the anodic current of the reduced rare earth ions, with the effect that the null potential should be shifted in a negative direction from the electrocapillary maximum potential. A linear shift of potential, of the order of 0.1 volt per 10^{-6} mole/liter of divalent rare earth ion, would be expected.

Using strontium amalgam as the reducing agent, in a nitrogen atmosphere, potential readings of the order of -0.8 volt (*vs.* the saturated calomel electrode) were observed both with neodymium sulfate solutions and with sulfuric acid blanks. With ytterbium sulfate solutions, a reading of the order of -1.2 volts was observed. In view of the fact that the cathodic half-wave potential of trivalent ytterbium ions is -1.4 volts,[6] and considering the insolubility of ytterbous sulfate in the presence of strontium sulfate, this value is of the expected order of magnitude.

Similar experiments using 3% sodium amalgam as the reducing agent gave potential readings of 0.0 to -0.12 volt for the blanks and for neodymium sulfate solutions. In these experiments, the removal of the last traces of oxygen from the solid sodium amalgam was difficult, and the blank readings were probably shifted to abnormally positive values by traces of residual oxygen.[5] With ytterbium sulfate, potential readings of -1.30 to -1.37 volts were observed, again in the expected range.

Attempts were made to effect reductions in an alkaline medium in the presence of complexing agents, with the hope of decreasing the rate of reoxidation of divalent neodymium by hydrogen ions. Using Nulapon A (tris-[carboxymethyl]-amine) and Nulapon B (ethylenediamine tetraacetic acid), a *p*H value of 13 could be reached without precipitation of rare earth hydroxides. Using ytterbium chloride with sodium amalgam in a nitrogen atmosphere, a series of color changes from black to brown to orange was observed. The potential of the dropping mercury electrode was about -1.8 volts (*vs.* the saturated calomel electrode). Using neodymium chloride, no color changes occurred, and a potential reading of -0.6 volt was observed.

All attempts to prove the existence of divalent neodymium occluded in strontium sulfate, or in solution under conditions favorable to the reduction of ytterbium, have failed.

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Degassing Low-Boiling Liquids by Liquid-Phase Condensation

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Low-boiling liquids have often been degassed by trap-to-trap distillation to liquid air, in high vacuum, with or without discarding of first fractions. This method has failed to remove last traces of permanent gas,[3,4] presumably because of adsorption and entrapment of gas on the nonvolatile condensate. The discarding of first fractions on distillation is generally ineffective when dealing with traces of dissolved gases. In these cases the vapors escaping the boiling liquid tend to be closer in composition to the liquid phase than to the gas-rich composition calculated on the assumption of continual equilibrium. By contrast, if one approaches liquid–vapor equilibrium from the opposite direction, *i. e.*, by condensing liquid from vapor containing traces of permanent gas, then the gas content of the resulting liquid phase will be equal to, or less than, the equilibrium value. Failure to attain equilibrium is in this case favorable for separation of gases. This principle, which was in effect used by Keyes[5] for degassing water, has been successfully applied by the authors to the degassing of chlorine and carbon tetrachloride for kinetic studies.[6,7] The method of condensation to the liquid phase should be readily adaptable for degassing low-boiling substances which can be conveniently liquefied. There is no reason to believe that the fraction of gas removed at each step decreases with decreasing gas content.

Experimental

An outline is given here of the degassing of chlorine, which represents the unfavorable case of a low-boiling liquid whose corrosive properties require a grease-free system. The apparatus consisted essentially of several traps which led through a U-bend to a waste trap (in liquid air) and a McLeod gage, and thence through a stopcock to a mercury diffusion pump. The system was evacuated, liquid air placed on the U-bend, and liquid chlorine, after a preliminary purification, introduced and sealed into the system. Chlorine froze in the bend to form a gas-tight plug which then allowed the pressure in the closed system to rise during the next step without loss to the waste trap. The trap containing liquid chlorine was exposed to the atmosphere and the resulting distillate condensed in another trap with Dry Ice–alcohol. Neither condensation temperature nor distillation rate was critical, as long as the condensed phase was a liquid. At the end of the distillation the partial pressure of permanent gas in the uncondensed vapor was estimated in the McLeod gage by closing the stopcock and removing the plug in the U-bend. The gas-rich vapor phase was then pumped out. Liquid air could now be used to freeze the chlorine and keep liquid losses low. The system was again closed at the bend and the distillation repeated. In accordance with expectations the measured residual pressures decreased in rapid progression and became unmeasurable in a gage sensitive to 10^{-5} mm.

Chlorine thus degassed was then sublimed in a closed system to melting ethyl bromide[3] at $-119°$, which should have released any gases present. No pressure increase was found indicating the chlorine had been degassed prior to the sublimation step. Chlorine thus prepared and carbon tetrachloride similarly prepared (but without subsequent sublimation) were found by Manes and Hill[7] to show no induction period in the photochlorination of (similarly degassed) benzal chloride. Control experiments set the sensitivity of this test to oxygen at about 0.005% for chlorine and 0.00005% for carbon tetrachloride. In no case was any positive indication of oxygen observed.

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