though the coal gas plant ceased operation about 1930, and the tar residues were exhumed in 1959, substantial amounts of coal tar compounds could have been leached into the aquifer during the intervening 30 years. The compounds identified in the water are entirely consistent with this source of contamination.

DISCUSSION AND CONCLUSIONS

The Rohm & Haas macroreticular resins XAD-2 and XAD-7 are efficient sorbers of a broad range of non-ionic organic compounds present in aqueous solution, even at concentrations in the parts-per-billion range. The simplicity of the extraction equipment makes it useful for field sampling as well as for laboratory experiments. Moreover, the sorption process appears to be completely reversible so that quantitative as well as qualitative results are possible.

In general, mixtures of trace organic compounds are so complicated that semi-automatic identification techniques must be employed to analyze the components. The most promising approach appears to be resin extraction followed by gas or liquid chromatography coupled with mass and infrared spectrometry of the separated effluents.

ACKNOWLEDGMENT

We wish to acknowledge the cooperation and advice given by Harris Seidel, Director, Water and Pollution Control, Ames, Iowa.

RECEIVED for review June 7, 1971. Accepted November 4, 1971. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Partial support of this work was supplied by the Ames Water Department.

Low-Temperature Electrochemistry

I. Characteristics of Electrode Reactions in the Absence of Coupled Chemical Kinetics

Richard P. Van Duyn1 and Charles N. Reilley

Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514

Electrochemical experiments such as cyclic voltammetry and the potentiostatic relaxation techniques, chronocoulometry and chronocoulometry, can be performed in cryogenic environments (\(> - 130 \, ^\circ\text{C}\)). Low-temperature electrochemical cells have been designed to perform these experiments with reasonable facility. A variety of solvent/supporting electrolyte systems have been evaluated for low-temperature use and butyronitrile/0.1M TBAP appears to be the best "all-purpose" low-temperature medium. Although the use of a low-temperature environment in electrochemistry results in some time response degradation, the electrical double layer can still be charged in less than 0.001 sec under all conditions tested. Double potential step chronocoulometry and chronocoulometry have the special advantage for low-temperature work that their characteristic ratio responses, \(i_t/i_0\) and \(Q_t/Q_0\), respectively, are temperature independent in the absence of coupled chemical reactions. Similar temperature independent ratios are formulated for other two-step electrochemical techniques.

Studies of the structure, thermodynamics, and kinetics of neutral and ionic free radicals generated by a variety of methods (viz., chemical redox, electrochemical redox, photolytic, and radiolytic) have received considerable attention in recent years (1-6). The widespread use of low-temperature environments for the observation of these highly reactive or inherently unstable species by optical spectrometry (1, 7), magnetic resonance spectrometry (1, 7), and, more recently, mass spectrometry (8) has proved to be of considerable value in the elucidation of their role as intermediates in chemical reactions. In contrast, comparatively little attention has been directed toward low-temperature studies of the intermediate species formed at the electrode/solution interface during an electrochemical reaction, perhaps because of the difficulty of finding satisfactory low-temperature electrolyte systems. Although no systematic studies of the low-temperature behavior of electrochemically generated radicals and their associated decay chemistries have been undertaken, several papers have appeared in which sub-ambient temperatures have been utilized in evaluating heterogeneous electron transfer kinetic parameters (9-15), conducting electrochemical

1 Present address, Department of Chemistry, Northwestern University, Evanston, Ill. 60201


syntheses (16–22), and increasing the lifetime of radical anions for electron spin resonance observation (23–27).

During the course of our low-temperature electrochemical investigations, two preliminary reports appeared in the literature in which cyclic voltammetric measurements were made at sub-ambient temperatures. Hawthorne et al. (28) were able to demonstrate the existence of the formally d4 nickel(IV) dication, \((\sigma-C_{6}H_{5})_{2}Ni^{2+}\), in the cyclic voltammogram of nickelocene run in acetonitrile solution at \(-40^\circ\text{C}\). The room temperature voltammetric behavior of the same solution was not shown for comparison; however, these authors implied that the nickel(IV) species rapidly decayed at room temperature. Very recently, Miller (29) has given evidence for a sigmatropic phenyl group migration in the cation radical of 1,1,3-triphenylindene using low-temperature electrolysis and cyclic voltammetry in liquid \(\text{SO}_{3}/0.2\text{M tetrabutylammonium perchlorate media}\). The investigations of Hawthorne and Miller are indicative of the potential utility of low-temperature techniques in electrode mechanism and radical ion characterization studies.

Realization of the potential value of the low-temperature adaptations of cyclic voltammetry and particularly the potential-step techniques of chronocoulometry and chronocoulometry in the study of complex electrode reaction mechanisms and the evaluation of thermodynamic and kinetic parameters of chemical reactions coupled to charge transfer requires:

First, the development of solvent-supporting electrolyte systems possessing reasonably high conductivity over a wide low-temperature range. This is necessary in order to produce substantial reaction rate changes with the relatively low activation energy reactions characteristic of radical ion decay processes.

Second, an assessment of the trade-off between low-temperature time response degradation of the cell-potentiostat and chemical reaction rate attenuation.

Third, a means of separating the temperature dependent factors involved in heterogeneous electron transfer and diffusion processes from those of the homogeneous chemical reactions coupled to charge transfer.

In this report, we quantitatively evaluate the extent of cell-potentiostat time response degradation in several low-temperature solvent-supporting electrolyte systems and examine the temperature dependences of all pertinent electrochemical parameters. The accompanying papers in this series are concerned with a theoretical description of the effects of coupled chemical reactions of low-temperature electrochemical responses for cyclic voltammetry and potential step techniques and with the applications of low-temperature electrochemical methods to the investigation of radical ion decay pathways involving fragmentation of the radical ion and/or its reactions with components of the electrogeneration environment.

**EXPERIMENTAL**

Low-Temperature Electrochemical Cells. The cells used for all low-temperature voltammetric and transient potential step experiments are shown in Figures 1 and 2. Both cells were designed with opposed, coaxial, working, and reference electrodes surrounded by a platinum coil auxiliary electrode. The cylindrical symmetry of this three-electrode configuration provides uniform current and potential distributions across the surface of the working electrode while the short interelectrode distances result in as small uncompensated and compensated cell resistances as are geometrically possible (30). Achievement of this nearly ideal electrode geometry for minimizing uncompensated ohmic drop between working and reference electrodes is especially important in low-temperature potentiostatic transient experiments since the solvent-supporting electrolyte media is of considerably higher resistance than in the corresponding ambient temperature situation.

The jacketed low-temperature cell (Figure 1) was used primarily for preliminary work and fixed, low-temperature measurements. The SCE reference electrode contacts the low-temperature test solution through an intermediate nonaqueous salt bridge and a Luggin capillary probe. The intermediate salt bridge serves two functions: protection against contamination of the nonaqueous test solution by water from the reference electrode; and thermal isolation of the SCE from the low-temperature environment (31). Reference electrode probe-working electrode spacing is adjustable (1 mm is usual) and the spherical joint permits precise electrode alignment. The small volume of the cell (approximately 10 ml) is advantageous in that consumption of difficult to purify nonaqueous solvents is low and thermal equilibrium is established fairly rapidly. Cell cooling is accomplished by immersion in an open top 4-liter dewar containing a solvent slush bath (dry-ice refrigerant) (32). Cell temperature is

![Figure 1. Low-temperature electrochemical cell for fixed temperature measurements](image-url)

---

(20) E. V. Kasatkin, A. A. Rakov, and V. I. Veselkovskii, Soc. Electrotech., 3, 923 (1967).

monitored by a copper-constantan thermocouple (0 °C reference junction) with read-out to a potentiometer (Rubicon Model 2730) or a strip-chart recorder (Sargent Model SR). For experiments conducted in the −60 °C range where solvent slush baths were sometimes inconvenient (or toxic), methanol coolant was circulated through the cell jacket using a thermostatically regulated bath (Beckman Thermocirculator 18100) fitted with a dry-ice/methanol heat exchanger (Haake Model K-60). A +40 to −59 °C contact thermometer provided ±1 °C regulation. Cell-jacket frosting and excessive heat losses to the surroundings were reduced by placing the entire cell assembly with a styrofoam insulating housing.

A variable temperature electrochemical cryostat (Figure 2) was constructed which retains the desirable features of the electrode configuration in the cell of Figure 1. Operation of this cryostat requires only about 4 ml of nonaqueous solvent and has low thermal mass, thus improving its thermal response time. Uniform temperature distribution as well as deaeration of the test solution is accomplished by passing highest purity nitrogen through the long stainless steel hypodermic needle immersed in the solution to be studied. The length of the reference electrode probe is adjusted to provide 1-mm working-reference electrode spacing. The reference electrode junction A consists of a cracked glass tip constructed by fusing a 0.5-mm diameter soft glass rod into a slightly larger hole formed at the tip of the borosilicate glass reference electrode probe. This junction has been found highly effective in preventing water contamination of the nonaqueous test solution while maintaining good electrical contact under low-temperature conditions. A planar platinum working electrode is shown in Figure 2, although a gold or amalgamated platinum electrode could have been used as well. In constructing platinum electrodes, it is important to avoid completely sealing the joint holding the electrode because, when cold, the partial vacuum created will force solvent through the nonvacuum tight borosilicate glass seal around the platinum. This problem is simply avoided by leaving a small hole in the exterior portion of the electrode holder. The vacuum jacketed cryostat dewar B has been strip silvered to facilitate viewing of the electrode arrangement under low-temperature conditions. This is quite valuable when working with a supercooled solvent that may accidentally crystallize or with a marginally soluble supporting electrolyte that may precipitate.

Cooling of the cryostat is achieved by passing compressed, dry nitrogen gas through a copper coil immersed in a liquid nitrogen (LN$_2$) heat exchanger (4-liter dewar); and then through the vacuum jacketed dewar of the cryostat. The cooling gas flow rate is indicated by a flowmeter (Gilmont No. 4) located at the cold LN$_2$ outlet and adjusted by means of a back pressure valve to a value slightly in excess of the cooling rate necessary to balance the heat leaks of the cryostat at the lowest control temperature desired. A 24-ohm, vacuum jacketed heater is located in the gas inlet line between the dewar B and the LN$_2$ heat exchanger. The heater is powered by a 55-watt programmable dc power supply (Kepco Model CK-36-1.5 M). The temperature of the cooling gas and, in turn, the cryostat is automatically regulated with a Leeds and Northrup Speedomax W recorder-controller (series 80 C.A.T. proportional controller) equipped with a copper-constantan sensing thermocouple. When the sensing thermocouple, which is located in the cold LN$_2$ gas space surrounding the low-temperature electrochemical cell, indicates a difference between actual gas temperature and controller set point temperature, the C.A.T. controller programs the heater power supply to provide a heater current proportional to the actual set-point temperature difference. This controlling action continues until the set point temperature is reached, at which point a steady state is established where heat and refrigeration fluxes just balance. With this system, any temperature in the range 300 to approximately 90 °K can be set and maintained to ±0.2 °C. A second thermocouple immersed in the test solution is used to measure the actual electrochemical cell temperature. The dynamic behavior of this controller-cryostat system is such that a 150 °K temperature excursion from thermal equilibrium at 300 °K to thermal equilibrium at 150 °K can be made in approximately 20 minutes and 10 °K changes can be made from one equilibrium set-point temperature to another in as little as 6–7 minutes.

Electrochemical Apparatus. The potentiostat used in these studies is similar in design to that described by Brown et al. (33). Potentiostat current output capability was boosted to 0.5 ampere by incorporating a Hewlett-Packard Model 467A power amplifier into the control amplifier (Philbrick P25A) feedback loop and a Philbrick/Nexus Model 2001 booster amplifier into the current transducer (Philbrick P25A) feedback loop. Compensation for ohmic drop

between the working and reference electrodes of the electrochemical cell was provided using the current transducer to supply a positive feedback signal proportional to the cell current. The voltage follower amplifier (Philbrick PS5A1U) was mounted in a small chassis external to that of the main potentiostat in such a fashion as to minimize the length (i.e., noise pick-up capability) of the high impedance reference electrode connection. A similar arrangement was described earlier by Schroeder (30). In the work to be described here, it was found useful to include a small (50 pfd) capacitor which acts as a high frequency bypass between the auxiliary electrode and the positive input of the voltage follower amplifier (33). This arrangement provided increased potentiostat stability for short time experiments. High-speed integration of the current-time transient for chronocoulometry experiments employed conventional circuitry (RC time constant = 10^{-2} \, \text{sec}). The integrator was armed and reset using a FET switch. This configuration minimized integrator drift and switching transients.

The signal generator used to drive the potentiostat with triangular waveforms for cyclic voltammetry, the potential step (both single and double) waveforms for chronomperometry and/or chronocoulometry is derived from a modification of the circuit developed by Fox and Reilley (34), which is described more fully elsewhere (35).

A Hewlett-Packard Model 7004-A X-Y recorder or a Tektronix Model 564 storage oscilloscope was used for signal monitoring purposes. For most of the experiments described, amplify high-speed transient signals was accomplished by photographically recording the oscilloscope trace and manually treating the data. However, during the latter stages of this investigation, a fully automated computer controlled data acquisition facility became available. This system, based on a Raytheon Model 706 computer, generates the potentiostat excitation waveforms, acquires and displays the experimental data, and performs on-line calculations to analyze the data rapidly. Hardware and software details of this system are described elsewhere (36).

Nonaqueous Solvents—Purification Procedures. Spectrograde acetonitrile (Eastman) as supplied usually contains 50–100 mM water depending on the batch. Two drying procedures were evaluated since water is a moderately strong nuleophile in acetonitrile and scavenes cation radicals while acting as a proton donor for the scavenging of anion radicals. Repetitive trap to trap distillation of acetonitrile from P_{2}O_{5} (2–3 g/150 ml) on a vacuum line reduced the water content to ca. 3 mM as determined by Karl Fischer amperometric titration and by gas chromatography; 6 ft \times \frac{1}{4}\text{-in. Porapak Q column (Waters Associates), column temperature 220 \, ^{\circ}\text{C}, He flow ca. 70 ml min^{-1}, detector temperature 225 \, ^{\circ}\text{C}}. The second method evaluated was a simplified version of the method previously described by Osa and Kuwana (37). A 100-ml volume of aluminum oxide (Merck reagent) activated at 350 \, ^{\circ}\text{C} in a muffle furnace for several hours and subsequently cooled in a vacuum desiccator was slurried with 1 liter of the spectrograde solvent, shaken at intervals, and allowed to stand 48 hours before use. Gas chromatographic examination of this "dry" solvent showed water content comparable to that obtained with the more laborious vacuum line technique. A small but readily detectable decrease in the water content can be effected by treating the ca. 3 mM water/acetonitrile with a second batch of activated alumina. This second and simpler drying method was adopted as standard procedure.

Butyronitrile (Eastman White Label) was found by the GC technique above to contain approximately 0.5% organic impurities, presumably unsaturated nitriles, as well as ca. 10 mM water. An adaptation of the acetonitrile purification method of O'Donnell et al. (38) was used to oxidatively remove the organic contaminants. Butyronitrile was twice heated at 75 \, ^{\circ}\text{C} and stirred for several hours with a mixture of 7.7 grams of Na_{2}CO_{3} and 11.5 grams of KMnO_{4}, performing butyronitrile. The mixture was then covered by distillation under a N_{2} pressure of 15 mm of Hg. The middle fraction (\frac{1}{2}\% volume) of the second distillation was dried over activated alumina as described above for acetonitrile. Examination of the "purified" solvent by gas chromatography showed less than 1 mM H_{2}O and drastically reduced organic impurity content. Water is essentially immiscible with BN, the saturation level being approximately 10–12 mM (by GC). One impurity, ca. 0.2 mM (by flame ionization detector) was not removale by this purification procedure.

Eastman White Label propionitrile (PN) was subjected to the permanganate distillation treatment using the same mole ratio of solvent to Na_{2}CO_{3} and KMnO_{4} as in the case of butyronitrile. This treatment was followed by distillation and drying over activated alumina as above. The resulting material showed negligible organic impurities and ca. 2 mM water.

Spectroquality dimethylformamide (DMF) supplied by Matheson, Coleman and Bell was further purified as described by Bard (39). Both methods A and B of Reference 39 were tested. No significant difference in the quality of DMF produced by the two methods was observed in our experiments; consequently, the simpler method A was used. Examination of the purified solvent by gas chromatography showed no detectable amount of water or dimethylamine to be present. On standing at room temperature for several weeks under N_{2}, solvent decomposition occurred with the formation of dimethylamine. Solvent decomposition can be arrested by storing the frozen solid at -78 \, ^{\circ}\text{C (dry-ice/ methanol)} under vacuum. Crystallization must be induced by rapid cooling to 77 \, ^{\circ}\text{K followed by warm-up to -78 \, ^{\circ}\text{C since DMF is readily supercooled. DMF can be stored in this manner for more than six months without detectable (by GC) dimethylamine formation.}

Spectroquality methylene chloride (Matheson, Coleman and Bell) was alumina dried and used without further purification. Water content was less than 2 mM by gas chromatography.

Reagent grade absolute ethanol (U.S. Industrial Chemicals Co.) and methanol (J. T. Baker Chemical Co.); and iso-propanol (J. T. Baker Chemical Co.) were used without additional purification.

Supporting Electrolytes and Chemicals. Tetraethylammonium perchlorate (TEAP) manufactured by Eastman and lithium perchlorate (G. F. Smith) were twice recrystallized from 50:50 (v:v) absolute ethanol/water. Tetrabutylammonium perchlorate (TBAP) from Southwestern Analytical Chemicals was used without further purification. All three salts were dried under vacuum at 70 \, ^{\circ}\text{C for at least 24 hours followed by prolonged pumping in a vacuum desiccator over P_{2}O_{5}. The P_{2}O_{5} was replaced at frequent intervals until it remained powdery. The salts were stored under vacuum over fresh P_{2}O_{5}.

Ferroene (Alpha Inorganics) was purified by repeated recrystallizations from cyclohexane, 9,10-Diphenylanthracene (DPA) from Aldrich Chemical Co. was recrystallized from ethanol. No difference in electrochemical behavior

---

(34) L. E. Fox and C. N. Reilley, unpublished work.
Table I. Solvent-Supporting Electrolyte Systems for Low-Temperature Electrochemistry (LTE)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>mp, °C</th>
<th>Dielectric constant</th>
<th>Supporting electrolyte</th>
<th>Low-temperature serviceability limit, °C</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Protic Solvents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-PrOH</td>
<td>-88</td>
<td>18.3</td>
<td>0.1M LiClO₄</td>
<td>-80</td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>-96</td>
<td>32.6</td>
<td>1.0M LiClO₄</td>
<td>-90</td>
<td></td>
</tr>
<tr>
<td>EtOH</td>
<td>-117°</td>
<td>24.3</td>
<td>0.5M LiClO₄</td>
<td>-100 to -105</td>
<td></td>
</tr>
<tr>
<td>B. Aprotic Solvents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CN</td>
<td>-45</td>
<td>36.7</td>
<td>0.1M TEAP or TBAP</td>
<td>-45</td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>-61°</td>
<td>36.7</td>
<td>0.1M TBAP</td>
<td>-78</td>
<td></td>
</tr>
<tr>
<td>CH₃Cl₂</td>
<td>-96</td>
<td>9.1°</td>
<td>0.1M TBAP</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>(PN)CH₂CH₂CN</td>
<td>-104</td>
<td>27</td>
<td>0.1M TBAP</td>
<td>-100</td>
<td></td>
</tr>
<tr>
<td>(BN) CH₃(C₂H₅)CN</td>
<td>-112</td>
<td>20.3</td>
<td>0.1M TBAP</td>
<td>-105</td>
<td></td>
</tr>
<tr>
<td>69 wt % BN</td>
<td>-132</td>
<td>?</td>
<td>0.1M TBAP</td>
<td>-118</td>
<td></td>
</tr>
<tr>
<td>31 wt % PN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 298 °K.
* Low-temperature limit for electrochemistry is determined by rapid increase in viscosity and electrical resistance.
* Supercools to -150 °C.
* Supercools to -80 °C.
* At -85 °C = 15.5.
* 0.1M TBAP precipitates.

was noted between recrystallized and unrecrystallized samples. Phenazine (Columbia Organic Chemicals) was used without further purification, and nitrobenzene (J. T. Baker Chemical Co.) was purified by vacuum distillation at 60 °C followed by passage through an alumina column.

RESULTS AND DISCUSSION

Low-Temperature Solvent-Supporting Electrolyte Systems. As discussed by Angell (40), the fundamental limitation imposed on a low-temperature electrolytic device whose successful operation depends on diffusive or convective mass transport of the electroactive species is the temperature \( T_0 \) at which crystallization or glass formation of the electrolyte occurs. Although \( T_0 \) is an absolute lower limit, usually above 100 °K, the maximum viscosity or solution resistance that can be tolerated in a particular application will generally raise the low-temperature limit. For use in low-temperature electrode mechanism studies where free radical species are likely to be intermediates, it is desirable that the solvent-supporting electrolyte have maximum potential span between anodic and cathodic limits, lowest possible freezing or glass point consistent with a solution resistance capable of providing millisecond or faster time resolution with transient electrochemical techniques, and minimum chemical reactivity with free radical intermediates. A variety of solvent-supporting electrolyte combinations were tested with respect to these criteria. Table I summarizes the properties of the most promising systems. The time response characteristics of these important solvents will be considered in the next section.

Butyronitrile (BN) and propionitrile (PN) are not commonly used electrochemical solvents, although some scattered reports of their use have appeared (41-43). In addition to their desirable low-temperature properties, they have several useful features which recommend them for ambient temperature studies as well. For example, in comparison with acetonitrile (AN), it is far easier to lower the trace water level of BN to less than 1 mM because of the greater BN/water size discrimination ratio when using molecular sieves as drying agents and because of the relatively high immiscibility of water in BN which increases its affinity for the surface of activated alumina drying agents. In addition, the solubility of many high molecular weight aromatic hydrocarbons is much greater in PN and BN than in acetonitrile, in some cases approaching their solubilities in DMF.

The anodic potential limit of BN is unfortunately not as large as can be attained with spectroquality (carefully dried) acetonitrile. We find that this is not due to oxidation of BN or TBAP but due to oxidation of a difficult to remove impurity having an \( E_c \) of +2.40 V vs. SCE. The UV spectrum of the "purified" BN reveals an impurity absorbing at \( \lambda_{max} \) 260 nm (o.d. = 1.0, 1-cm path length). An impurity level of 0.1 mM is estimated using an extinction coefficient of 10°. All attempts to remove this apparently aromatic impurity have been unsuccessful to date; however, no significant influence on the results of this work is expected due to its presence. The cathodic potential limit of BN, on the other hand, is substantially more negative on a bright platinum electrode than either AN or DMF. Since all

(42) A. Stanienda and G. Bieli, Z. Phys. Chem. (Frankfurt am Main), 52, 254 (1967).

146 • ANALYTICAL CHEMISTRY, VOL. 44, NO. 1, JANUARY 1972
Table II. Potentiostat-Cell Time Response at Low-Temperatures. Potential-Step Excitation

<table>
<thead>
<tr>
<th>Solvent supporting-electrolyte</th>
<th>Temperature °C</th>
<th>iR Compensation</th>
<th>95% Response times, µsec</th>
<th>95% Response times, µsec</th>
<th>99% Response times, µsec</th>
<th>99% Response times, µsec</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN/0.1M TEAP*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.0</td>
<td>60.5</td>
<td>105</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>263.0</td>
<td>93</td>
<td>104</td>
<td>64</td>
<td>156</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>247.8</td>
<td>124</td>
<td>128</td>
<td>68</td>
<td>180</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>238.0</td>
<td>151</td>
<td>152</td>
<td>72</td>
<td>220</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>228.5</td>
<td>161</td>
<td>...</td>
<td>88</td>
<td>...</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>DMF/0.1M TBAP*</td>
<td>300.0</td>
<td>370</td>
<td>240</td>
<td>92</td>
<td>...</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>238.0</td>
<td>1073</td>
<td>300</td>
<td>148</td>
<td>...</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>215.1</td>
<td>2150</td>
<td>670</td>
<td>220</td>
<td>...</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>194.5</td>
<td>5900</td>
<td>3200</td>
<td>5000</td>
<td>380</td>
<td></td>
</tr>
<tr>
<td>BN/0.1M TBAP*</td>
<td>298.0</td>
<td>760</td>
<td>150</td>
<td>34</td>
<td>265</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>194.2</td>
<td>5500</td>
<td>250</td>
<td>118</td>
<td>340</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>181.4</td>
<td>15400</td>
<td>3000</td>
<td>210</td>
<td>4600</td>
<td>500</td>
</tr>
<tr>
<td>69% BN-31% PN/0.1M TBAP*</td>
<td>295.7</td>
<td>620</td>
<td>108</td>
<td>28</td>
<td>186</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>190.5</td>
<td>6270</td>
<td>960</td>
<td>100</td>
<td>2000</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>176.9</td>
<td>12350</td>
<td>1750</td>
<td>170</td>
<td>3500</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>170.2</td>
<td>22800</td>
<td>4200</td>
<td>370</td>
<td>7300</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>161.6</td>
<td>d</td>
<td>6400</td>
<td>...</td>
<td>10000</td>
<td>...</td>
</tr>
</tbody>
</table>

* From +0.2 V to +0.7 V vs. SCE.
* Electrode area = 0.035 cm².
* Electrode area = 0.030 cm².
* Too high resistance to compensate. Loss of potential control occurred.
* Reference (48).

Three solvents have essentially identical cathodic limits on mercury, provided that careful purification procedures have been followed, this probably indicates that reduction of BN is platinum surface controlled and is more difficult than that for AN or DMF. As expected, propionitrile exhibits intermediate behavior with respect to ease of drying, solubility, and cathodic potential limit. Provided that the anodic potential limit difficulty can be eliminated, BN appears to be an excellent solvent for electrochemiluminescence studies where solubility limitations have hampered the use of AN and the proximity of the sequential oxidation and reduction processes to the background limits of DMF have been a problem. The low-temperature behavior of the anodic and cathodic background potential limits for a TBAP/DMF solution at a platinum electrode is unique among the solvents studied to date. Figure 3 shows a comparison between a background cyclic voltamogram for a DMF solution containing 0.1M TBAP taken at room temperature and a similar scan taken at 194 °K. Clearly a substantial increase in the available potential “window” is realized at low-temperatures. The possibility exists that this potential span increase is due to the formation of a cyclic DMF dimer which has been suggested to have the structure (44):

![Dimer Structure]

The dimeric species would have to be both more difficult to oxidize and difficult to reduce than the monomer to account for this observation. From the thermodynamic parameters for the DMF dimerization (45), we calculate that DMF is more than 97% in the dimer form at 195-200 °K. DMF dimer formation may also be the reason for the substantial supercooling behavior noted in Table I.

**Time Response Degradation at Low Temperatures.** A potentially serious problem in obtaining high speed transient electrochemical measurements at low-temperatures is the iR drop due to uncompensated resistance between the working and reference electrodes. This resistance depends on both the geometric configuration of the cell and the conductivity of the solvent-supporting electrolyte medium. Potentiostat electrochemical cell design factors which permit iR drop compensation using the positive feedback approach have been discussed in detail (30, 33, 46); however, quantitative

---


---

![Figure 3](image-url)
Figure 4. Effect of $iR$ compensation on time response of single potential step chronocoulometry at 194 °K: 2.87 mM ferrocene/0.1 M TBAP/DMF/platinum electrode; potential step from +0.2 V to +0.7 V vs. SCE
A. No $iR$ compensation  
B. 5 Kohms $iR$ compensation

indications of the maximum obtainable time resolution following a potential step excitation have been limited to low impedance dummy cells or highly conducting aqueous media. Smith (47) has demonstrated nearly complete $iR$ compensation in high resistance aprotic media (a few Kohms) enabling ac polarographic measurements to be made approaching 1 KHz frequencies.

Measurement of the resistance between working and auxiliary electrodes of the low-temperature cells in 0.1 M TBAP solutions of DMF, BN, and BN/PN at 194 °K indicates that uncompensated resistances as high as 3-5 Kohms will be encountered in low-temperature electrochemical studies. Table II summarizes the nonfaradaic response times obtained from current-time transients measured following application of a 0.5-volt potential step to the cell. Charging current decay times to 95 and 99% completion, which place a lower time limit on when the earliest faradaic current measurements may be taken, were measured for both zero and maximum $iR$ compensation. The necessity of employing positive feedback $iR$ compensation under these conditions in order to effect rapid double layer charging is illustrated. The results presented in Table II indicate that for temperatures down to 190 °K double layer charging can be effected within 0.3 millisecond for the nitrile systems (slightly longer for DMF) so that faradaic measurements should be feasible in the 1-2 millisecond range. In the temperature range 190 to 160 °K a more rapid increase in time response degradation is observed. Faradaic measurements are still possible after 2-5 milliseconds. The time response degradation is correlated with a drastic increase in solvent viscosity over this same temperature range. Further support for this observation is obtained from the dielectric behavior of these solvents in an ESR cavity cooled to 190 °K. As the temperature is lowered to 160 °K, substantial increase in the dielectric loss of the sample is observed whose temperature dependence is distinctly nonlinear.

Further verification of the feasibility of performing potentiostatic transient experiments at low-temperatures is obtained from response time measurements under faradaic conditions. In a potential step chronocoulometry experiment, short time deviations from linear $Q$ vs. $t^{1/2}$ behavior are indicative of $iR$ drop difficulties if an ideally behaved electrochemical system is studied and a sufficiently large potential step has been applied to the electrode to cause the electron transfer reaction to proceed under diffusion controlled conditions (48). The results of such a chronocoulometry experiment employing the reversible oxidation of ferrocene on a platinum electrode as the model system are illustrated in Figure 4. With no $iR$ compensation applied at 194 °K, deviations from the linear $Q$ vs. $t^{1/2}$ relation are observed for the first 60 milliseconds of the transient. However, at full $iR$ compensation, $Q$ vs. $t^{1/2}$ linearity is extant after only 1 millisecond following application of the potential step. The low-temperature chronocoulometric behavior of ferrocene in the other solvent supporting electrolyte systems shown in Figure 5 indicates that under all low-temperature conditions tested, faradaic current or charge data, corrected for $iR$ drop effects, may be acquired at times as short as 1-3 milliseconds. This does not represent any theoretical short time limit but merely reflects the bandwidth, stability, and voltage output limitations of the potentiostat used in these studies when coupled to very high resistance, low-temperature cells.

**FACTORS GOVERNING FARADAIC ELECTROCHEMICAL RESPONSE**

Temperature Dependence in the Absence of Chemical Kinetic Complications. In all electrochemical methods involving total or partial mass transport control of the measured response, both the potential at which the electrode reaction takes place and the flux of electroactive species impinging on the electrode surface are temperature dependent. If the electrochemical experiments for a particular low-tempera-


ture investigation are all carried out isothermally, then these temperature dependent factors can be ignored and the results of conventional electrochemical diffusion theory may be applied to their interpretation.

Isothermal operation unnecessarily restricts the utility of low temperature techniques in electrode mechanism studies. The approach conceived in the present study is to employ the variable temperature cryostat so that primary electron transfer processes can be isolated via a "cryoquench" of the coupled chemical reactions. Kinetic complications can then be reintroduced in a controlled fashion as ambient thermal conditions are subsequently approached. In comparison, conventional studies of complex electrode mechanism using techniques such as cyclic voltammetry, current reversal chronopotentiometry, ac polarography, etc., isolation of the primary electron transfer is achieved by increasing the frequency of the excitation signal to the extent that coupled chemical reactions cannot significantly influence the measured response during the short observation time. Sufficiently high frequency measurements are not always possible because of capacitive or ohmic drop degradation of the observed response. It is conceivable then that low-temperatures or a combination of low-temperatures and high frequencies would be advantageous for studying coupled chemical reactions. In order to be able to define these situations, a quantitative appreciation of the low temperature behavior of some important electrochemical techniques is desirable.

Consider first those temperature dependences that are technique specific and are characteristic only of the mass transport and heterogeneous electron transfer processes for the simple reaction

\[ O + ne^- = \frac{\Delta G_{b}}{\Delta G_{e}} R \]  

(1)

Chemical reactions taking place on the electrode surface and adsorption will not be considered.

Cyclic Voltammetry. In a cyclic voltammetry experiment, two groups of temperature dependent factors may be identified: those related to electrode potential: the standard electrode potential, \( E^0 \), and the liquid junction potential in the reference electrode salt bridge; and those related to the flux: diffusion coefficients of oxidized and reduced species, electrode area (Hg electrodes), and concentration of electroactive material [through the solvent density temperature coefficient (49)].

When \( k_{b,0} \) and \( k_{b,1} \) in Equation 1 are sufficiently large that Nernstian behavior is maintained at all times during the potential sweep, the standard potential at which the reaction takes place is related to the peak potential of the voltammogram through (50):

\[ E_p = E^0 + \frac{RT}{nF} \left( \ln \frac{D_s}{D_b} + 1.109 \right) \]  

(2)

in which the temperature dependent factors are \( D_s \), \( D_b \), and \( E^0 \). Since diffusion is an activated rate process (51), \( D_s \) and \( D_b \) will follow a Boltzmann temperature dependence:

\[ D_s = D_s' \exp\left(-\frac{E_{s,0} \text{diff}}{RT}\right) \]  

(3)

where \( D_s' \) is the frequency factor for diffusion and \( E_{s,0} \text{diff} \) is the diffusional activation energy. The standard potential of an electrode reaction is proportional to the free energy change accompanying the electron transfer; its temperature dependence is, therefore, simply:

\[ E^0 = \frac{1}{nF}(TA\Delta S - \Delta H^0) = T \frac{\Delta G^0}{RT} \frac{\Delta H^0}{nF} \]  

(4)

Combining Equations 2-4 gives:

\[ E_p(T) = T \frac{\partial E_0}{\partial T} + \frac{R}{nF} \ln \left( \frac{D_s'}{D_b'} \right) + \frac{E_{A,0} \text{diff} - E_{A,0} \text{diff}}{2RT} \left( \frac{\Delta H^0}{RT} - 1.109 \right) \]  

(5)

Under the simplifying assumption that the diffusion coefficients of O and R are equal at all temperatures, the temperature shift of \( E_p \) will be controlled principally by the magnitude and sign of \( \Delta S^0 \), \( \Delta S^0/nF = \Delta E^0/\partial T \); \( \Delta S^0 \) is positive for an oxidation and is negative for a reduction, provided the initial state is a neutral species and the entropy change due to solvent reorganization is less than the entropy change of the electron transfer proper. Extensive measurements of \( \Delta E^0/\partial T \) for inorganic redox processes have been tabulated (52). Typical values are \( \pm 1 \) mV/deg. Hoiitink (53) measured the temperature shift of the polarographic \( E_{1/2} \) for a few aromatic hydrocarbon reductions and found at most a 0.4 mV/deg shift over the temperature range 298–348 °K.

Inclusion of quasi-reversible or irreversible charge transfer in Equation 1 alters the low-temperature behavior of the observed voltammogram. Equation 5 now becomes:

\[ E_p = E^0 - \frac{RT}{nF} \left( 0.780 + \ln \frac{D_s' \text{diff}}{D_b'} - \ln k_{s,1} \right) \]  

(6)

\[ k_{s,1} = k_p \left[ \frac{kT}{2\pi m} \right]^{1/2} e^{-\lambda_1 kT} \]  

(7)

where the expression for \( k_{s,1} \) is that derived from Marcus' quantum mechanical theory of electron transfer at an electrode (54). The reorganization free energy parameter \( \lambda_1 \) may be calculated from a suitable model which describes the energies of solvent reorganization and bond length distortion accompanying charge transfer, but generally is taken as \( 1/2 \) of the value of \( \lambda \) for the corresponding homogeneous electron exchange process. An estimate for \( \lambda_1 \) of 8 Kcal/mole is obtained from the electrode exchange data for Wurster's Blue cation radical (55). The extent of heterogeneous rate constant temperature dependence may conceivably be augmented, however, through the action of specific effects such as adsorption of an electron transfer blocking agent or modification of the physical state of the electrode surface at low temperatures.

In the experimental arrangement used for all studies in this investigation, the reference electrode temperature shift has been effectively minimized by thermostating it at room temperature and noting that the temperature coefficient of the liquid junction potential caused by the temperature gradient along the reference electrode probe is probably \( \sim 10^{-2} \) mV/deg. The thermodynamic arguments and the

The temperature variation to be expected for cyclic voltammetry has been computer simulated for both reversible and quasi-reversible charge transfer cases using a modified, explicit finite difference calculation (36) embodying Equations 2-8. This calculational scheme is patterned after the approach of Feldberg (57); however, in this study, provision has been made to allow independent selection of the time step/distance step ratio and the diffusion coefficient. In this way the stability parameter of the finite difference scheme is independent of the temperature. These calculations specifically account for the temperature dependences of the diffusion coefficients of the reacting species, the $E^\circ$ shift, solvent density leading to increased concentration at low-temperatures, and the heterogeneous rate constant; however, the simplification is made that the transfer coefficient, $\alpha$, is temperature independent.

The results of the finite difference calculations are displayed in Figure 6 where the current function $\chi(at)$ defined by (59):

$$\chi(at) = \frac{1}{nF} \frac{\pi d_{a}FV^{1/2}}{(RT)^{1/2}} C_{0} e^{-\frac{1}{2}}$$

is plotted vs. an $(E - E^{\circ}_{298} + \Delta E)$ potential scale.

For the reversible charge transfer case (Figure 6A), the peak potential shift toward more positive potentials (calculated for a reduction) controlled by the entropy change of the electron transfer process is shown along with a decrease in the anodic–cathodic peak potential separation, $\Delta E_{p}$, as the temperature is lowered. In addition the low-temperature voltammograms exhibit much narrower peaks than their room temperature counterparts.

In contrast cyclic voltammogram morphology for quasi-reversible charge transfer shows an increase in anodic–cathodic peak separation (Figure 6B); and a competition between peak broadening due to a smaller $k_{eq}$ and the normal peak narrowing as the temperature is lowered. The $E^\circ$ shift is identical to the reversible case. The finite difference simulations for this situation were made assuming a $\lambda_{eq}$ value of 20 Kcal/mole. This is probably too large for heterogeneous electron transfer involving extensively delocalized π aromatic systems; however, it is likely to be reasonable for many inorganic or organometallic systems which involve substantial inner-sphere reorganization free energy in addition to the solvent reorganization free energy. Primarily $\lambda_{eq} = 20$ Kcal/mole was chosen to emphasize the qualitative effects one might expect in low-temperature peak voltammetry resulting from slow electron transfer. Including double layer effects in Equation 7 as outlined by Mohlner (58) would have allowed a smaller $\lambda_{eq}$ to produce similar low-temperature effects.

The cyclic voltammetric behavior of several “perfectly” reversible “model” 1e− transfer systems at a platinum “bead” electrode was investigated in 0.1 M TBAP solutions of AN, DMF, and BN over the available temperature range of each solvent in order to experimentally supplement the theoretical calculations. The oxidation of ferrocene in the three solvents showed an expected cathodic peak potential shift corresponding to a $\Delta E^{\circ}$ of 0.31 mV/deg, a decrease in $\Delta E_{p}$.


and diffusional peak narrowing only if \( iR \) compensation was employed. These results were found to be highly dependent on the history of the platinum surface. On an oxidized platinum surface, prepared by immersion of the electrode in concentrated nitric acid or by rapidly scanning the electrode potential at \( \sim 10 \) V/sec from 0 to +3.0 V vs. SCE in a solution not containing ferrocene, reversible behavior was observed at room temperature; however, extensive peak broadening and \( \Delta E_p \) increase occurred at temperatures lower than 253 °K. The electrode could be consistently "regenerated" by scanning the electrode potential from 0 to +3.0 V vs. SCE at \( \sim 10 \) V/sec in a deaerated solution. On a reduced surface prepared in this manner, the theoretical \( \Delta E_p \) separation was observed down to about 200 °K. Further lowering of the temperature produced increasing \( \Delta E_p \) separation. In BN at \(-100 \) °C, for example, \( \Delta E_p \) was 110 mV at a scan rate of 135 mV/sec which rapidly increased as the freezing point was approached. Similar results were observed for the \( 1e^- \) irreversible oxidation of 9,10-diphenylanthracene to its monocation radical \( \Delta E_p/\Delta T = 0.33 \text{ mV/deg} \) and the \( 1e^- \) reductions of nitrobenzene and phenazine with \( \Delta E_p/\Delta T \) of 0.36 mV/deg and 0.45 mV/deg, respectively.

The peak widths and \( \Delta E_p \) separations for these systems were very much less sensitive to platinum surface history than ferrocene although narrower peaks could definitely be obtained when the electrode was electrochemically cleaned by scanning into the anodic background prior to a reduction or into the cathodic background prior to an oxidation. No attempt was made in the present work to quantitatively evaluate the relative contributions of residual ohmic drop and slow charge transfer to peak broadening and the larger than theoretical \( \Delta E_p \) separations observed at low-temperatures. Qualitatively, however, some heterogeneous slow charge transfer control is indicated by virtue of the platinum surface effect and an \( iR \) drop contribution is suggested by the similarity in the peak potential separations observed for different redox couples. Consequently, a word of caution is in order concerning attempts to measure heterogeneous rate constants at low-temperatures. Extreme care must be taken to ensure that the electrode surface can be prepared in a reproducible and hopefully understood state, and that the technique used to measure \( \alpha \) is minimally affected by \( iR \) drop problems. Furthermore, one must be prepared to deal with adsorbed solution components, possibly nulelectroactive, which may act as electron transfer blocking agents.

**Chronoamperometry and Chronocoulometry.** Although cyclic voltammetry possesses considerable utility for making qualitative measurements, the complex nature of its associated temperature dependences limits the quantitative usefulness of this technique for studies of coupled chemical reactions at low temperatures. By comparison the potential step techniques, chronoamperometry and chronocoulometry, are more suitable for such quantitative studies since all electrode potential temperature dependences can be eliminated from the measured response by proper selection of the step potentials. \( E_{	ext{initial}} \) and \( E_{	ext{final}} \) are selected from voltammetric studies. In a low-temperature environment, the voltammetric wave will be shifted from its room temperature position. \( E_{	ext{initial}} \) will have to be reset to a less negative (less positive for an oxidation) potential by an amount corresponding to the voltammetric wave shift in order to prevent the electrode reaction from occurring. \( E_{	ext{final}} \) is then adjusted to a value \( \sim 60-100 \text{ mV} \) beyond the peak potential of the low-temperature voltammogram. The double potential step mode has identical low-temperature requirements for readjusting the room temperature initial and final potentials.

With the potential step limits set in this manner, only the diffusion coefficient, concentration, and electrode area temperature dependences enter into the \( i \) vs. \( t \) and \( Q \) vs. \( t \) responses:

\[
i(t < \tau) = \frac{nFA D_{0} v^{1/2} C_{0}^*}{\pi^{1/2} t^{1/2}} \quad (9)
\]

\[
i(t > \tau) = \frac{nFA D_{0} v^{1/2} C_{0}^*}{\pi^{1/2}} \left[ \frac{1}{(t-\tau)^{1/2}} - 1 \right] \quad (10)
\]

\[
Q(t < \tau) = \frac{2nFA D_{0} v^{1/2} C_{0}^*}{\pi^{1/2}} \left[ (t)^{1/2} - (t-\tau)^{1/2} \right] \quad (11)
\]

\[
Q(t > \tau) = \frac{2nFA D_{0} v^{1/2} C_{0}^*}{\pi^{1/2}} \left[ (t)^{1/2} - (t-\tau)^{1/2} \right] \quad (12)
\]

The simple temperature dependence of the single potential step \( Q \) vs. \( t^{1/2} \) or \( i \) vs. \( t^{1/2} \) plots can be used to evaluate diffusion coefficient activation energies. Arrhenius plots of chronocoulometric slopes, corrected for concentration temperature dependence, obtained from 2.87mM ferrocene/0.1M TBAP solutions of AN and DMF are shown in Figure 7. Activation energies for ferrocene diffusion are 2.13 Kcal/mole in AN and 3.27 Kcal/mole in DMF.

Double potential step techniques allow complete elimination of temperature dependences other than those due to chemical kinetics through the use of characteristic ratio measurements. With chronocoulometry for example, formation of the ratio of Equation 11 evaluated at \( t = \tau \) and Equation 12 evaluated at \( t = 2\tau \):

\[
\frac{Q_{\tau}}{Q_{2\tau}} = \frac{Q_{\tau} - Q_{2\tau}}{Q_{\tau}} = |2 - \sqrt{2}| = 0.5858 \quad (13)
\]

results in an easily measured temperature independent parameter. In general, two-step electrochemical methods

---

Table III. Temperature Independent Parameters for Two-Step Electrochemical Techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Temperature independent parameter</th>
<th>Characteristic value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double potential step</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chronocoulometry</td>
<td>$\frac{Q(t) - Q_e}{Q_e} = 1 - \left( \frac{1 + \theta}{\theta} \right)^{1/2} + \theta^{1/2}$</td>
<td>0.5858 for $\theta = 1$</td>
</tr>
<tr>
<td>Double potential step</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chronoamperometry</td>
<td>$i_a = 1 - \left( \frac{\theta}{1 + \theta} \right)^{1/2}$</td>
<td>0.2929 for $\theta = 1$</td>
</tr>
<tr>
<td>Double potential step</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chronoabsorptometry</td>
<td>$\frac{A(t) - A_e}{A_e} = 1 - \left( \frac{1 + \theta}{\theta} \right)^{1/2} + \theta^{1/2}$</td>
<td>0.5858 for $\theta = 1$</td>
</tr>
<tr>
<td>Thin-layer</td>
<td>$Q_a$</td>
<td>1.00</td>
</tr>
<tr>
<td>chronocoulometry</td>
<td>$Q_e$</td>
<td>1.00</td>
</tr>
<tr>
<td>Reversal coulometry in</td>
<td>$Q_e$</td>
<td>1.00</td>
</tr>
<tr>
<td>bulk solution</td>
<td>$i_b^p/i_p^s$</td>
<td>3.00</td>
</tr>
<tr>
<td>Cyclic voltammetry</td>
<td>$\tau_e$</td>
<td></td>
</tr>
<tr>
<td>Current reversal</td>
<td>$\tau_n$</td>
<td></td>
</tr>
<tr>
<td>chronopotentiometry</td>
<td>$N = \frac{i_{ring}}{i_{disk}}$</td>
<td>0 &lt; $N$ &lt; 1^e</td>
</tr>
<tr>
<td>Rotating ring-disk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>voltammetry</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In the absence of chemical kinetics.
* With equal forward and reverse current densities.
* Exact value of $N$ depends on electrode geometry.

Table IV. Experimental Verification of Temperature Independence in the Absence of Coupled Chemical Kinetics

<table>
<thead>
<tr>
<th>$\tau$ (msec)</th>
<th>$Q_e/Q_i$ at 298 °K</th>
<th>$Q_e/Q_i$ at 233 °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.554</td>
<td>0.557</td>
</tr>
<tr>
<td>8</td>
<td>0.557</td>
<td>0.568</td>
</tr>
<tr>
<td>20</td>
<td>0.569</td>
<td>0.565</td>
</tr>
<tr>
<td>40</td>
<td>0.570</td>
<td>0.572</td>
</tr>
<tr>
<td>80</td>
<td>0.575</td>
<td>0.568</td>
</tr>
<tr>
<td>200</td>
<td>0.573</td>
<td>0.565</td>
</tr>
<tr>
<td>400</td>
<td>0.574</td>
<td>0.557</td>
</tr>
<tr>
<td>800</td>
<td>0.575</td>
<td>0.541</td>
</tr>
</tbody>
</table>

* Potential step: +0.2 V to +0.7 V vs. SCE for both temperatures. Solution conditions: 1.67mM ferrocene with 0.1M TEAP in acetonitrile.

provide temperature independent ratios in the absence of chemical kinetics. The appropriate ratios and their characteristic values are listed in Table III for several popular techniques.

Experimental confirmation of the $Q_e/Q_i$ temperature independence was obtained through a series of measurements on 1.67mM ferrocene/0.1M TEAP solutions at a platinum "bead" electrode in acetonitrile. Table IV compares $Q_e/Q_i$ at 233 and 298 °K over step times, $\tau$, from 4 to 800 msec and shows that the temperature independence of Equation 12 is obeyed within experimental limits. Double layer charging corrections were made to all $Q_e/Q_i$ ratios using (60):

$$\frac{Q_e}{Q_{i,corr}} = \frac{Q_e - Q_{i,corr}}{Q_e - Q_{i,corr}}$$

where $Q_{i,corr}$ and $Q_{i}$ are the least squares intercepts of the $Q_e(t > \tau) = Q_e(t > \tau)$ vs. $t^{1/2}$ and $Q_e(t < \tau)$ vs. $t^{1/2}$ plots, respectively. With $iR$ compensation applied, at room temperature, these plots showed linear behavior after only 500 μsec following step application and return to the initial potential; while at 233 °K, 850 μsec was required.

Received for review March 29, 1971. Accepted August 2, 1971. One of the authors (R.P.V.D.) wishes to acknowledge support of a National Aeronautics and Space Administration Fellowship (1967-1970). In addition, various aspects of this work were supported by the U.N.C. Materials Research Center under contract DAHC15 67 C 0223 with the Advanced Research Projects Agency and the Air Force Office of Scientific Research, USAF (AFSC), Grant AF-AFOSR-69-1625.