The time-interval between successive values of potential was several minutes. If, however, the potential was kept constant, the film continued to grow very slowly with a logarithmic dependence on time. Thus after 1,000 min at 1·74 V the film thickness was observed to be ~ 20 Å. The fact that optical changes occurred while the potential was constant indicates that these changes were due to film growth rather than to changes in optical parameters occurring in the solution at the metal-solution interface produced by a change in the potential of the metal surface.

Once the film had begun to form in the solution containing 4 g/l. of $Na_2C_2O_4$ the rate of oxalate oxidation decreased. Lowering the potential from 1·74 V to 1·24 V resulted in a fairly slow first-order decay of the film. The same was true on open circuit. The film was easily reduced by setting the potential to values below 1·1 V with the potentiostat. Essentially the same results were obtained in 1 M sulphuric acid alone, but the film was not readily removed by the acid either on lowering the potential to about 1·2 V or on open circuit. With a sodium oxalate concentration of 20 g/l. the rate of reaction of oxalate with the film was so rapid that no film formation was observed up to 1·94 V, within the limit of detection of the ellipsometer.

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Infra-red Spectra of Aqueous Solutions by the Attenuated Total Reflectance Technique

IT has recently been suggested[1,2] that the attenuated total reflectance (ATR) technique is superior to the conventional transmission technique for obtaining the infra-red spectra of aqueous solutions, with the implication that the intense absorption bands of liquid water appear to be relatively weaker in ATR spectra. We have examined the spectra of a number of aqueous solutions by both methods and have in no case found the ATR spectra to be superior.

It is generally accepted that in the ATR system the radiation beam interacts only with the surface layer of the sample although the exact depth of penetration is a function of the complex refractive index, angle of incidence and wave-length. Parker[2] reports an apparent transmission of about 50 per cent for pure water by ATR methods at the 6·3 μm absorption peak. The transmission spectra of Ackermann[3] show that a path length of the order of 5 μm does in fact allow 50 per cent transmission at this wave-length.

It seems, therefore, that the ATR technique possesses no inherent advantage over the transmission technique for the examination of aqueous solutions. For concentrated solutions in regions of intense water absorption, the ATR technique circumvents the practical difficulties of filling and cleaning very short path length transmission cells. Where adsorption on the ATR prism surface allows higher solute concentrations to be established, the multi-reflexion ATR technique could probably be used with advantage, although the spectrum of the adsorbed material will not necessarily be the same as that of the material in true solution. These observations in no way detract from the value of the ATR technique for obtaining the spectra of intractable water containing samples which would be difficult or impossible to examine by transmission methods.

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Electronic Structures of Kryptates and Xenates

THE recent preparation of kryptates[1] and xenates[2] by Grosse et al. opens a new chapter in rare-gas chemistry. Up to now the compounds that have been made have presented no new problems in chemical bonding; no problems that were not already present in the chemistry of iodine and tellurium, etc. Most of the fluorine and oxygen compounds of xenon that have been prepared have isoelectronic analogues in the chemistry of iodine, for example, $XeF_6(IF_6^-)$, $XeF_4(IF_4^-)$, $XeF_2(ICl_2^-)$, XeO_3 (IO_3^-) and $XeO_6^{4-}(IO_6^{5-})$. Xenates based on XeO_6^{6-} are therefore a new type of compound. Similarly krypton forms $KrO_3(BrO_3^-)$, but kryptates (KrO_4^{--}, KrO_6^{6-}?) have no isoelectronic counterparts.

Rubidium and cæsium follow krypton and xenon in the periodic sequence, and in these elements the circum-rare-gas electron is in a $5s$ or a $6s$ orbital. While these electrons are loosely bound (Rb, 4·2 eV; Cs, 3·9 eV) it seems reasonable to suppose that such orbitals may play some part in bonding in rare-gas compounds. Calculations by Craig and Zauli[3] have shown that many ligands and especially electron attracting ligands can, by polarizing the valency-shell electrons of a non-transitional element, confer on the diffuse and loosely bound d orbitals an enhanced bonding potential. The empty $5s$ and $6s$ orbitals that surround krypton and xenon should be similarly affected by ligands such as oxygen and fluorine. These ligands will also enable the krypton $4d$ and the xenon $5d$ and $4f$ orbitals to play some part in bonding. Oxygen's $2p$ orbital is less tightly bound than fluorine's. It is, therefore, nearer in energy to the $5s$ (Kr) or $6s$ (Xe) orbitals and, being more diffuse than the fluorine orbital, it will overlap better with the loosely bound rare-gas orbitals. These two effects combine[4] in making the outer orbitals of krypton and xenon more important in bonding to oxygen than to fluorine.

In the tetrahedral oxy-anions, germanate, arsenate, etc., the four oxygen ligands may be thought of as each having one p orbital directed towards the central atom. These four p orbitals will belong to irreducible representations a_1 and t_2 of the point group Ta. The a_1 oxygen orbital will, therefore, interact with the valency $4s$ orbital and the empty $5s$ orbital in these anions. Ignoring the possible effect of the $5s$ orbitals it has been argued[5] that since the $4s$ orbital becomes more tightly bound in going from germanium to bromine the efficiency of a_1-type bonding will decrease. In BrO_4^- only the bromine $4p$ orbitals contribute effectively to the bromine–oxygen bonds. Thus BrO_3^- is stable, but, in the absence of other effects, BrO_4^- should be unknown. (In isoelectronic ClO_4^-, $3d$ orbitals