordinate even at the lowest melt temperatures and the co-ordination-number does not change as a function of temperature.[18] The intensity decrease appears to be related to subtle changes in the covalency of the Co–Cl bond.

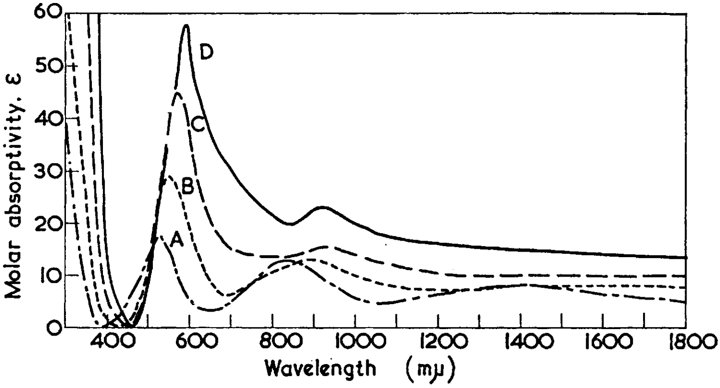

FIG. 4. *Temperature variation of the absorption spectrum of* V^{II} *in* LiCl–KCl *eutectic:* $A = 400°$, $B = 600°$, $C = 800°$, $D = 1000°$.

Spectra of Lanthanide Ions and the Analysis of Lanthanide-ion Mixtures in Fused-salt Solutions

Studies of the absorption spectra of Pr^{3+} and Nd^{3+} in $LiNO_3$–KNO_3 eutectic at 184°C showed that the narrow bands so characteristic of aqueous-solution spectra of the rare-earth ions are largely preserved in fused-salt solutions.[19] In addition to nitrates, fused chlorides are also suitable as solvents in which to carry out spectrochemical studies of rare-earth ions. The usefulness of fused-salt solvents for spectroscopic studies is due to the wide region of optical transparency extending into the infrared. For example, LiCl–KCl eutectic at 400°C is transparent in the range *ca.* 30,000 to *ca.* 1000 cm.$^{-1}$. For the study of rare-earth mixtures the main problem is to find spectral regions in which characteristic bands due to ions of one element are not overlapped or masked by those of another. It is very desirable, therefore, to be able to make measurements over as wide a spectral range as possible.

The ability to measure transitions in the region 7000 to 4000 cm.$^{-1}$ is particularly useful, since many 4*f* ions possess electronic transitions in this energy range. Water absorbs strongly at wave-numbers less than 7000 cm.$^{-1}$ and cannot serve as a solvent in the infrared. By studying the absorption spectra of the lanthanides in molten nitrate systems, for

[18] D. M. Gruen and R. L. McBeth, *Pure and Appl. Chem.*, 1963, **6**, 23.
[19] D. M. Gruen, *J. Inorg. Nuclear Chem.*, 1957, **4**, 74.

example, one extends the region accessible to measurement from the 7000 cm.$^{-1}$ limit imposed by the presence there of an intense water-absorption band to *ca.* 4000 cm.$^{-1}$, where a strong nitrate ion absorption band is located. Carnall[9] has pointed out that in the 7000 to 4000 cm.$^{-1}$ interval there are some two dozen excited multiplets and multiplet components above the ground states of the ions Pr^{3+} to Yb^{3+}. Since there are only about a dozen additional excited multiplet components at energies below 4000 cm.$^{-1}$, the rewards to be gained by pushing further into the infrared region are proportionately much less from the point of view of analytical chemistry.

Stewart and Kato[20] and Banks *et al.*[21a] have made detailed studies of the aqueous-solution spectra of the lanthanides. Banks *et al.*,[21b] Carnall,[9] and Young and White[22] have recently studied $4f$ ion spectra in chloride, nitrate, and fluoride melts, respectively. The advantage of molten-salt solvents for these studies due to the extension of measurements to the near-infrared region has already been pointed out and is confirmed by the work of these investigators. However, the problems in working with molten-salt solvents needs to be pointed out as well. The first consists of the increased difficulty in experimental technique with regard to solvent and solution preparation, temperature control, and container materials. A second disadvantage is due to the observation that the bands in the fused-salt solvents often tend to be less intense than their counterparts in aqueous solutions of equal concentrations. However, several exceptions to this generalisation occur and give rise to potentially important analytical possibilities. Carnall[9] has concluded from his spectrophotometric study that "by having recourse to both aqueous and molten $LiNO_3$–KNO_3 solutions, the quantitative analysis of even relatively complex mixtures of heavy and light lanthanides should be possible".

Spectrophotometric Determination of Mixtures of Oxidation States in Fused-salt Solutions

Each oxidation state of a transition-metal ion possesses a different electronic configuration and is therefore characterised, at least in principle, by a unique absorption spectrum. Because of this fact, it is possible to analyse spectrophotometrically not only mixtures of cations of different elements but also mixtures of different oxidation states of the same element.

The law of additive absorbances states that in a solution of several light-absorbing species, each species contributes additively to the absorbance. If this law holds and if the spectra of the different oxidation states are

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[20] D. C. Stewart and D. Kato, *Analyt. Chem.*, 1958, **30**, 164.

[21] (*a*) C. V. Banks, J. L. Spooner, and J. W. O'Laughlin, *Analyt. Chem.*, 1958, **30**, 458; (*b*) C. V. Banks, M. R. Heusinkveld, and J. W. O'Laughlin, *Analyt. Chem.*, 1961, **33**, 1235.

[22] J. P. Young and J. C. White, *Analyt. Chem.*, 1960, **32**, 799.

sufficiently different from each other, spectrophotometric analysis is possible.

Only one illustrative example will be cited here. Swanson[23] has studied the spectra of plutonium in various oxidation states in the LiCl–CsCl eutectic. He was able to characterise the III, IV, V, and VI oxidation states of Pu spectrophotometrically. Only absorbance data are given in this paper, but there appear to be spectral regions in which absorption is due predominantly to one oxidation state and it may be feasible therefore to determine the relative concentrations of Pu oxidation states in fused chloride melts.

Spectra of Intermetallic Compounds in Fused-salts

The interesting phenomenon of solubility of intermetallic compounds in molten salts was first described by Heymann and his collaborators.[24,25,26] Earlier, Zintl *et al.* observed that a large number of intermetallic compounds form solutions in liquid ammonia.[27] Absorption spectra of Li_3Bi dissolved in LiCl and in LiCl–LiF mixture were reported by Foster *et al.*[28] and of alkali-metal tellurides dissolved in molten alkali halides by Gruen *et al.*[29]

The spectra of the alkali-metal tellurides have absorption bands in the region 22,000 to 15,000 cm.$^{-1}$. These transitions can be interpreted, in first approximation, as essentially atom-like excitations of the sort $5p^6 \rightarrow 5p^56p$ centered on tellurium. Trends of atomic energy levels with degree of ionisation in this region of the Periodic Table lead to the conclusion that the absorbing species carry a negative charge and are probably to be identified with entities such as MTe^-, where M is an alkali metal.

Molar extinction coefficients of the coloured species in these solutions have been obtained but further work is required to establish the functional relation between absorptivity and concentration.

Spectra of Non-metallic Species in Fused-salts

A number of spectra of non-metallic ions have been characterised in molten salts. By far the most extensively studied non-metallic ion is the nitrate ion. An exhaustive study of the effect of the cation on the energy of the lowest-lying nitrate ion transition at ~ 300 mμ has been carried out by Smith and Boston.[30,31] Rhodes and Ubbelohde[6] have studied the energy

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[23] J. L. Swanson, *J. Phys. Chem.*, 1964, **68**, 438.

[24] E. Heymann and H. P. Weber, *Nature*, 1938, **141**, 1059.

[25] E. Heymann and H. P. Weber, *Trans. Faraday Soc.*, 1938, **34**, 1492.

[26] E. Heymann, J. L. Martin, and M. F. R. Mulcahy, *J. Phys. Chem.*, 1943, **47**, 473.

[27] E. Zintl, J. Goubeau, and W. Ropt, *Z. physik Chem.*, 1931, **154**, *A*, 1—46.

[28] M. S. Foster, C. E. Crouthamel, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.*, 1964, **68**, 940.

[29] D. M. Gruen, R. L. McBeth, M. S. Foster, C. E. Crouthamel, Abstracts of the 148th National American Chemical Society Meeting, Chicago, Illinois, September 1964.

[30] G. P. Smith and C. R. Boston, *Ann. New York Acad. Sci.*, 1960, **79**, 930.

[31] G. P. Smith and C. R. Boston, *Discuss. Faraday Soc.*, 1961, **32**, 14.

change of the maximum of one of the nitrate absorption bands which occurs on melting. These workers also studied the spectrum of the thiocyanate ion in molten KSCN.[6]

The energies and oscillator strengths of the nitrate ion absorption bands depend on the ionic potential of the melt cations. A detailed understanding of these spectral changes is important to a better understanding of theories of melting and of melt structure as shown by the recent work of Rhodes, Smith, and Ubbelohde.[6b]

The spectrum of nitrite ion has been studied[30] in molten KNO_2. The band maximum occurs at 359 mμ with $\epsilon = 30{\cdot}6$. In dilute aqueous solutions these values are 366 mμ and 21·9 mμ respectively while in crystalline KNO_2 the band maximum occurs at 360 mμ.

Solutions of halogen gases in molten alkali-metal halides have been measured by Greenberg and Sundheim[32] and were interpreted to show the presence of trihalide ions. Chlorine gas dissolved in the LiCl–KCl eutectic and bromine dissolved in the LiBr–KBr eutectic gave spectra that were similar to the trihalide spectra in aqueous solutions.[33,34] The spectrum of sulphur dissolved in molten LiCl–KCl, LiBr–KBr, and KSCN has been studied.[35] The sulphur solutions are blue, and it was postulated that diatomic S_2 molecules give rise to the colour.

Spectrophotometers for High-temperature Measurements

The chief instrumental problem that arises in measurements of absorption spectra at high temperatures is due to the emission of radiation by the sample, sample container, and furnace. It will be instructive to follow the development of instrumentation to cope with this problem. The first instruments used in fused-salt spectrophotometry were manually operated devices modified by replacing standard sample compartments by heated compartments. The sequence of major components in these instruments is:

Light source → Monochromator → Sample → Detector

(CONFIGURATION I)

Measurements of transition-metal ion spectra in nitrate melts[36,37] showed that emission of radiation did not constitute a problem up to 250°C. However, with Configuration I, the detector "sees" the entire spectrum of emitted radiation in addition to the transmitted monochromatic beam. The signal (monochromatic beam) to noise (emitted radiation) ratio rapidly diminishes in the range 250—500°C.[38]

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[32] J. Greenberg and B. R. Sundheim, *J. Chem. Phys.*, 1958, **29**, 1029.
[33] L. I. Katzin, *J. Chem. Phys.*, 1952, **20**, 1165.
[34] G. Zimmerman and F. C. Strong, *J. Amer. Chem. Soc.*, 1957, **79**, 2063.
[35] J. Greenberg, B. R. Sundheim and D. M. Gruen, *J. Chem. Phys.*, 1958, **29**, 461.
[36] D. M. Gruen, *Nature*, 1956, **178**, 1181.
[37] D. M. Gruen, *J. Inorg. Nuclear Chem.*, 1957, **4**, 74.
[38] B. R. Sundheim and J. Greenberg, *Rev. Sci. Instr.*, 1956, **27**, 703.

The effect of emitted radiation on instrument performance is somewhat improved by adopting the sequence:

Light Source → Monochromator → Chopper → Sample → Detector →
A.C. Amplifier → Recorder

(CONFIGURATION II)

Most recording spectrophotometers provide this sequence. Adaptations of several automatically recording spectrophotometers for fused-salt work have been described.[39,40,41] The reduction of interference from emitted radiation with Configuration II is due to the fact that the light beam is pulsed before passing through the heated sample. In principle, this system should operate successfully even at very high temperatures since only the A.C. output of the phototube detector is amplified. In practice, however, the upper temperature of operation is limited to about 750°C because the detector is heated by the complete spectrum of thermal radiation from the furnace, sample, and sample container. Although the signal from this radiation is not amplified, because of the nature of the circuit, the heating of the detector increases its noise level and diminishes the resolution.

Substantial gains in extending the range of measurements to higher temperatures were made by adopting the following configurations:

Light Source → Sample → Monochromator → Detector

(CONFIGURATION III)

Light Source → Sample → Chopper → Monochromator → Detector →
A.C. Amplifier → Recorder

(CONFIGURATION IV)

Modifications to operate in Configurations III[42] and IV[17] made it possible to measure absorption spectra to temperatures of about 1050°C.

As a consequence of operating an instrument in Configuration IV, the emitted radiation is made to pass through the monochromator before striking the detector. The intensity of the emitted radiation to which the detector is exposed is therefore greatly reduced at temperatures comparable with those encountered in Configurations I and II. However, since the thermal radiation is chopped in Configuration IV at the same frequency as the transmitted beam, it will be picked up by the detector and amplified as part of the signal.

Planck's equation for black-body radiation allows one to make an approximate calculation[17,43] of the ratio I_E/I_O where I_E is the intensity of the furnace and sample radiation and I_O is the intensity of radiation from

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[39] C. R. Boston and G. P. Smith, *J. Phys. Chem.*, 1958, **62**, 409.

[40] J. P. Young and J. C. White, *Analyt. Chem.*, 1959, **31**, 1892.

[41] J. R. Morrey and A. W. Madsen, *Rev. Sci. Instr.*, 1961, **32**, 799.

[42] D. M. Gruen and R. L. McBeth, *J. Inorg. Nuclear Chem.*, 1959, **9**, 290.

[43] J. R. Morrey and E. E. Voiland, *Spectrochim. Acta*, 1962, **18**, 1175.

the tungsten lamp. At a given furnace temperature T, the ratio I_E/I_O is, of course, wavelength dependent. For example, at a furnace temperature of 2400°C, I_E/I_O has the values 0·02 and 0·09 at 1500 mμ and 2500 mμ respectively. Suppose, however, that a fused-salt solution of a transition metal ion at 1000°C has an optical density of 1 and this absorbs 90% of the incident light at a wavelength of, say, 1500 mμ. The intensity of the thermally emitted radiation under these conditions constitutes 20% of the signal. Since the instrument does not discriminate against the (monochromatised) emitted radiation, a correction has to be applied to the measured spectrum at every wavelength.

The virtual elimination of emitted radiation from the signal detection and amplification system can be achieved by using the sequence:

Light Source → Chopper → Sample → Monochromator → Detector →
A.C. Amplifier → Recorder

(CONFIGURATION V)

This arrangement which has, for example, been used in atomic-absorption spectroscopy,[44] and is the conventional mode of operation of some infrared spectrometers, has two advantages. It eliminates emitted radiation except at the wavelength transmitted by the monochromator and amplifies only the radiation emanating from the light source.

The performance of an instrument embodying these features,[45] the Cary 14H, has recently been tested.[46,47] A tungsten filament light bulb was placed in the sample light beam and the "spectrum" was measured with the filament at room temperature and then at 2200°C. The bulb filament simulated a glowing furnace and sample assembly at that temperature. The only effect on the performance was a slight increase in noise level showing that the instrument discriminates essentially 100% against emitted radiation. With an instrumental arrangement such as given in Configuration V, absorption spectra can be measured up to 2200°C and probably well above that temperature.

The special optical arrangement of this instrument results in a lowered light intensity at the detector. However, by substituting a Sylvania Sun Gun for the more conventional tungsten lamps, the light intensity in the near infrared and visible region of the spectrum is increased sufficiently so that normal slit widths are obtained.

Furnaces for Spectrophotometers

A variety of furnace designs for use in fused-salt spectrophotometry have been described.[41]

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[44] B. J. Russell, J. P. Shelton, and A. Walsh, *Spectrochim. Acta*, 1956, **8**, 317.

[45] Described in Bulletin No. 114-H, Applied Physics Corporation, Monrovia, California.

[46] C. R. Boston and G. P. Smith, *Rev. Sci. Instr.*, 1965, **36**, 206.

[47] D. M. Gruen, unpublished observations.

A furnace operating at temperatures up to 1450°C has recently been designed and operated successfully using Pt–20% Rh wire as the heating element.[46]

An exploded view of a furnace with excellent temperature stability at temperature up to 1050° is shown in Fig. 5. The water-cooled furnace

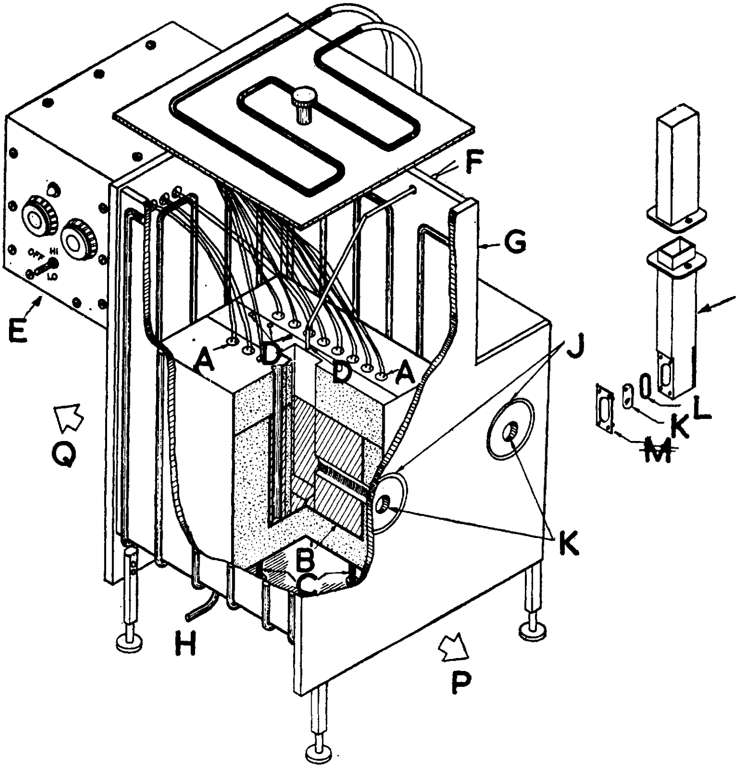

FIG. 5. *Exploded view of furnace assembly for absorption spectra measurements at temperatures up to* 1000°.

A, 400w firerod heaters.
B, 310 Stainless steel inner and outer walls of insulation container.
C, Positioning screws for furnace.
D, Thermocouple wells.
E, Terminal box.
F, Pt–Pt:10% Rh thermocouple leads to temperature controller.
G, Water-cooled brass furnace housing.
H, To supply of inert gas.
J, O ring seals.
K, Quartz windows.
L, Gold gasket.
M, Keeper plate.
N, 310 Stainless steel cell holder.
P, To light source.
Q, To Cary Model 14 Spectrophotometer.

Dotted regions represent powdered zirconia insulation, and hatched regions the 310 stainless steel furnace block.

compartment (22·9 × 26·7 × 40·7 cm.) is made of 0·64 cm. brass through which the cooling water flows.[17] The light ports in the furnace compartment have quartz discs sealed into the openings. A lucite box (not shown) fits on the top of the furnace compartment and is connected to a laboratory exhaust duct, thus providing a leak-proof system for obtaining spectral measurements on radioactive samples.

The furnace itself is constructed of 310 stainless steel and is made in three parts. The two outside sections each contain eight 400-watt Firerod heaters while the centre section is machined to accommodate a cell holder for 1 cm. square absorption cells. The furnace is so designed that the centre section can be removed and replaced with other sections designed to hold cells of 2, 5, or 10 cm. light path. These three parts of the furnace are contained in a double-walled 310 stainless steel container filled with powdered zirconia insulation. Insulation on top of the furnace is provided by three sealed 310 stainless steel cans also filled with zirconia insulation.

Only the sample chamber is maintained at the high temperature.

Power to the furnace is controlled through a self-saturating saturable reactor (choke) with a chopper amplifier. A Pt–Pt:10% Rh thermocouple is used as a sensing element bucked against a reference source which is a 12 mv manganin wound helipot. An anti-oscillation control on the amplifier prevents hunting and large overshoots. Provisions exist for pre-heating the furnace rapidly with an automatic switchover to the temperature controller as the temperature approaches a predetermined point. A waterflow interlock system controlled by a solenoid valve turns off the power to the heaters, reactor, light, and water sources should a leak develop anywhere within the system. The heater block is connected so that only 12 heaters are controlled and four heaters are available for auxiliary heat.

The excellent stability of the controller coupled with the high heat capacity of the furnace resulted in temperatures which were constant to ±0·1° for periods of several hours over the entire temperature range.

Temperature Measurement.—Temperature of the molten salt inside a quartz cell was determined and controlled in the following way: A Pt–Pt:10% Rh thermocouple was calibrated according to the method reported by Roeser and Wensel[48] of the National Bureau of Standards using standard samples of tin, lead, zinc, aluminium, and copper metals, and a secondary standard of silver metal. This thermocouple was inserted in a thin-wall quartz tube immersed in molten salt in a cell in the operating position of the furnace. The e.m.f. of this thermocouple was measured on a Leeds and Northrup Double Range Potentiometer, Model No. 8662, against a number of settings of the helipot on the temperature controller. After applying the corrections to the e.m.f., a graph was constructed showing the temperature of the molten salt as a function of the helipot settings.

[48] W. F. Roeser and H. T. Wensel, in "Temperature—Its Measurement and Control in Science and Industry," American Institute of Physics, vol. 1, Reinhold Publ. Corp., New York, N.Y., 1941, pp. 284—314.

Although any temperature setting is maintained within 0·1° by the controller, it is calculated that the temperature within the cell is ±1° from any desired temperature.

Spectrophotometric Determination of Solute Concentrations in Fused-salts

For a particular fused-salt solvent medium and a given temperature, the spectrophotometric determination of the concentration of a solute species involves the Lambert–Beer law of ideal behaviour. It is conventional in solution work, where the interest is in the absorption by the solute apart from that by the solvent, to define the absorbance, A, as

$$\mathrm{A} = \log P_{\mathrm{soln}}/P_{\mathrm{solv}} \qquad (1)$$

where P_{soln} and P_{solv} is the radiant power transmitted through equal thicknesses of solution and solvent when both are irradiated with the same incident power. The Lambert–Beer law states that for a sample path-length, b, the absorptivity, a,

$$a = A/cb \qquad (2)$$

If b is in centimetres and c is in units of moles/litre, one can write

$$A = \epsilon bc \qquad (3)$$

where ϵ is the molar absorptivity at a particular frequency ν.

It is often desirable to measure the integrated absorption of a single electronic absorption band. The oscillator strength or f number of that band is given by

$$f = 4{\cdot}32 \times 10^{-9} \int_0^{\infty} \epsilon \mathrm{d}\nu$$

The integral is taken over the range of ν-values for which ϵ is appreciable. The oscillator strength defined in this way does not take into account the effect of the medium on the incident light wave and a small correction term depending on the particular fused-salt solvent must be introduced. For allowed transition, f numbers are near unity. However, the inner-shell electronic transitions of the transition-metal ions for example have varying degrees of forbiddences and their f numbers range from *ca.* 10^{-2} to *ca.* 10^{-4}.

In order to do quantitative spectrophotometry A, b, and c must be accurately determined and it must be shown that ϵ is independent of c in the concentration range of interest.

In conventional aqueous-solution spectrophotometry, the absorbance of the solvent is automatically subtracted from that due to the solute species by having pure solvent in the reference path. Furthermore, at ambient temperatures no complications arise owing to emitted radiation. In addition, aqueous-solution work allows one to use quartz or Pyrex cells with well defined path lengths. It is also usually relatively simple to make independent determinations of solute concentrations and to verify the linear relationship between A and c.

The situation in the case of fused-salt spectrophotometry is not nearly so straightforward. Nonetheless, the development of instrumentation and techniques for high-temperature spectrophotometry does make it possible to measure molar absorptivities to high accuracy in fused-salt media. In some cases, such as the determination of molar absorptivities of transition-metal ions in chloride melts at temperatures up to 1000°C, the same accuracy has already been achieved as on aqueous solutions at room temperature.

The full exploitation of the technique for quantitative spectroscopic measurements on melts, however, necessitates a detailed consideration of the special problems which arise in connection with fused-salt spectrophotometry. These problems will be dealt with in the subsequent sections of this Review.

(1) Measurement of Absorbance at High Temperatures.—At high temperatures, absorbance measurements are complicated by the emission of radiation from the sample, sample container, and furnace. There are three mechanisms by which emission occurs: (1) Spontaneous, discrete emission; (2) Induced, discrete emission; and (3) Thermal emission. Spontaneous and thermal radiation are not, while induced emission is, dependent on the intensity of external radiation. In an earlier section it was noted that proper design of instrumentation allows one to discriminate 100% against spontaneous and thermal radiation. When operating a spectrometer in Configuration V, spontaneous and thermal radiation appear as D.C. signals and are not registered in the A.C. detection-amplification system. No correction for emission from these two sources need therefore be applied to absorbance measurements made under these experimental conditions.

Induced emission on the other hand exhibits the same chopped frequency and direction as the incident light and will be detected by the instrument. This problem has been considered by Morrey and Voiland[43] who found that the correction for induced emission is less than 1% when $\nu(\text{cm.}^{-1})/T/°\text{K}) > 3{\cdot}15$. No appreciable error is therefore introduced by neglecting this correction at temperatures below 1000°C and wavelengths less than 2500mμ.

It is frequently experimentally convenient to measure the absorption spectra of the solution and solvent separately against an air reference. This is due to the fact that it is far easier to design a furnace in such a way as to heat only the cell containing the solution while leaving the reference path unheated and unobstructed. With such an experimental set-up, the solute absorbance is obtained by subtraction. The subtraction procedure is relatively simple if all spectra are digitised on cards or tape since the subsequent calculations can then be carried out by a computer.

Using a properly designed spectrophotometer and furnace and employing a careful subtraction technique for solvent absorbance, solute absorbance can be measured at wavelengths less than 2500 mμ and at temperatures up to 1000°C with the same accuracy as at ambient temperatures.

(2) High-temperature Optical Cells.—A container for solutions on which quantitative spectrophotometric measurements are to be performed at high temperatures must meet four basic requirements: (1) It must be transparent to electromagnetic radiation in the wavelength region in which measurements are to be made; (2) its softening or melting point must be considerably above the highest temperature at which measurements are contemplated; (3) it must be chemically inert to attack by the fused-salt solutions; (4) it must have either a precisely defined optical path length or one which can be determined by calibration.

It is not surprising that these requirements are, to some extent, mutually exclusive and that they limit the choice of container materials which have been used or have been suggested for use together with their range of applicability both insofar as temperature and type of melt is concerned. Since requirements 1 and 3, optical transparency and inertness to chemical attack, are found only infrequently in one and the same material, considerable efforts have been devoted to developing "windowless" cells. In Table 2, materials of construction for "windowless" cells are grouped in a separate category.

TABLE 2. *Container materials for high-temperature optical cells.*

Material	Solvents and solutions	Upper temp. limit
Pyrex	Nitrates	500°
Quartz	Sulphates, chlorides, bromides, iodides, solutions of some intermetallics	1200
Sapphire	Chlorides, chloride–fluoride mixtures, metal–molten salt solutions	1800
Magnesium oxide	Same as sapphire but useful for alkali-fluoride melts	2500
Diamond	Unvaluated	

Windowless cells.

Material	Solvents and solutions	Upper temp. limit
Gold	Hydroxides	800°
Platinum	Fluorides, oxides, carbonates, borates, silicates	1400

In order to determine molar absorptivities using the relation $A = \epsilon bc$, one must know the optical path through the sample. The path length is well defined when it is determined by the distance between plane parallel windows. In "windowless" cells, however, it is not simple to determine the path length accurately and calibration procedures must be employed.

(*a*) *Cells with plane parallel windows.* As outlined in Table 2 a number of optically transparent oxidic materials can serve as container materials for fused salts. The Pyrex or fused silica absorption cells used with aqueous solutions are unsuitable for fused-salt work because they are not vacuum tight and the edges are usually cemented with a material which either decomposes or melts at elevated temperatures. Rectangular, 1 cm. path length fused silica cells for high temperature work are now available commercially.* These cells are made of 100% fused silica and are vacuum tight at least up to 1000°C. The 1 cm. path length of these cells can be reduced by using readily available fused silica spacers. Procedures for filling cells of this type with fused-salt samples have been described in the literature.[17]

Cells for solutions which attack fused silica can be machined from single crystal sapphire or magnesium oxide. Both of these materials have been shaped into rectangular cells having rectangular or square wells with plane parallel sides.[29,40] Ultrasonic machining techniques have been employed for this purpose.

(*b*) "*Windowless cells*". Molten hydroxides, oxides, silicates, certain fluoride melts and some metal–molten salt solutions attack sapphire as well as MgO. To study highly corrosive liquids of this sort "windowless" metal cells have been developed. The most thorough study of this subject is due to Young and his collaborators,[40,49,50] although several other methods have also been described.[10,51,52] In the "captive liquid cell" developed by Young,[50] light is transmitted through the side of a vertical column of liquid which is held in a metal cylinder container of special design. No window material or mirrors are necessary to the operation of the cell. The path length of liquid samples held in this cell is independent of the weight, or volume, of sample initially placed in the cell but is postulated to be dependent on the surface tension and density of the liquid. Based on absorbance measurements in 0·250 inch (0·635 cm.) outside diameter cells, the path length of aqueous solutions is 0·68 ± 0·02 cm.; the path length of the molten eutectic LiF–NaF–KF at 540°C is 0·77 ± 0·02 cm. The cell has been used for spectrophotometric studies of molten fluoride salts.

(3) Concentration of Solute Species.—The concentration of a solute species must be determined by an independent method before its molar absorptivity can be calculated. However, determining the concentration of a solute species in a salt matrix is often not a trivial analytical problem. Indeed, the difficulty associated with such determinations serves as a

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* Fisher and Porter Company, Warminster, Pennsylvania; Pyrocell Manufacturing Co., New York.

[49] J. P. Young and J. C. White, *Analyt. Chem.*, 1960, **32**, 1658.

[50] J. P. Young, *Analyt. Chem.*, 1964, **36**, 390.

[51] W. Bues, *Z. anorg. allgem. Chem.*, 1955, **279**, 104.

[52] J. Greenberg and L. J. Hallgren, *Rev. Sci. Instr.*, 1960, **31**, 444.

stimulus to using fused-salt spectrophotometry as a quantitative analytical method.

In whatever way the amount of solute present is determined, it is convenient to express its concentration in a fused salt solution in the conventional units of moles/litre of solution. To make this calculation, the density of the melt as a function of temperature must be known and unless available, must be obtained in separate experiments.

Finally, to apply the relation $A = \epsilon bc$ for quantitative determinations of concentration, Beer's law which states that at a fixed wavelength A and ϵ are constants independent of concentration must be verified. Only a few studies have been made to check Beer's law in a precise way for solutions in melts. In one instance, Boston and Smith[39] measured the visible spectrum of $NiCl_2$ in the fused LiCl–KCl eutectic at seven concentrations, ranging from 0·01 to 0·4M. Beer's law was accurately obeyed at all wavelengths.

(4) Preparation and Purification of Fused-salt Solutions.—The need to prepare fused-salt solutions of high purity is of concern for investigations of the basic physical chemistry of these systems as well as for purposes of analysis. It would carry us too far afield here to describe in detail the various and often ingenious methods that have been developed for the preparation and handling of fused-salt solvents and solutions. A survey of some of this work with literature references is given by Corbett and Duke.[53] The original literature should be consulted for specific procedures.

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[53] J. D. Corbett and F. R. Duke, "Technique of Inorganic Chemistry," ed. H. B. Jonassen and A. Weissberger, ch. on "Fused Salt Techniques," vol. I, Interscience Publishers, New York, 1963.