Atomic Energy of Canada Limited

PROGRESS REPORT
CHEMISTRY AND MATERIALS DIVISION
April 1 to June 30 1972

PR-CMa-21

Chalk River, Ontario
August 1972

AECL-4259
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PROGRESS REPORT
April 1, 1972 - June 30, 1972

CHEMISTRY AND MATERIALS DIVISION

Director - T. A. Eastwood
Secretary - Mrs. A. E. Goodale

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# 1. REPORT OF SOLID STATE SCIENCE BRANCH

by

F. Brown

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F. Brown

Secretary

Mrs. T. LaBelle

J.A. Böttiger\(^1\)
F. Chemin\(^2\)
J.A. Davies
L.M. Howe
D.P. Jackson
W.D. Mackintosh
I.V. Mitchell
J.R. Parsons
D.C. Santry
F.W. Saris\(^3\)
M.L. Swanson\(^4\)
J.L. Whitton

G.R. Bellavance (Tg)
C.W.K. Hoelke (Rt)
D. Lanteigne (Tg)
J. Lori (Tg)
H.H. Plattner (Tg)
A.F. Quenneville (Tg)
M.H. Rainville (Rt)
G.A. Sims (Rt)
C. Sitter (Tg)
D.A.S. Walker (Tg)
R.D. Werner (Tg)
O.M. Westcott (Rt)

Shop

L. Dixon (Rt)
B. McGilvray (Rt)

Stores, Services

K.W. Dunlop (LSS)
M.D. Frivalt (LA)
L. Graveline (LA)
W.M. Hartwick (LA)
W.J. Sullivan (LA)

1 NRC Post Doctoral Fellow, arrived 5 April, 1972.
2 Attached Staff from the University of Bordeaux, arrived May 23, 1972.
3 NRC Post Doctoral Fellow, arrived December 29, 1971
4 On leave of absence at University of Utah, U.S.A. from August 16, 1971.
1.2 ION PENETRATION

1.2.1 Dechanneling of MeV Protons
- J.A. Davies, L.M. Howe and J.L. Whitton

The investigation of the dechanneling of protons in germanium (PR-CMa-20, Section 1.2.1) has been continued. Detailed back-scattered energy spectra have been obtained at room temperature for 0.3, 0.6, 1.5 and 2.5 MeV protons incident along the <111>, <110> and <112> axes as well as along the [110] plane. Data have been obtained for the perfectly aligned case as well as for small off-axis tilts (but still within Lindhard's characteristic angle $\theta_f$). An analysis of the experimental data is in progress. However, visual comparison of the spectra suggests that the apparently anomalous dechanneling behaviour for the <111> and <110> axes at 1.5 MeV, as noted in PR-CMa-20, will not be confirmed by the newer and more extensive data.

1.2.2 Determination of Oxygen in Natural Oxides on Group III-V Compound Semiconductor Crystal Surfaces
- I.V. Mitchell and J.L. Whitton

The amounts of oxygen on the [111] and [111] faces of a variety of single crystal compound semiconductors have been measured. The method is essentially that recommended by Amsel$^1$, namely determination via the $^16\text{O}(d,p)^{17}\text{O}$ reaction. Relative yields are converted to absolute amounts through use of a standard, in this case, an anodic tantalum oxide film 300 ± 5Å thick on a tantalum backing. A deuteron beam of 200nA at 850 kev energy was used and the current measured by a beam wobbler$^2$ capable of better than 1% accuracy. Scattered deuterons were filtered out with an aluminum foil.

For most specimens, protons from the $^{14}\text{N}(d,p)^{15}\text{N}$ reaction were clearly resolved, permitting estimates of the amounts of nitrogen present. A 370Å thick silicon nitride film served as a standard in this case.

Our results show that, for specimens prepared by vibratory polishing and a quick chemical etch, oxygen was present at a level of 1 to 3 x $10^{16}$ atoms/cm$^2$ on GaP, InSb, InP, InAs and GaAs. We also see different concentrations on the A and B faces e.g. the Ga face of GaAs shows twice
as much oxygen as the As face.

All specimens showed nitrogen present in an amount corresponding to approximately one monolayer coverage.


1.2.3 2.5 MV Positive Ion Van de Graaff
- G.A. Sims

Three unsoldered resistors were found to be the cause of the magnet power supply instability when operating at high currents (> 10 amps). Normal operating currents were 8 amps or less. One day's running was lost due to fouling of the cooling water system by algae.

The accelerator operating schedule for the past three months is summarized below:

<table>
<thead>
<tr>
<th>Month</th>
<th>Operating time (hours)</th>
<th>Days lost due to failure</th>
<th>Source gas refilling (days)</th>
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<tr>
<td>March</td>
<td>128</td>
<td>1</td>
<td></td>
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<td>April</td>
<td>139</td>
<td>1</td>
<td>1/2</td>
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<td>May</td>
<td>190</td>
<td>1</td>
<td>1/2</td>
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1.3 ELECTRON MICROSCOPY

1.3.1 High Resolution Electron Microscopy Investigation of Defects in Irradiated and Deformed Crystals
- L.M. Howe and M. Rainville

Studies are continuing on the perturbing influence of end-on dislocations on the lattice fringe images obtained by combining the transmitted and one of the diffracted beams. \{111\} lattice fringe images have been obtained in deformed germanium single crystals in the vicinity of dislocations viewed virtually end-on in the foil. Experiments have been performed in which the fringe images have been
obtained under different diffraction conditions. Detailed measurements of the electron micrographs will now be performed to determine to what extent the fringe distribution in the vicinity of the end-on dislocations is dependent upon the diffraction geometry.

1.3.2 Electron Microscopy Studies of Zr₃Al
- L.M. Howe and M. Rainville in collaboration with E.M. Schulson (Materials Science Branch)

Electron microscope investigations are continuing on Zr-Al alloys which have been heat treated to produce a large volume fraction of Zr₃Al. Transmission electron diffraction experiments confirmed that the Zr₃Al was present as an ordered f.c.c. structure. Recent experiments have also revealed that it is not possible to quench disorder into the system, at least by the conventional techniques used to date. Extended dislocations and stacking faults have been observed which suggest that the stacking fault energy is fairly low in Zr₃Al whereas the antiphase boundary energy is probably very high. Diffraction contrast experiments are being undertaken to determine the nature of the stacking faults as well as the Burgers vectors of the dislocations.

1.3.3 Atom Imaging by Phase Contrast
- J.R. Parsons, C.W. Hoelke and H.M. Johnson (Health Physics Branch)

As described in PR-CMa-20 atomic sites occupied by heavy atoms in biological and metallurgical structures can be imaged with the electron microscope by phase contrast. This method of single atom imaging is unique in that atomic sites occupied by heavy atoms can be detected by reversing the heavy atom contrast. This is accomplished by imaging the same area at two different defocus values. If the microscopist selects the correct two defocus values, the heavy atoms will have black contrast in the smaller defocus image and white contrast in the larger defocus image.

In any one of these defocus image pairs there are at least six factors working against good heavy atom contrast. If all six factors are properly controlled by the microscopist, a good image pair results. These factors and the tests used to detect their presence are as follows:
(1) Electron-beam source incoherence; single crystal pointed filaments are used and their optical brightness on the image plane tests their degree of coherence.

(2) Carbon contamination; its presence generates "wings" on the diffractogram (i.e. on the optical diffract: on pattern of the image structure recorded photographically).

(3) Objective lens astigmatism; the diffractogram rings are elliptic.

(4) Specimen motion; the diffractogram rings fade out in a direction parallel to the motion.

(5) Incorrect defocus; tested by the number and position of the diffractogram rings.

(6) Substrate thickness and structure; these contribute to the "noise" in the images. (The present substrates are 10Å thick evaporated carbon films.)

Figures 1.3.3.1(a) and (b) show a good quality defocus pair and their corresponding diffractograms. The diffractograms indicate the absence of image astigmatism, specimen motion and correspond to image defocus values of 1029Å in (a) and 1596Å in (b). Note also that these diffractograms illustrate that for phase contrast imaging the electron microscope acts as a spatial filter.

In Fig. 1.3.3.1 uranium atom images are superimposed on the phase contrast image structure of the thin carbon support film. The expected contrast reversal and the triangular arrangement of uranium atoms in "stained" molecules of melilitic acid can be seen by comparing image detail within corresponding areas in Fig. 1.3.3.1(a) and 1.3.3.1(b).

These images are the best obtained to date and clearly illustrate the potential of this technique for imaging heavy atoms.

1.3.4 Calculations of Heavy Atom Image Contrast
- J.R. Parsons and R.R. Hosbons (Metallurgical Engineering Branch)

A very necessary part of this program is the need to calculate the optimum defocus values and the corresponding
By comparing image detail within corresponding areas on Fig. 1.3.3.1(a) and 1.3.3.1(b) the expected contrast reversal of uranium atom images and their triangular arrangement in "stained" molecules of mellitic acid can be seen. The diffractograms (insets) indicate the absence of image astigmatism and correspond to image defocus values of 1029Å in (a) and 1596Å in (b).
heavy atom image contrast.

As described in PR-CMa-20, these calculations have been done for 100 keV electrons and an objective lens whose spherical aberration constant $C_s = 2.01 \text{ mm}$. During the last quarter these calculations were redone for the other \textit{Elmiskop 101} accelerating voltages of 40, 60 and 80 kV and for an objective lens with $C_s = 1.3 \text{ mm}$. No marked improvement in heavy atom image contrast was evident in these more recent calculations. In general, it could be seen that the higher the accelerating voltage and the lower the $C_s$ value the better was the heavy atom image contrast.

1.4 NUCLEAR METHODS OF ANALYSIS

1.4.1 Movement of Implanted Foreign Atoms During Anodic Oxidation of Aluminum

- F. Brown, W.D. Mackintosh and H.H. Plattner

A report, describing the Rutherford scattering method for studying the migration of implanted foreign atoms during the anodic oxidation of aluminum, has been prepared for publication. This includes the results for implants of the inert gases, Xe, Kr and Ar; the alkali metals, Cs, Rb and K and the halides, I, Br and Cl (PR-CMa-20).

In PR-CMa-17, it was reported that implants of the aluminum analogues, Tl, Ga and In into aluminum metal were substantially retained at the metal oxide interface on anodizing (in contrast to the alkali metals which move towards the oxide surface). These experiments are now being continued. Tl, Ga and In were implanted into pre-formed oxide layers $11 \mu\text{g/cm}^2$ thick and the location and amount retained were determined. After anodization none of the implanted atoms were detected.

At first sight these results, taken with the earlier ones on metal implants, suggest that Tl, Ga and In in the metal will not pass easily into the oxide during anodizing but that any that do enter the oxide will be rapidly lost to the electrolyte. Considering that practically no aluminum is lost during anodizing this latter behaviour would be rather surprising. However, there remains the possibility that the sensitivity of the Rutherford scattering analysis,
with the doses used, would not be sufficient to detect the Tl, Ga or In if they were not concentrated in a fairly narrow depth region. To test this possibility a series of experiments with radioactive Tl implants was instituted. The amount of activity retained in a specimen of aluminum metal implanted with the tracer remained almost constant through oxidation up to 100μg/cm². About half of it was still retained in the metal when the oxide layer was stripped. These specimens were re-anodized and stripped and the process repeated several times. The fraction of activity lost during each cycle became less as the cycles were repeated and tended to level off at about 10% loss per cycle after 5 or 6 cycles. All of these results agree, at least semi-quantitatively, with the results obtained by Rutherford scattering. On the other hand specimens with Tl implanted into a 11μg/cm² thick oxide layer retained at least 80% of the activity on anodizing to a thickness of 100μg/cm². On stripping, all activity disappeared from the specimen. This result suggests that, as suspected, the scattering analysis had failed to detect the foreign atoms which were, in fact, still contained in the oxide layer. The scattering experiments will be repeated using larger amounts of implants; the radiotracer work will eventually be extended to include Ga and In.

1.5 NUCLEAR CHEMISTRY

1.5.1 Thermal Neutron Capture Cross Section of ¹³⁶Xe
- D.C. Santry and R.D. Werner

Recently we examined the use of an activity depletion method for determining neutron capture cross sections for radioactive nuclides(1). The use of high resolution gamma-ray spectrometry to analyze thin radioactive samples of high purity, prepared by mass separation and ion implantation, provided a means of measuring cross sections for ³²Na and ⁵⁸Co with an estimated error of 3 to 6%.

We have extended our investigation to see if the method was applicable to the fission product gas ¹³⁶Xe (see PR-CMa-18, Section 1.6.1). Activity depletion measurements were made on ¹³⁶Xe samples irradiated in the pneumatic carrier positions of the NRX and NRU reactors. Effective capture cross
sections determined, $\hat{\sigma}$, are given in Table 1.5.5.1. Our data were used to estimate $\sigma_0$, the 2200m/sec value, from the relationship $\hat{\sigma} = \sigma_0(g+rs)$ as described by Westcott. The epithermal index, $r$, for each irradiation position was measured from Cd ratios of Au neutron flux monitors. Values of $g$ were taken from Smith et al. for a spin state $g^* = 5/8$. The $s$ value was obtained by extrapolating values given by Story. Values of $g$ and $s$ depend on the neutron temperature at which $\hat{\sigma}$ was measured. In our work the neutron temperature was obtained by measuring the reactor moderator temperature and applying a small correction, recommended by Bigham, for hardening of the neutron spectrum due to neutron absorption in the vicinity of the irradiation facility. Calculated values for $\sigma_0$ are given in Table 1.5.1.1 and are to be compared with the ENDF/B recommended value of $2.63 \times 10^6$ barns.

We have observed that the activity depletion method can be useful in obtaining accurate neutron cross section data for radioactive nuclides. Such information would be useful in calculating storage and shielding requirements for irradiated fuels and components of nuclear power reactors.

Table 1.5.1.1

<table>
<thead>
<tr>
<th>Reactor</th>
<th>T</th>
<th>r</th>
<th>g</th>
<th>s</th>
<th>$\hat{\sigma}$</th>
<th>$\sigma_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°K)</td>
<td></td>
<td></td>
<td></td>
<td>(10^6 barns)</td>
<td>(10^6 barns)</td>
</tr>
<tr>
<td>NRX</td>
<td>332°K</td>
<td>0.0158</td>
<td>1.187</td>
<td>-1.0</td>
<td>3.28±0.13</td>
<td>2.80</td>
</tr>
<tr>
<td>NRU</td>
<td>318°K</td>
<td>0.0036</td>
<td>1.175</td>
<td>-1.0</td>
<td>3.10±0.10</td>
<td>2.65</td>
</tr>
</tbody>
</table>

(4) J.S. Story, Appendix to AEHW rept. RL16(1962) by H.M. Sumner.
(6) National Neutron Cross Section Center, Brookhaven National Laboratory.
1.5.2 Thermal Neutron (n,\(\alpha\)) Reactions
- D.C. Santry and R.D. Werner

From our earlier studies (PR-CMa-20, Section 1.5.3) we concluded that the \(^{68}\text{Co}(n,\alpha)^{55}\text{Mn}\) reaction was not responsible for the anomalously large He production observed in neutron irradiated Ni and stainless steel. Further measurements were made to determine the amount of \(^{55}\text{Mn}\) produced by the thermal neutron irradiation of \(^{68}\text{Co}\) activity ion implanted into high purity Al foils. The results indicated that the \(^{55}\text{Mn}\) content, as determined by activation analysis, was no greater in the irradiated \(^{68}\text{Co}-\text{Al}\) samples than the natural Mn content of the high purity Al foils, i.e. 0.061 ppm. Consequently, \(\sigma_{\text{th}}\) for the \((n,\alpha)\) reaction of \(^{68}\text{Co}\) is set at < 3 mb.

Kangilaski and Bauer\(^{(1)}\) had suggested that the source of He was the \(^{59}\text{Ni}(n,\alpha)^{56}\text{Fe}\) reaction (Q-value 5.1 MeV) which is energetically possible with thermal neutrons. The \(8 \times 10^4\) year \(^{59}\text{Ni}\) is produced by the \(^{58}\text{Ni}(n,\gamma)\) reaction (\(\sigma_{\text{th}} = 4.8\) barns). The nuclide decays only by electron capture and has no characteristic gamma ray. The identity of the \(^{59}\text{Ni}\) which we obtained was established by measuring its characteristic Co X-ray with a high resolution X-ray spectrometer. The amount of activity obtained was considered too small for processing in the isotope separator, therefore sources were prepared by electroplating the activity on Cu disks. Similar control samples were prepared using natural Ni containing no radioactivity. The \(^{59}\text{Ni}\) and control samples were irradiated along with cellulose nitrate \(\alpha\) track detectors in the S-6-1 thermal neutron self serve position of the NRX reactor. After an irradiation the cellulose nitrate was etched in NaOH solution. A high track density was observed for the \(^{59}\text{Ni}\) samples while no tracks were observed for the Ni control sample, which indicated that the \(^{59}\text{Ni}(n,\alpha)\) reaction was very likely occurring.

A set of standard samples were prepared by ion implanting known amounts of \(^6\text{Li}\) and \(^{10}\text{B}\), of known \((n,\alpha)\) cross sections, into Al disks. A simultaneous irradiation of the \(^{59}\text{Ni}\) samples and the standard samples was performed. It was hoped that a comparison of track densities of the standards with \(^{59}\text{Ni}\) sources would permit an evaluation of the \(^{59}\text{Ni}(n,\alpha)\) cross section. Unfortunately, by using a densitometer, we were not able to correlate the track densities of the standards with their known concentrations of Li and B. These measurements will be repeated using lower concentrations of both \(^{59}\text{Ni}\) and
the standards and the tracks will be counted in a microscope. In addition, it will be necessary to produce an ion implanted $^{59}$Ni source to confirm that the observed tracks are in fact due to $^{59}$Ni and not to the presence of natural B present in the $^{59}$Ni sources.


1.5.3 Fast Neutron Cross Sections

C. Santry

Studies have begun on the use of the $^{127}$I(n,2n)$^{126}$I reaction as a fast-neutron flux monitor. The high reaction threshold energy ($\sim 9.2$ MeV) and the 13-day half-life of the product provide attractive features for a threshold detector. In monitoring 14 MeV (D + T) neutrons from a neutron generator, the $^{127}$I(n,2n) reaction is not influenced by the presence of extraneous 2.9 MeV (D + D) neutrons produced by the D build-up in T targets. For a nuclear reactor, changes in the shape of a neutron spectrum as well as the flux could be monitored by using the $^{127}$I(n,2n) reaction in conjunction with a low threshold detector, i.e. $^{32}$S(n,p)$^{32}$P (threshold $\sim 1.5$ MeV). For this pair of reactions the resulting products have similar half lives, 14.22 day for $^{32}$P and 13.0 day for $^{126}$I.

Hexaiodobenzene ($C_6I_6$) was pressed into pellets 4.8 mm in diameter and 0.09 mm in thickness. This material has the advantages of high iodine content (91.4%) and is not hygroscopic as are many of the other iodine compounds. A 30 minute irradiation of the material in the X-rod pneumatic carrier of the NRX reactor indicated no weight loss and no visible signs of radiation damage. Longer neutron exposure times will be investigated. It was shown that the reactor irradiated $C_6I_6$ could be analyzed for $^{126}$I by measuring the 389-keV $\gamma$ transition with a Ge(Li) $\gamma$-ray spectrometer.

Cross sections for the $^{127}$I(n,2n) reaction are to be measured from threshold energy up to 20 MeV relative to the known cross section for the $^{32}$S(n,p)$^{32}$P reaction. An irradiation of $C_6I_6$ for 30 minutes with 14.7 MeV neutrons produced sufficient $^{126}$I activity to permit analysis using NaI and Ge(Li) $\gamma$-ray detectors. Using discs of S as flux monitors a preliminary cross-section value for the $^{127}$I(n,2n) reaction at 14.7 MeV was found to be $1335 \pm 260$ mb. This value is
in agreement with a value of $1320 \pm 132 \text{ mb}$ measured by Bormann\textsuperscript{(1)}.


1.6 COMPUTATIONS

1.6.1 \textbf{The Use of Computers to Simulate the Trajectories of Energetic Ions in Crystals}
- D.P. Jackson and D.V. Morgan (University of Leeds)

Morgan and Van Vliet\textsuperscript{(1)} have successfully used computer programs to study a number of problems connected with the channeling and dechanneling of energetic ions in crystals. It is intended to have similar facilities available at CRNL and, at the same time, to extend the program considerably. To this end, work has commenced both at CRNL and at the University of Leeds and will be continued during Dr. Morgan's forthcoming summer visit to CRNL. The work has two objectives.

(a) To generalise the concepts of reference (1) to produce a program package with a broad choice of options. These include a choice of:

(i) Thomas-Fermi or Bohr interatomic potential. Large and small angle collisions.

(ii) Lindhard or Firsov electronic stopping models for ion energy losses.

(iii) Inclusion of directional deflections in the ion trajectory due to electronic stopping resulting from either of (ii) above.

(iv) A triangular or Gaussian model for lattice atom vibrations due to temperature.

(v) A choice of lattice type: face-centered cubic, body-centered cubic, diamond (silicon) and zinc-blende (mixed diamond) lattices.

Various portions ((i), (iii) and part of (v)) of this total package have already been generated.

(b) In particular to extend the models of reference (1) to study dechanneling in III-V semi-conductors. The following modifications are being undertaken.
(i) A master program has been written for the study of dechanneling. It follows a large number of ions starting at the surface into the solid, steps them through the lattice and determines the depth at which dechanneling occurs. Finally, a table of number dechanneled as a function of depth is constructed from totalling the results from the complete set of trajectories tested.

(ii) The stepping program has been extensively modified to the III-V lattice configuration. This meant putting in routines to identify the type of a lattice atom involved in a collision. Note that an essential feature of these programs to date has been their ability to rapidly detect the presence of a lattice atom in a position to collide with the ion based solely upon the coordinates of the ion. Therefore the changes referred to here have not only implied the most complex lattice type used thus far but also the further complication of determining the species of the lattice atom. At this point this part of the program has apparently performed successfully.

(iii) When a lattice consists of two species their thermal amplitudes of vibration will in general be different. The equipartition of energy implies the same average energy resident in atoms of each species but the difference in masses gives rise to the difference in amplitudes. These thermal effects are considered to be important in dechanneling; crudely speaking they make the channel walls appear "routhier" to the ion. A routine is now being written which takes into account these differences. A further modification involves the introduction of Gaussian distributions of thermal amplitudes which we consider more realistic than the triangular approximation used in reference (1).

(iv) The collision solving routine has not only been modified to handle two atomic species but has been simplified to consider only small angle deflections. Large angle deflections are assumed to give rise to immediate dechanneling. The locally available Bessel functions have been incorporated into this routine.
1.6.2 Computer Studies of the Ejection of Low Energy Atoms from Crystal Surfaces
- D.P. Jackson

Modifications to the main computer program have been made so that it can now handle the six crystal surface configurations of most interest i.e. the (100), (110) and (111) surfaces of both b.c.c. and f.c.c. crystals. Ejection thresholds are being calculated for the f.c.c. metals Pb, Ag, Ni, Cu, Al, Ca, Sr, and for the b.c.c. metals Mo, Cr, W, Fe, Ba, K, Na, Cs and Rb. However there has been difficulty in getting a self-consistent field for the b.c.c. (111) surfaces. The approximation\(^{(1)}\) for the semi-infinite lattice potential used has not been good enough at the very low interplanar spacings involved in this case (.289d, d = lattice spacing). It has been necessary to use interpolation on a table of exactly calculated semi-infinite solid potential values. A routine for doing this has been tested and appears to be successful, but more work on this method is required before results can be quoted with confidence.


1.7 PUBLICATIONS AND LECTURES

1.7.1 Publications

Low Temperature Recovery of Plastically Deformed Cadmium, Indium, Tin and Lead.
- M.L. Swanson and A.F. Quenneville, phys. stat. sol. (a) 9, 135 (1972).

Neutron Capture Cross Sections of \(^{22}\)Na and \(^{58}\)Co.
Temperature Dependence of the Hyperfine Field at $^{181}$Ta Nuclei in a Nickel Field.


New Campaigns for a Veteran Technique: Alpha-Particle Backscattering Microscopy.

Ion Implantation Damage and Annealing in GaP.

1.7.2 Lectures


Ion Bombardment and Channeling: a unique combination for surface studies.
- J.A. Davies, Esso Research Laboratories, Newark, N.J., April 21, 1972.

Atomic Collisions in Solids: a review of current CRNL work on channeling and heavy ion induced X-ray emission.
- J.A. Davies, B.A.R.C., Trombay, India, June 1, 1972.

Ion Implantation, Channeling and Atomic Collision Studies in Solids. (A series of 10 lectures at a summer school organized by the Tata Institute of Fundamental Research, Bombay).
- J.A. Davies, Ootacamund, India, June 5-19, 1972.
2.0 REPORT OF GENERAL CHEMISTRY BRANCH

by

W.H. Stevens

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GENERAL CHEMISTRY BRANCH

2.1 STAFF

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Secretary
Mrs. L. Wachsmann

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Tg - Technologist
RT - Research Technician
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SS - Summer Student
2.2 ANALYTICAL CHEMISTRY

2.2.1 Emission Spectrography

- G. Zotov, J. Munch

(1) Carrier Distillation Techniques

Two types of electrodes are being investigated to improve carrier distillation techniques. The electrodes are illustrated in Fig. 2.2.1.1. One, (a), is designed to hold a solid sample between two graphite "filters" above a solid "carrier". The vapours resulting from reaction between decomposing "carrier" (e.g. Teflon powder) and sample pass into the arc discharge in the usual manner. The second type of electrode, (b), is designed to use a reactive carrier gas such as CF₄. The aim is to prevent carry-over of solid sample into the arc and improve the ratio of impurity signal to background.

(2) Pre-Evaporation Techniques

Two new approaches are being tried to improve the transfer of impurity elements from interfering matrices by distillation from a sample holder to the electrode used for analysis. One involves the use of an electrode similar to that shown in Fig. 2.2.1.1(b) as sample holder, through which a reactive gas such as CF₄ can be passed to give more complete chemical reaction with the sample impurities and better transfer of these impurities to a collecting electrode.

In the second approach the previously used pre-evaporation electrode assembly was modified by placing a graphite cylinder of the same diameter as the graphite sample holder on top of the sample cup. Inside the graphite tube is placed a series of graphite rings to act as collectors for the material evaporated from the sample. Since the temperature will vary along the length of the tube, fractionation of the vapour and some separation of the components should result. The collector rings will be used separately as electrodes for analysis of the condensates. Some fractionation has already been observed but further experimentation is required.

(3) Direct Excitation of Deposits on Millipore Filters

Good reproducibility of results has not been obtained by this technique (cf. PR-CMa-20, Sec. 2.2.1 (2)) due to
Fig. 2.2.1.1. Electrodes for "Carrier Distillation" arc excitation (dimensions in mm)
lack of homogeneity of the graphite cylinders available and consequent variability of removal of excess filter material. This method has been dropped in favour of other more promising methods.

(4) Filter Electrodes

An electrode has been designed which provides conventional filtering action for transferring solids from a liquid phase to an electrode in which they are excited and analyzed using a complete burn technique. A special filter funnel has been constructed to hold these electrodes for such transfers. The electrode and filtering assembly are shown in Figs. 2.2.1.2 and 2.2.1.3. A filtering medium (e.g. cellulose fibre) is placed at the bottom of the electrode cups and covered with graphite powder. Solid samples are thus retained in the electrode for analysis. The weight of sample can be obtained by weighing the dried electrode.

The following applications are being investigated:

i) Collection of solids from liquids.

ii) Transfer of solids from Millipore filters - Samples can be transferred from Millipore filters to the electrode by dissolving the filter in acetone and filtering the resulting slurry through the electrode.

iii) Analysis of ion exchange resins - It has been found that ion exchange resins can be arced in filter electrodes which suggests a method for analyzing for trace concentrations of elements in solution. The appropriate quantity of resin is contacted with the solution to pick up the elements required, then transferred to the electrode and analyzed.

(5) Use of the Glowmax Hollow Cathode Source in Spectrographic Analysis

A preliminary investigation has been made into the use of the Glowmax tube as a source for emission spectrography. Tests have been made with He and Ne as ionizing gases and for Fe, Ni, Cu and Ti as both self electrodes and in graphite electrodes. Results to date are not entirely satisfactory in that sensitivities are only moderately good. Further work will be done as time permits.
Fig. 2.2.1.2. Filter Electrode for "Complete Burn" arc excitation of solids
Fig. 2.2.1.3. Filtering Assembly for Collection of Solids in Electrode
2.2.2 Flame Spectroscopy

- M. Hurteau, D. Bellavance

(1) Sequential Multi-Element Determination by Flame Emission Methods

The automatic wavelength selector has been received and tested for reproducibility of settings. For five sequential wavelengths the reproducibility was found to be <0.5 Å. Mixed solutions of five elements (Fe, Cu, Ni, Co and Cr) were prepared and analyzed several times by this system. The variation in measured peak heights was less than 2%.

Mutual interference was found when the most sensitive lines for Ni and Co were used, i.e. Ni = 3525 Å, Co = 3528 Å, so the Co line at 3455 Å was chosen for the analysis. The contribution from Ni was much less but still occurred with this line so direct determination of Ni and Co was not possible. However, the emission intensities were found to be additive at the wavelengths chosen and a treatment of the data by simultaneous equations has proven applicable. In the concentration range from 1 to 10 µg/ml the variations in the results were found to be ± 0.2 µg/ml for Ni and ± 0.4 µg/ml for Co.

The equipment has been found to operate very satisfactorily. It can be adapted for any combination of elements whose wavelengths lie within a range of 1300 Å and can be used in either the emission or absorption mode.

(2) Interferences in Determination of Zirconium by Atomic Absorption

Recent discrepancies in results for zirconium between atomic absorption and emission spectrographic analyses have led to a review of interference effects in the atomic absorption analysis. The effects of hydrochloric, hydrofluoric, nitric and sulfuric acids at different concentrations are being examined as are those of the cations expected to be present in the samples analyzed, i.e. Fe, Cu, Ni, Cr, Co, Al and Na.

2.2.3 Gas Analysis

- T. Longhurst

(1) Analysis of Freons

Analysis of Freons has been required from time to
time in the past and has been attempted by mass spectro-
metry. This has not been entirely satisfactory because
of the similarities of the mass patterns, so a program
to investigate gas chromatographic analysis was under-
taken. The gases investigated were Freon 11 (CCl₃F),
Freon 12 (CCl₂F₂), Freon 13 (CClF₃) and the most commonly
encountered impurities CF₄ and CCl₄.

Unsatisfactory separations were obtained with both
Carbowax 20M and OV-225. A 6 ft column of Porapak Q,
programmed from 60° to 180°C at 10°/min. gave separations
of air, CF₄, Freon 13, H₂O, Freon 12, Freon 11 and CCl₄
although the latter two components gave broad, tailing
peaks. Calibrations have been made for this system.

(2) Analysis of SF₆

The Accelerator Physics and NRX Branches have re-
quired analyses for impurities in the SF₆ used as in-
sulating gas in the accelerators which would contribute
to the breakdown of insulating capability. Mass spectro-
metry has been difficult to apply to this problem so
attention was turned to gas chromatography.

The main impurity in SF₆ samples received to date
has been air. The supplier lists SF₄ and H₂O as the
main impurities. An attempt to separate these chromato-
graphically was successful using a 6 ft column of
Porapak Q, programmed from 60° to 180°C at 10°/min.
The retention times are, air = 59 sec., CF₄ = 1 min.
12 sec., and H₂O = 5 min. 15 sec. SOF₂ was also separated
and has a retention time of 3 min. 10 sec.

2.2.4 Analytical Support for the Heavy-Water Process Development Program

(1) Amine - Hydrogen Exchange Process
    - R.W. Ashley, J.P. Mislan, T. Bruce, S. Elchuk,
      W. Grondin

Work is described in an unpublished CRNL report.

(2) Hydrogen Sulfide - Water Exchange Process
    - R.W. Ashley, J.P. Mislan, G. Jarbo, T. Longhurst

a) Determination of Hydrogen Sulfide in Water by
   Autoanalyzer

Automated chemical analysis for sulfide in water
in concentrations up to 1 ppm using the ethylene blue reaction is now being used regularly. Experience with glass bead mixing coils indicated the need for extended wash periods between samples. Replacing these with standard mixing coils without air segmentation gave considerable improvement in mixing and a reduction in the wash time. Sensitivity was also increased.

Samples from H₂S saturating and stripping experiments were found to oxidize rapidly, precipitating free sulfur. Stabilization immediately after sampling with 1M NaOH containing 5% hydrazine is considered necessary to give accurate results for dissolved H₂S. Subsequent dilution to meet the requirements of the method is so great that any effect of the NaOH-hydrazine on the color development is eliminated.

b) Analysis of H₂S by Gas Chromatography

Gas chromatography is being examined as an alternative method of analysis for H₂S in water at concentrations higher than possible by the colorimetric procedure, and for impurities in H₂S gas.

Preliminary examinations of CP grade H₂S gas have been made on a 6 ft column of Porapak Q programmed from 60° to 180°C at 10°/min. Eight peaks were observed of which air, H₂S and H₂O have been identified. Identification of the remaining peaks and comparisons of various cylinders of H₂S are being carried out at present.

The separation of H₂S and H₂O on Porapak Q was unsatisfactory when the response from H₂O exceeds that from H₂S. For the analysis of H₂S in water, therefore, a different column or set of conditions is required. This is to be investigated.

2.2.5 Special Analyses

- T. Bruce, G. Jarbo, P. Hardy

(1) Analysis of Cruds

Recoveries in the solution techniques tested were acceptable and the following method of digestion is to be adopted for routine analysis:

i) Nitric acid decomposition of the filter followed by perchloric acid solution of the crud, evaporation almost to dryness to get rid of the bulk of the perchloric acid,
redissolution and dilution to a known volume with 1M nitric acid.

ii) Insoluble residue from i) above, treated with sulfuric acid and hydrofluoric acid to determine silicon content, followed by fusion with sodium tetraborate. The fused melt is dissolved in 1M nitric acid and made up to a known volume.

Where sample size and solution volumes permit, the analysis is done by atomic absorption. In the case of small samples, i.e. less than one milligram, the majority of the element determinations will be done by spectrographic analysis.

Calibration curves for the determination of iron and nickel by X-ray fluorescence have also been prepared. Attempts to do the same for zirconium have not been very successful but it is hoped to achieve better results with the recently acquired and rebuilt molybdenum target tube.

(2) Spectrophotometric Analyses

a) Gold in Aluminum - Gold Alloy

The stannous chloride method was applied to the analysis for gold in a sample of aluminum - gold wire submitted by the Solid State Science Branch. A calibration curve has been established and a procedure written. The method will serve as an alternative to atomic absorption analysis.

b) Yttrium in Calcium Fluoride

Analysis for yttrium in a calcium matrix by flame spectroscopy proved unsuitable. The spectrophotometric analysis using pyrocatechol violet was successfully applied to this analysis. Calcium can be tolerated in amounts up to 100 times the yttrium present. A procedure has been written.

(3) Mercury Analysis with a Coleman Mercury Analyzer, MAS-50

The control of mercury contamination at CRNL is the responsibility of the Radiation and Industrial Safety Branch. This branch recently acquired a Coleman Mercury Analyzer, MAS-50, to make the measurements required. Testing and evaluation of this analyzer was undertaken at their request.

The analyzer is based on the conversion of mercury
in the sample to mercury vapour and measurement of the absorption of the 2537 Å mercury line by this vapour. The instrument is being evaluated with standard solutions prepared from mercuric chloride. To date, some difficulties have been encountered in balancing the instrument to give the proper readings on the direct reading scales. It is proposed to carry out a calibration using the % transmission scale to see if better results are obtained.
### 2.2.6 Service Analyses

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<td>H₂</td>
</tr>
<tr>
<td></td>
<td>SF₆</td>
<td>2</td>
<td>M.S. analysis</td>
</tr>
<tr>
<td></td>
<td>Heat exchanger water</td>
<td>2</td>
<td>Fe</td>
</tr>
<tr>
<td>Received from</td>
<td>Type of Sample</td>
<td>No. of Samples</td>
<td>Type of Analysis Done</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------------------------------------</td>
<td>----------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Neutron and Solid State Physics</td>
<td>MnF₂/ZnF₂ crystal</td>
<td>3</td>
<td>Mn, Zn, Ni, O₂, F</td>
</tr>
<tr>
<td>Special Projects</td>
<td>Rubber</td>
<td>1</td>
<td>Identification of elastomer type</td>
</tr>
<tr>
<td>NRX Reactor Loops</td>
<td>SF₆</td>
<td>2</td>
<td>M.S. analysis</td>
</tr>
<tr>
<td>Reactor Loops</td>
<td>Solid deposit</td>
<td>3</td>
<td>NH₄⁺, Na, general spectrographic F, Cl</td>
</tr>
<tr>
<td>Cutting fluid</td>
<td></td>
<td>1</td>
<td>Cl, NH₄⁺, loss on ignition</td>
</tr>
<tr>
<td>Deposit from Douglas Point</td>
<td></td>
<td>3</td>
<td>General spectrographic</td>
</tr>
<tr>
<td>Wear test particle</td>
<td></td>
<td>1</td>
<td>General spectrographic</td>
</tr>
<tr>
<td>Particulate matter in H₂O</td>
<td></td>
<td>3</td>
<td>Mg</td>
</tr>
<tr>
<td>Engineering Research</td>
<td>Freon-12</td>
<td>1</td>
<td>M.S. analysis</td>
</tr>
<tr>
<td>Electronics</td>
<td>Solder</td>
<td>2</td>
<td>Cu, Sn</td>
</tr>
<tr>
<td>Al wire</td>
<td></td>
<td>2</td>
<td>Identification (spectrographic)</td>
</tr>
<tr>
<td>Mechanical Equipment Development</td>
<td>Gas</td>
<td>3</td>
<td>General M.S.</td>
</tr>
<tr>
<td>Mechanical Design</td>
<td>Crud from electrolyte cell</td>
<td>1</td>
<td>Fe, Cu, general spectrographic</td>
</tr>
<tr>
<td>Received from</td>
<td>Type of Sample</td>
<td>No. of Samples</td>
<td>Type of Analysis Done</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>Radiation and Industrial Safety Stores</td>
<td>Swipes</td>
<td>8</td>
<td>Be</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>1</td>
<td>General M.S.</td>
</tr>
<tr>
<td>Nuclear Power Demonstration</td>
<td>Al alloy</td>
<td>2</td>
<td>Identification (spectrographic)</td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>25</td>
<td>Fe, Cu, Ni, Co, Mn, Li</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>1</td>
<td>M.S. analysis</td>
</tr>
</tbody>
</table>

Total number of samples = 848

<table>
<thead>
<tr>
<th>Type of Analysis</th>
<th>No. of Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrographic</td>
<td>1666</td>
</tr>
<tr>
<td>Atomic Absorption</td>
<td>1037</td>
</tr>
<tr>
<td>Gas Analyses</td>
<td>758</td>
</tr>
<tr>
<td>Other</td>
<td>311</td>
</tr>
</tbody>
</table>

Total = 3772
2.3 HYDROGEN-WATER EXCHANGE

- W.H. Stevens, A.S. Denovan

Work is described in an unpublished CRNL report.

2.4 RADIOACTIVITY MEASUREMENTS

2.4.1 Fission Product Deposition - Laboratory Studies

- W.J. Edwards

The adsorption of tellurium by nickel oxide is believed to result in the formation of direct bonds between nickel ions of the substrate and \( \text{TeO}_3^- \) ions from solution. Information on the stability of such bonds may be inferred from the ionization of pure nickel tellurite in solution. An attempt has been made therefore to determine the solubility parameters of pure nickel tellurite.

Nickel tellurite was prepared by slow precipitation over a 16 hour period by mechanically adding and mixing equivalent portions of nickel chloride and potassium tellurite, labelled with Te-132, in dilute solutions at room temperature. The pH of the solution was maintained near neutrality. After being filtered and washed, portions of the \( \text{NiTeO}_3 \) product were suspended in a few ml of various dilute \( \text{Ni(NO}_3)_2 \) solutions and stirred for 1 hour with nitrogen bubbles. The solutions were then filtered and the tellurium determined from the Te-132 activity. The solution conditions are given in Table 2.4.1.1 and the solubility curve is plotted in Fig. 2.4.1.1.

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Concentration of ( \text{Ni(NO}_3)_2 ) (M)</th>
<th>Concentration of Tellurium gm-atomic wts./l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.7</td>
<td>0</td>
<td>2.07 x ( 10^{-4} )</td>
</tr>
<tr>
<td>2</td>
<td>6.8</td>
<td>0.01</td>
<td>4.95 x ( 10^{-5} )</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>0.02</td>
<td>1.92 x ( 10^{-5} )</td>
</tr>
<tr>
<td>4</td>
<td>6.9</td>
<td>0.10</td>
<td>2.39 x ( 10^{-5} )</td>
</tr>
<tr>
<td>5</td>
<td>6.7</td>
<td>0.20</td>
<td>2.08 x ( 10^{-5} )</td>
</tr>
</tbody>
</table>
Fig. 2.4.1.1

Solubility of Nickel Tellurite
The data in Fig. 2.4.1.1 are interpreted with the aid of equations -

1. \[ \frac{k_1}{H_2TeO_3 \rightleftharpoons HTeO_3^- + H^+} \]

2. \[ HTeO_3^- \rightleftharpoons \frac{k_2}{H^+ + TeO_3^=} \]

3. \[ NiTeO_3_{solid} \rightleftharpoons NiTeO_3_{solution} \]

4. \[ NiTeO_3_{solution} \rightleftharpoons \frac{k_4}{Ni^{++} + TeO_3=} \]

where \[ k_1 = \frac{[H^+][HTeO_3^-]}{[H_2TeO_3]} = 10^{-3} \] (1)

\[ k_2 = \frac{[H^+][TeO_3^=]}{[HTeO_3^-]} = 10^{-8} \] (1)

\[ NiTeO_3_{solution} = [NiTeO_3] \] (molecular solubility of NiTeO_3)

\[ k_4 = \frac{[Ni^{++}][TeO_3^=}]{[NiTeO_3]} \] (ionization constant)

The first two equations are necessary to account for the hydrolysis of TeO_3^- as a function of pH. The third expresses the molecular solubility of nickel tellurite. Fig. 2.4.1.1 shows that the solubility becomes approximately constant at \[ \approx 2.1 \times 10^{-3} \text{ M} \] as the nickel concentration increases. This is interpreted as the molecular solubility level (equation 3) with ionization repressed by the high nickel concentrations. If this level is subtracted from the first two points it is possible to obtain two estimates of \[ k_4 \], the ionization constant by means of the expression,
\[
\frac{[\text{Ni}^{+2}] \cdot ([\text{Te}] - [\text{NiTeO}_3])}{([\text{NiTeO}_3])} = \frac{(1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2})}{[\text{NiTeO}_3]}
\]

In the preceding expression \([\text{Te}]\) represents the total concentration of all forms of tellurium in solution from the measured activity. The concentration of nickel in the first solution where no nickel nitrate is added is taken as \([\text{Te}]\).

From the first two data points \(k_4\) is calculated as \(6.0 \times 10^{-9}\) and \(8.6 \times 10^{-9}\) respectively. The best estimates at present therefore can be summarized as -

- Molecular Solubility = \(2.1 \times 10^{-5}\) M
- Ionization Constant = \(7.3 \pm 1.3 \times 10^{-4}\)


2.4.2 Activated Corrosion Product Deposition - Laboratory Studies

- R.C. Hawkings, L.P.V. Corriveau

Investigations on the kinetics of the deposition of cobalt from aqueous solution have been continued. In the upper range of concentration (>\(10^{-6}\) M \(\text{Co}^{2+}\)), where deposits onto Teflon surfaces from pH 10 solution under oxygen-free nitrogen are visible, the deposited material is dark brown in colour. No brown precipitates of \(\text{Co}^{2+}\) have been reported in the literature. Benson, Briggs and Wynne-Jones (1) have reported a brown cobaltic hydroxide formed by air oxidation of \(\text{Co(OH)}_2\), which they claim is identical, by X-ray diffraction, with a compound \(\text{CoH}_6\) described by Kondrashev and Fedorova (2).

If our material is a cobaltic hydroxide, then the oxidation must take place in alkaline solution in the absence of oxygen, slowly at pH 10 (order of hours) and more rapidly as the pH is increased. It is formed from either \(\text{NO}_3^-\) or \(\text{ClO}_4^-\) solutions of \(\text{Co}^{2+}\) with either \(\text{NaOH}\) or \(\text{LiOH}\). The material formed from \(\text{Co(OH)}_2\) precipitated with \(\text{LiOH}\) differs from that formed from \(\text{Co(OH)}_2\) precipitated with \(\text{NaOH}\) in that the latter material appears to peptize in pure water to yield a yellow-brown solution. When
passed through a 0.6 micron filter a gray solid is left on the filter and the filtrate is clear and colourless.

Efforts to characterize the brown material are continuing.


2.4.3 Special Problems

Identification of Defected Fuel Elements


One technique for locating a defected fuel element in a suspected bundle is to heat each element separately in a small amount of water and look for fission-products in the water.

In one test of this procedure six irradiated UO$_2$ elements were examined, one of which was known to be defected. Three of the six yielded essentially pure solutions of fission-product cesiums at levels almost four orders of magnitude higher than the other three (Fig. 2.4.3.1). Furthermore, the ratio of $^{134}$-Cs to $^{137}$-Cs was shown to agree with the ratio of the fuel burnups for the elements.

This out-reactor application of the thermal cycling technique used in the reactor loops is apparently an extremely sensitive and reliable technique for the detection of small defects in irradiated UO$_2$ fuel elements.

2.4.4 Counting Room

A total of 1052 samples was received. These were analyzed as follows:

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>decay curves beta</td>
<td>18</td>
</tr>
<tr>
<td>gross beta</td>
<td>178</td>
</tr>
<tr>
<td>Nal(Tl) gamma spectra</td>
<td>421</td>
</tr>
<tr>
<td>Ge(Li) gamma spectra</td>
<td>652</td>
</tr>
<tr>
<td>Total</td>
<td>1073</td>
</tr>
</tbody>
</table>
Relative Counts fission-product in Wash Water

Fig. 2.4.3.1
### DISTRIBUTION OF BETA ANALYSES

<table>
<thead>
<tr>
<th>Loop</th>
<th>X-1</th>
<th>X-2</th>
<th>X-3</th>
<th>X-5</th>
<th>U-2</th>
<th>U-1</th>
<th>X-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decay</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>-</td>
<td>8</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gross</td>
<td>36</td>
<td>36</td>
<td>30</td>
<td>36</td>
<td>38</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

### DISTRIBUTION OF GAMMA ANALYSES

<table>
<thead>
<tr>
<th>Loop</th>
<th>U-1</th>
<th>U-2</th>
<th>U-3</th>
<th>X-2</th>
<th>X-5</th>
<th>X-6</th>
<th>X-7</th>
<th>General</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
<td>456</td>
<td>2</td>
<td>21</td>
<td>73</td>
<td>23</td>
<td>19</td>
<td>22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other</th>
<th>NRU</th>
<th>NRX</th>
<th>NPD</th>
<th>Douglas Point</th>
<th>Special Analyses</th>
<th>Co sorption</th>
<th>Te sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>43</td>
<td>18</td>
<td>177</td>
<td>7</td>
<td>11</td>
<td>131</td>
<td>15</td>
</tr>
</tbody>
</table>
2.5 DEUTERIUM ANALYSIS

2.5.1 Mass Spectrometer System Using An AEI-MS-20

- W.M. Thurston, R.W. Jones, M. James

The design of the mass spectrometer analysis system for D/H ratio determinations is to be frozen for the next year or so as a result of the excellent performance of the systems built for the Pt. Tupper and Bruce Heavy Water Plants. Several more systems are required in the near future in the Heavy Water program, but all requirements can be met by the most recent design which is capable of doing one D/H analysis every 35 seconds and the analysis of one water sample for D/H ratio every minute.

2.5.2 THN-202 Mass Spectrometer

- W.M. Thurston, R.W. Jones, M. James

An automatic sample line sequencer has been installed on the THN-202 mass spectrometer to allow programmed operation of 1 to 6 lines on a 15 minute interval, unattended overnight or weekends. With a standard included in the sample sequencer, accurate analyses can be obtained day and night.

Summary of Analysis

<table>
<thead>
<tr>
<th>No. of Samples</th>
<th>Branch</th>
<th>Program</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,800</td>
<td>General Chemistry</td>
<td>Mass spectrometer development and testing</td>
</tr>
<tr>
<td>4,375</td>
<td>General Chemistry</td>
<td>H₂-H₂O Exchange</td>
</tr>
<tr>
<td>11,885</td>
<td>Physical Chemistry</td>
<td>H₂-H₂O Exchange</td>
</tr>
<tr>
<td>13,345</td>
<td>Chemical Engineering</td>
<td>Heavy-Water Process Studies</td>
</tr>
<tr>
<td>15</td>
<td>Heavy Water Plants</td>
<td>Effluent and Process Water Analysis</td>
</tr>
<tr>
<td>35,420</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.6 ELECTROCHEMISTRY

2.6.1 Electrochemical H/D Separation

- M. Hammerli, W.J. Olmstead

Measurements of the electrolytic H/D separation (cf. PR-CMa-20) on polished iron cathodes of different surface areas in 1M KOH - 10% D₂O electrolyte at 25°C have been continued. Additional results to support and expand the observations and conclusions of PR-CMa-20 have been obtained. These are summarized briefly:

a) The steady-state electrolytic H/D separation factor, $\alpha$, decreases with the cathodic overpotential, $|\eta|$, but appears to reach a plateau at $\eta > |\eta| = 950$ mV relative to the hydrogen electrode in the same solution. However, when the measured overpotentials are corrected for the IR-drop (due to the resistance of the electrolyte-gas mixture between the Luggin capillary and the iron cathode) $\alpha$ decreases approximately linearly with the corrected cathodic overpotential over the whole overpotential range studied to date. These results are shown in Fig. 2.6.1.1. Experiments are in progress to extend the overpotential range to smaller absolute values.

b) The $\alpha$ versus $\eta$ relationship is independent of the shape of the cathode since data for rectangular cathodes (5 cm x 1 cm) and for a wire electrode (0.159 cm in diameter and 0.5 cm long) overlap (see Fig. 2.6.1.1).

c) It was also observed that changes in the real surface area of an iron cathode, possibly due to electrolysis, are reflected in a change in the cathodic overpotential with a corresponding change in $\alpha$. Thus it is important to measure the overpotential corresponding to each $\alpha$ value if good reproducibility is to be expected.

d) The initial decrease in $\alpha$ at a given constant current has been confirmed and appears to be independent of electrode size or current density. Thus, this short-term time effect may be due to a diffusion controlled reaction involving the dissolution of an impurity or impurities from the Pyrex glass. More experimental work is planned to pin-point the cause of this effect.

e) Steady-state Tafel plots have been measured before and after separation factor experiments. A typical curve is shown in Fig. 2.6.1.2. The general lack of hysteresis between ascending and descending current densities in
Fig. 2.6.1.1. Electrolytic H/D separation factor on Fe cathodes versus overpotential in 1M KOH - 10% D_2O @ 25°C.

- •,○ - Fe wire cathode (0.27 cm^2 of geometric surface)
- ■,□ - Fe paddle cathodes (10 cm^2 each of geometric surface)

open symbols represent data uncorrected for IR-drop; closed symbols represent data corrected for IR-drop.
Fig. 2.6.1.2. Tafel plot for a polished iron cathode in 1M KOH - 10% D₂O electrolyte at 25°C. (O) increasing current density; (●) decreasing current density. Notes: (a) current density is based on geometric surface area; (b) overpotentials have not been corrected for IR-drop.
these plots is indicative of a "clean" system. The Tafel slope of about -130 mV could be indicative of a slow discharge mechanism viz:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{MH} + \text{HO}^- \quad \text{(slow)}
\]

followed by,

\[
2\text{MH} \rightarrow 2\text{M} + \text{H}_2 \quad \text{(fast)}
\]

where M denotes the metal-hydrogen (deuterium) adsorption site.

f) Based on the geometric surface areas, tentative conclusions from Fig. 2.6.1.1 and 2.6.1.2 are that the cells of the CRNL Upgrading Plant are operating in the overpotential range -650 mV to -735 mV corresponding to \(i = 350 \text{ mA cm}^{-2}\) to 470 mA cm\(^{-2}\) where the separation factor is about 7.9 to 7.7. Of course, the real surface areas could easily differ sufficiently to accommodate a much wider range in \(\alpha\).

2.6.2 Mass Spectrometer and Secondary HD Standard Calibration

- M. Hammerli, W.J. Olmstead

Since the accuracy of our primary HD standards preparation procedure (based on dissociation of a heavy-water standard over hot uranium metal) is known to be better than the short-term reproducibility of mass spectrometer analyses of \(\pm 0.3\%\), we produced several HD standards for J.H. Rolston of the Physical Chemistry Branch for calibration of his CEC model 21-614 Residual Gas Analyser. At the same time we also established two new secondary HD standards and determined the HD sensitivity factor of the Bendix MA-1 time-of-flight mass spectrometer. This factor was found to be linear over the range 0.4 to 8 mole \% HD, which covers the separation factor range 2 to 40 in the electrolytic process based on 10\% D\(_2\)O electrolyte.
2.7 MASS SPECTROMETRY AND FUEL ANALYSIS

2.7.1 Spark Source Mass Spectrometer Operation

- I.H. Crocker, C.H. Knight

Work on several operational facets of the mass spectrometer that has been described in earlier progress reports was continued in this quarter.

The cause of photoplate fogging in the analyzer is almost certainly static charge build-up on the photoplate followed by discharge to metal of the analyzer chamber. A complete cure has not been found. We have discovered that it can be minimized by avoiding the first six of the sixteen photoplate positions. This is considered an expedient and not a final solution.

The focus of the MS-702 was checked and found to be as good as ever. Tests were continued on the cryogenic source pump, and its beneficial effects on background during sparking of standard copper samples was ascertained. Significant reductions in C, N, O, H₂O and CO₂ mass peaks were observed. Several new sample holders of various designs were fabricated and tested. These are intended mainly as aids in surface analyses of materials. Several minor but time-consuming electronic faults occurred and were repaired in this quarter. These were in the magnetic and electrostatic analyzer circuit, the autospark unit, and the analyzer ion gauge circuit.

2.7.2 Thoria-Urania Fuel

- I.H. Crocker, F.C. Miller, J.A. Schruder

In PR-CMa-20 we reported that an insoluble residue remained after a prolonged ammonium bisulfate fusion of pellet C-249 from highly irradiated flux peaking rod bundle THC. Two more prolonged fusions of the residue with ammonium bisulfate and ammonium nitrate put most of the residue into solution. Spectrographic analysis by G. Zotov of the Analytical Chemistry Section showed that the solution from the first fusion contained mostly Mo, Tc, Pd, Ru and Sr. No U or Th were detected. The solution from the second fusion contained mostly Si and Sr. This agrees with J.H. Goode and B.F. Rider, in reports ORNL-3754 and GEAP-5354 respectively, that in highly irradiated fuel, very insoluble metal inclusions are formed from Mo, Ru, Tc, Pd and Zr fission products.
Thorium was determined by differential colorimetry using thoronal, while U was determined by controlled potential coulometry. The results are listed in Table 2.7.2.1 along with the results for earlier, less-irradiated specimens for comparison. The mass spectrometric analyses for U are given in Table 2.7.2.2.

Table 2.7.2.1

Summary of Chemical Analyses for Thoria-Urania Fuel

<table>
<thead>
<tr>
<th>Fuel Pellet</th>
<th>Irradiation (MWd/kg)</th>
<th>Th (mg/g)</th>
<th>U (mg/g)</th>
<th>U/Th (wt. ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated #42</td>
<td>0</td>
<td>863</td>
<td>13.23</td>
<td>$1.533 \times 10^{-2}$</td>
</tr>
<tr>
<td>THB (outer) #62</td>
<td>4.6</td>
<td>860</td>
<td>13.77</td>
<td>$1.601 \times 10^{-2}$</td>
</tr>
<tr>
<td>THE (inner) #99</td>
<td>11.4</td>
<td>852</td>
<td>14.41</td>
<td>$1.691 \times 10^{-2}$</td>
</tr>
<tr>
<td>THE (outer) #98</td>
<td>16.7</td>
<td>843</td>
<td>14.65</td>
<td>$1.738 \times 10^{-2}$</td>
</tr>
<tr>
<td>THC (outer) #C-249</td>
<td>~49</td>
<td>818</td>
<td>17.47</td>
<td>$2.136 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Table 2.7.2.2

Summary of Mass Analyses for Thoria-Urania Fuel in Atom %

<table>
<thead>
<tr>
<th>Fuel Pellet</th>
<th>Mass No. 233 (unirradiated)</th>
<th>THB62 (outer)</th>
<th>THE99 (inner)</th>
<th>THE98 (outer)</th>
<th>THC C-249 (outer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#42</td>
<td>0</td>
<td>24.95</td>
<td>49.39</td>
<td>57.14</td>
<td>67.99</td>
</tr>
<tr>
<td>234</td>
<td>0.783</td>
<td>1.196</td>
<td>2.990</td>
<td>4.138</td>
<td>14.68</td>
</tr>
<tr>
<td>235</td>
<td>93.017</td>
<td>63.73</td>
<td>34.18</td>
<td>24.58</td>
<td>3.27</td>
</tr>
<tr>
<td>236</td>
<td>0.235</td>
<td>4.221</td>
<td>7.943</td>
<td>8.932</td>
<td>10.09</td>
</tr>
<tr>
<td>238</td>
<td>5.965</td>
<td>5.915</td>
<td>5.497</td>
<td>5.213</td>
<td>3.97</td>
</tr>
</tbody>
</table>

2.7.3 PuO₂-UO₂ Fuel Analyses

- F.C. Miller

The methods currently used for precise analysis of uranium and plutonium are based on controlled potential
coulometry in a cell containing a stirred mercury electrode for the uranium analysis and in a different cell containing a platinum working electrode for plutonium. There are two main disadvantages to the use of the mercury cell. First, efficient stirring of the mercury pool is very critical for optimum performance and secondly, mercury dissolves under slightly oxidizing conditions thus preventing the coulometric oxidation of U(IV), Fe(II) or Pu(III) in the usual mineral-acid containing electrolytes. Neither of these affect the platinum electrode and it would be convenient to use this electrode for uranium analysis. Davies, Gray and McLeod (1) have done preliminary work on this, establishing an electrolyte in which U(VI) can be reduced to U(IV) at a platinum electrode without hydrogen evolution, and by addition of Bi(III), eliminate most of the surface poisoning effects at the potential needed to reduce U(VI) to U(IV).

An analysis carried out in a dry box line should be done with the minimum amount of essential equipment. Thus, an effort has been made to use the single platinum cell for uranium and plutonium. To check the operation of the cell at the potential necessary for the oxidation-reduction of Pu(III)-Pu(IV), the highly reversible Fe(II)-Fe(III) couple which operates at approximately the same potential was used. Standard solutions of iron and uranium were analyzed separately, and in the presence of each other with satisfactory results.

<table>
<thead>
<tr>
<th>Fe Taken</th>
<th>U Taken</th>
<th>Analyzed</th>
<th>No. of Determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 5.272 mg</td>
<td></td>
<td>5.270 ± 0.011</td>
<td>5</td>
</tr>
<tr>
<td>(2)</td>
<td>96.9 mg</td>
<td>96.89 ± 0.19</td>
<td>5</td>
</tr>
<tr>
<td>(3) 5.272 mg</td>
<td>96.9 mg</td>
<td>5.269 ± 0.009</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96.83 ± 0.005</td>
<td>5</td>
</tr>
</tbody>
</table>

The sequential determination of plutonium and uranium in the same solution appears to be possible. However, the effects of surface poisoning of the electrode by minor contaminants, and of interference from elements which reduce under similar conditions need to be studied further before the technique can be used routinely to analyze PuO₂-UO₂ pellets.

2.7.4 Uranium Ore Samples

- F.C. Miller, J.A. Schruder, I.H. Crocker

Two samples of uranium ore were received from Dr. I.M. Szöghy, attached staff, Nuclear Physics Branch. The ore samples were ground to pass a twenty mesh sieve and leached with hot concentrated nitric acid. The uranium content was purified by reversed phase chromatography on a TBP-Kel F column and analyzed mass spectrometrically for isotopic composition. The column effluents from the purification process were concentrated by evaporation and sources were prepared for gamma scanning. Sources were also prepared from the purified uranium fractions for gamma scanning. Results are reported in PR-P-94 (AECL-4257).

2.7.5 Burnup Measurements

- W. Cherrin, F.C. Miller, J.A. Schruder, S.R. Bokwa

Dissolution and purification for mass spectrometric analyses of the uranium isotopes were completed on 13 samples from experimental fuel programs. In the same period 20 uranium mass analyses of starting material and irradiated fuel pellets were completed.

2.8 LECTURES

"Electrolytic H/D Separation Factors on Cathode and Diffusion Sides of Iron Membranes in H₂SO₄" by M. Hammerli, B.L. Muju, W.J. Olmstead and F.R. Smith. Presented by M. Hammerli at the Chemical Institute of Canada 55th Chemical Conference and Exhibition, Laval University, Quebec, June 4-7, 1972.
3. REPORT OF PHYSICAL CHEMISTRY BRANCH

by

D.R. Smith

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<th>Title</th>
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</thead>
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PHYSICAL CHEMISTRY BRANCH

3.1 STAFF

Branch Head                  D.R. Smith
Secretary                    Miss M. Andreas

RADIATION CHEMISTRY

A.W. Boyd                     O.A. Miller (Rt)
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W.A. Seddon                   F. Sopchyshyn (Tg)
                             J. Jevcak (Tg)
                             J. Reid*

ISOTOPE CHEMISTRY

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P.R. Norton                   F. Molson (Rt)
J. Halliday                   P.J. Richards (Tg)
                             P.E. Bindner (Tg)

*Summer Student from University of Waterloo
3.2 RADIATION CHEMISTRY

3.2.1 Pulsed Electron Radiation Chemistry

- A.W. Boyd, O.A. Miller and J.A. Reid

(a) Hydrogen Yields in the Radiolysis of Vanadate Solutions - in collaboration with W.A. Seddon

H.E. Zittel at ORNL has reported that the radiolytic hydrogen yield is markedly reduced by relatively small concentrations of VO$^-$ in water at pH > 7 (1), e.g., in 2 x 10^{-3} M VO$^-$ G(H$_2$) = 0.04. Peled and Czapski (2) have shown that the reduction in hydrogen yield in water by many solutes can be correlated with their concentrations and rate constants for their reactions with the hydrated electron. We have determined the value of the rate constant for reaction [1]:

\[ \text{[1]} \quad e^{-}_{aq} + \text{VO}^-> \text{VO}^3_{aq} \]

at pH = 13 by standard pulse radiolysis techniques and find $k_1 = 8 \times 10^9$ M$^{-1}$s$^{-1}$. As a check, the rate constant for reaction [2]:

\[ \text{[2]} \quad e^{-}_{aq} + \text{CrO}_4^{2-} \rightarrow \text{CrO}^{3-}_{aq} \]

was also measured and $k_2$ was found to be $1.6 \times 10^{10}$ M$^{-1}$s$^{-1}$ in good agreement with the previously reported value of $1.8 \times 10^{10}$ M$^{-1}$s$^{-1}$ (3). Since in 10^{-2} M CrO$_4^{2-}$ G(H$_2$) = 0.32 (2), it does not appear that the effect of VO$^-$ on G(H$_2$) is due to scavenging of e$_{aq}^-$. To study this effect further we have irradiated both VO$^-$ and CrO$_4^{2-}$ solutions at pH = 13 with single Febetron pulses and measured the hydrogen yields. The dosimetry was based on a yield of G(H$_2$) = 1 in pure water at a dose rate of $10^{27}$ eV g$^{-1}$s$^{-1}$ and a dose of $6 \times 10^{19}$ eV g$^{-1}$ (4). The results are shown in Figure 3.2.1.1. Zittel's results were obtained at conventional low dose rates of $\sim 10^{17}$ eV g$^{-1}$s$^{-1}$. As can be seen our high dose rate values are markedly different and are close to those predicted by Peled and Czapski's correlation. That the change in the yields in VO$^-$ solutions is not a general effect due to high dose rates is shown by the agreement between our values and Peled and Czapski's for the yields in CrO$_4^{2-}$ solutions.
Figure 3.2.1.1 Hydrogen Yields from the Radiolysis of NaVO$_3$ and Na$_2$CrO$_4$ Solutions.

- $\times$ NaVO$_3$ 0.15 NaOH dose $4 \times 10^{19}$ eV g$^{-1}$
- $\circ$ Na$_2$CrO$_4$ dose rate $0.8 \times 10^{27}$ eV g$^{-1}$s$^{-2}$
- $\bullet$ Na$_2$CrO$_4$ dose $1.6 - 5.0 \times 10^{18}$ eV g$^{-1}$
  dose rate $8 - 20 \times 10^{13}$ eV g$^{-1}$s$^{-1}$ (1)
We are now determining the hydrogen yields in 10^{-2} M VO_3^- solutions containing radical scavengers at low dose rates following irradiation with a Febetron pulse.

(1) H.E. Zittel in ORNL Nuclear Safety Research and Development Program Reports, e.g., ORNL-TM-2984, ORNL-TM-3411.


(b) Water Vapour Radiolysis - in collaboration with C. Willis (University of the West Indies)

The yields of hydrogen and the deuterium separation factor, \( \alpha \), for the hydrogen from radiolysis of H_2O-D_2O water vapour mixtures reported in PR-CMa-19 were determined at 160°C. Further work has shown that there is no change in either G(H_2) or \( \alpha \) from 135 - 225°C in a 2:1 mixture of H_2O and D_2O. These results support our assumptions that the H atoms and OH radicals react only as in reactions [1] - [3],

\[
\begin{align*}
[1] & \quad H + OH \rightarrow H_2O \\
[2] & \quad OH + OH \rightarrow H_2O_2 \\
[3] & \quad H + H \rightarrow H_2
\end{align*}
\]
as the rate of any radical-molecule reaction would be expected to change over this temperature range. Gordon and Mulac (1), have reported a value of \( k_1 + k_2 = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \) in water vapour at \( \sim 1 \) atmosphere. Using this value, our yield of G(H_2) = 1.65 ± 0.15 in pure H_2O, G(H_2) = 0.90 ± 0.15 in H_2O with 1 mole% SF_6, and the previously reported (2) values of G(H_2) unimolecular
= 0.45, \( G(H) = G(OH) = 7.3 \) in pure \( H_2O \) and \( G(H) = 4.0 \), \( G(OH) = 7.3 \) in \( H_2O + SF_6 \), the values of \( k_1 \) and \( k_2 \) are:

- Pure \( H_2O \):
  \[ k_1 = 1.42 \pm 0.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \]
  \[ k_2 = 0.58 \pm 0.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \]

- \( H_2O + SF_6 \):
  \[ k_1 = 1.25 \pm 0.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \]
  \[ k_2 = 0.75 \pm 0.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \]

(1) S. Gordon and W.A. Mulac at the CIC symposium on Pulse Radiolysis, Pinawa Manitoba, October 1971.


(c) **Neutralization Reactions In \( H_2S \) Radiolysis**

The preliminary value of \( G(H_2) = 8 \) in the radiolysis of \( H_2S-SF_6 \) mixtures at \( 2 \times 10^{28} \text{ eV g}^{-1}\text{s}^{-1} \) reported in PR-CMa-20 has now been confirmed. We have also measured the hydrogen yields in \( H_2S \) and \( H_2S-SF_6 \) mixtures at \( 1 \times 10^{26} \text{ eV g}^{-1}\text{s}^{-1} \). The results for the pure compound and the mixtures as a function of dose rate are shown in Table 3.2.1.1. As can be seen, though the yield in the presence of electron scavengers stays the same the yield in pure \( H_2S \) increases from 11.0 to 13.0. This increase is presumably due to ionic processes and as stated in PR-CMa-20 it is most easily explained by the production of two \( H \) atoms in the neutralization of \( H_2S^+ \) and one in the neutralization of \( H_3S^+ \). Increasing the dose rate favours reaction [1] over [2].

\[
\begin{align*}
[1] & \quad H_2S^+ + e \longrightarrow H + H + S \\
[2] & \quad H_2S^+ + H_2S \longrightarrow H_3S^+ + SH
\end{align*}
\]

In PR-CMa-20 it was stated that the values \( k_1 = 10^{14} \) to \( 10^{15} \text{ M}^{-1}\text{s}^{-1} \) were consistent with this mechanism. However the value of \( k_2 \) used in the earlier calculations was too low. If a more accurate figure of \( k_2 = 5 \times 10^{11} \text{ M}^{-1}\text{s}^{-1} \) (1) is used, then \( k_1 \) turns out to be
greater than $10^{16} \text{M}^{-1}\text{s}^{-1}$. This seems somewhat improbable and we are re-examining our mechanism.

\textbf{TABLE 3.2.1.1}

Hydrogen Yields from $\text{H}_2\text{S}$ and $\text{H}_2\text{S} - 1\text{Mole}\% \text{SF}_6$

Mixtures as a Function of Dose Rate

<table>
<thead>
<tr>
<th>Dose Rate $10^{27} \text{eV g}^{-1}\text{s}^{-1}$</th>
<th>$G(\text{H}_2)$ $\text{H}_2\text{S}$</th>
<th>$G(\text{H}_2)$ $\text{H}_2\text{S-SF}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>$11.1 \pm 0.2$</td>
<td>$8.0 \pm 0.2$</td>
</tr>
<tr>
<td>2</td>
<td>$12.0 \pm 0.3$</td>
<td>$7.9 \pm 0.3$</td>
</tr>
<tr>
<td>20</td>
<td>$13.1 \pm 0.4$</td>
<td>$7.8 \pm 0.2$</td>
</tr>
</tbody>
</table>


(b) \textbf{Febetrons}

The thirteenth tube for the Febetron 705 was installed and has delivered 317 pulses bringing the grand total for the 705 to 13,937. The total number of pulses from the first tube in the Febetron 706 is now 2194. The combined total is 16,133. (The combined total at the end of the last period was 15,723, not 13,710 as given in PR-CMa-20.)

\textit{3.2.2 Pulse Radiolysis of Liquid Systems}

- W.A. Seddon, J.W. Fletcher, F. Sopchyshyn and J. Jevcak

(a) \textbf{Alkali Metal Amides in Liquid Amines}

Previously reported results (PR-CMa-20) are consistent with a mechanism involving three species in the radiolysis of alkali metal solutions in amines. These species appear to be a solvated electron ($e^-_s$), a metal-electron dimer ($M^+ - e^-_s$) and metal anion ($M^-$) in equilibrium with each other.

$$[1] \quad e^-_s + M^+ \xrightleftharpoons[k_1]{k_-1} (M^+ - e^-_s)$$
The \( e_\text{S}^- \) and \( (M^+ - e_\text{S}^-) \) species have similar absorption spectra with the extinction coefficient \( \varepsilon(M^+ - e_\text{S}^-) \) being approximately twice that of \( \varepsilon(e_\text{S}^-) \).

A recent pulse radiolysis study by Dye et al. (1), on the kinetics of formation of \( \text{Na}^- \) in ethylenediamine (EDA) suggested a mechanism involving the formation of an electron-electron dimer, \( e_2^- \)

\[
\begin{align*}
[2] & \quad e_\text{S}^- + (M^+ - e_\text{S}^-) \rightleftharpoons M^- \\
[3] & \quad (M^+ - e_\text{S}^-) + (M^+ - e_\text{S}^-) \rightleftharpoons M^- + M^+
\end{align*}
\]

Dye's results showing \( k \), the pseudo second order rate constant for the formation of \( \text{Na}^- \) are given in Figure 3.2.2.1. The dotted line represents their calculated curve using \( k_4 = 1.66 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \) and \( \gamma_4/kg = 3.5 \times 10^{-3} \text{ M} \).

The solid curve was calculated by us using reactions [1] - [3] where

\[
k = \frac{k_2k_1 + k_3}{(1 + K_1)^2}
\]

and

\[
K_1 = \frac{k_{-1}}{k_1 [\text{Na}^+]}\]
Figure 3.2.2.1 Variation in Observed Rate of Formation of Na\(^-\) in EDA As a Function of Na\(^+\) Concentration.

The experimental points are those of Dye et al (1). The dotted line calculated by Dye et al. (1) using e\(_2^+\) as an intermediate. The solid line calculated using (e\(^-\)Na\(^+\)) dimer as an intermediate.
The rate constants used are given in Table 3.2.2.1. It can be seen that our mechanism fits their data equally well.

<table>
<thead>
<tr>
<th>TABLE 3.2.2.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated Rate Constants for the Na/EDA System Using (e^- - Na^+) Dimer as an Intermediate and the Data of Dye et al. (1)</td>
</tr>
</tbody>
</table>

\[
k_1 = 3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \\
k_2 = 5 \times 10^5 \text{ s}^{-1} \\
k_2 = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \\
k_3 = 1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} 
\]


(b) 2.5 MeV Electron Van de Graaff

Several minor component failures in the high voltage terminal and bearing seizure on the turbo molecular pump results in several "tank offs" after more than nine months' trouble-free operation. About three weeks' accelerator time was lost while repairs were effected. Operation is now back to normal.

3.3 ISOTOPE CHEMISTRY

3.3.1 Nuclear Magnetic Resonance Studies of Amine Solutions - J.D. Halliday and P. Bindner

3.3.2 Analysis of Total Deuterium in Amines - J. Denhartog, J.P. Butler and J.H. Rolston

3.3.3 Measurements of the Isotopic Separation Factor Between Hydrogen and Liquid Water - J.H. Rolston, J.P. Butler and J. Denhartog

3.3.4 Measurements of the Isotopic Separation Factor Between Hydrogen and Liquid Amines - J. H. Rolston, J.P. Butler and J. Denhartog
3.3.5 Surface Area Measurements of Catalysts
- J.H. Rolston and J.W. Goodale

3.3.6 Isotopic Exchange Between Hydrogen and Water
- J.P. Butler, F.W. Molson and J. Denhartog

3.3.7 Kinetic Studies of the Isotopic Exchange Between HDO Vapour and Hydrogen
- J.H. Rolston and J.W. Goodale

The results of the research in Sections 3.3.1, 3.3.2, 3.3.3, 3.3.4, 3.3.5, 3.3.6 and 3.3.7 are given in an unpublished CRNL report.

3.3.8 Hydrogen Isotope Chemisorption and Equilibration on Platinum
- P.R. Norton and P.J. Richards

The chemisorption of H\(_2\) and the equilibration of H\(_2\) + D\(_2\) mixtures were studied in an ultra-high vacuum (UHV) flow system. The purpose is to establish the kinetics of hydrogen chemisorption on a clean, polycrystalline platinum surface with a view to eventually elucidating the state of adsorbed hydrogen under conditions pertaining to the H\(_2\)/H\(_2\)O exchange reaction.

(a) Kinetics of Chemisorption of H\(_2\)

The kinetics of chemisorption of hydrogen were studied over the range 77° < T < 350°K by measuring the pumping speed of the filament (15 cm x 0.0075 cm diameter) in a constant flow of hydrogen. The pressures during the experiments were \(\approx 10^{-7}\) Torr H\(_2\) (background pressures \(\approx 10^{-10}\) Torr). The experiment measured the net rate of adsorption and not the true rate. Only when the rate of desorption is zero, does the net rate equal the true rate. The results were similar to those observed previously (1), in that there was an initial region of high sticking coefficient (S) followed by a region in which S approaches zero, S being defined as net rate of adsorption/collision number.

The values of S as the coverage of H\(_2\) tends to zero (S\(_0\)) are shown in Figure 3.3.8.1. The decrease with temperature has been observed in other chemisorption systems but was missed in the work of Eley et al. (1) because of a deficiency in the earlier techniques. The decrease is attributable either to poorer momentum transfer to hydrogen molecules at the surface or to heterogeneity of the surface with high
INITIAL STICKING COEFFICIENT $S_0$ vs $T\, (^{\circ}K)$ FOR HYDROGEN ON PLATINUM

Figure 3.3.8.1
sticking coefficient states being associated with low values of the heat of adsorption. The latter explanation looks more tenable, in the light of the equilibration kinetics.

(1) D.D. Eley, P.R. Norton and R.J. Breakspere, J. Catalysis, to be published.

(b) **Equilibration of H\textsubscript{2} + D\textsubscript{2}**

At a known flow rate (molecules sec\textsuperscript{-1}) the average residence time, \( t \), of \( \text{H}_2 + \text{D}_2 \) in the system could be calculated by equation (1).

\[
t = \frac{V}{C} \text{ sec}
\]  

(1)

where

\[ V = \text{volume of system in litres} \]
\[ C = \text{conductance of exit valve in litres sec}^{-1}. \]

The mass spectrometric analysis of the deuterium content of the gas at steady state could then give the first order rate constant at a particular temperature and pressure. The efficiency \( \eta \), could be defined as:

\[
\eta = \frac{\text{HD}_{\text{out}} - \text{HD}_{\text{in}}}{\text{HD}_{\text{eq}} - \text{HD}_{\text{in}}}
\]

where \( \text{HD}_{\text{in}}, \text{HD}_{\text{out}}, \text{HD}_{\text{eq}} \) are the concentrations of HD at the inlet, outlet and at equilibrium respectively. Experimental checks on \( \text{HD}_{\text{eq}} \) agreed well with theory. The first order rate constant, \( K_y \) could then be defined as:

\[
K_y = \frac{1}{t}(-\ln(1 - \eta)) \text{ sec}^{-1}
\]

The absolute rate, \( K_m \) could then be calculated as:
\[ K_m = K_y \cdot \frac{N}{A} \text{ molecules cm}^{-2} \text{ sec}^{-1} \]

where

\[ N = \text{number of molecules in system at T, P}. \]
\[ A = \text{geometric area of filament in cm}^2. \]

The apparent activation energy, \( E \), could be calculated from the usual Arrhenius equation:

\[ K_m = B_m \exp \left( \frac{-E}{RT} \right). \]

The pressure dependencies of the reaction at various temperatures were measured by the above method over the range \( 10^{-8} < P < 5 \times 10^{-5} \text{ mm, Hg} \). A reaction that is first order with respect to the pressure gives \( K_m \propto P^{1} \); zero order gives \( K_m \propto P^{0} \).

The Arrhenius plot is shown in Figure 3.3.8.2. Also plotted is the fraction of collisions that lead to reaction. At temperatures > 300°K the activation energy decreases almost to zero and at 870°K the fraction of active collisions is 0.18 which is very close to the measured value for \( S_0 \) of 0.16 at 77°K (see Figure 3.3.8.1). Figure 3.3.8.3 shows the pressure dependency at 870°K. The reaction is accurately first order over the range \( 10^{-8} \) to \( 10^{-5} \text{ Torr} \).

Figure 3.3.8.4 gives the pressure dependency at 244°K. The value of the slope is the exponent in the Freundlich Isotherm

\[ K_m \propto P^n \]

or \( \log K_m = \text{constant} + n \log P \). At 244°K, \( n = 0.7 \), while at 228°K \( n \approx 0 \) within experimental error.

Several conclusions may be drawn from the data:

1) At high temperatures adsorption is the rate limiting step in the equilibration reaction. This is
D, EQUILIBRATION QN PLATINUM

Figure 3.3.8.2

PRESSURE DEPENDENCY: H₂ - D₂ EQUILIBRATION ON PLATINUM. T = 870°K

SLOPE = 1.0

Figure 3.3.8.3
PRESSURE DEPENDENCY: $H_2 + D_2$ EQUILIBRATION ON PLATINUM. $T = 244^\circ K$

$\log_{10} K_m$

$(\text{mols. cm}^{-2}\text{ sec}^{-1})$

SLOPE $= 0.71$

Figure 3.3.8.4
shown by the equality of $S_o$ and the collision efficiency (within experimental error) and the first order pressure dependency, i.e.,

$$K_m = S Z$$

where $Z$ is the collision number in mols. cm$^{-2}$ sec$^{-1}$.

2) At $T < 250^\circ K$ some surface process is rate limiting with $E = 5.8$ kcals mole$^{-1}$. This activation energy could be characteristic of an energy of desorption or of a diffusion process. At $P \sim 10^{-7}$ Torr, $T = 240^\circ K$ one would not expect to populate adsorption states with heats of adsorption of $\sim 6$ kcals mole$^{-1}$ to any extent, while the zero order pressure dependency indicates that the population of the states responsible for equilibration is complete. It seems unlikely that the activation energy for diffusion could be as high as $\sim 6$ kcals mole$^{-1}$ but this is not impossible. A possible explanation is, therefore, that in the range $200 - 270^\circ K$ the mechanism is that of diffusive mixing of H and D atoms on the surface followed by desorption from a few weakly held states. We are at present measuring the heat of adsorption, $q$, at the coverage at which the equilibration measurements were made. The value of $q$ so obtained (from isosteres) will be compared with $E$ to further elucidate the mechanism.

### 3.4 REPORTS, PUBLICATIONS AND LECTURES

#### 3.4.1 Publications

ESR Study of $\gamma$-Irradiated Alcohols Adsorbed on Magnesium Oxide Powders.

3.4.2 Lectures

ESR Study of γ-Irradiated Alcohols Adsorbed on Magnesium Oxide Powders.

Neutralization Reactions in the Radiolysis of Gases.

Hydrogen Yields and Isotope Effects in the Radiolysis of H₂O-D₂O Vapour with High Intensity Electron Pulses.
- A.W. Boyd and C. Willis, CIC 55th Annual Conference and Exhibition, Laval University, Quebec City, June 4 - 7, 1972.

Intermediates Formed in the Pulse Radiolysis of Methylamine and Ethylamine.

Hydrogen Chemisorption and Exchange on Platinum.
- R.J. Breakspere, D.D. Eley and P.R. Norton, CIC 55th Annual Conference and Exhibition, Laval University, Quebec City, June 4 - 7, 1972.
4. REPORT OF MATERIALS SCIENCE BRANCH

by

B. Cox

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MATERIALS SCIENCE BRANCH

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4.2 SURFACE CHEMISTRY

4.2.1 Environmentally Induced Cracking of Zirconium Alloys
- B. Cox

(a) In nitrate-iodide melts

Earlier studies (PR-CMa-18) have shown that shot-peening increases considerably the lifetime of Zircaloy split-ring specimens in nitrate-iodide melts. Since the majority of the time to failure of chemically polished specimens is due to the time for crack initiation, it was hoped that by a comparison of shot-peened and chemically polished surfaces at the point of crack initiation some information on the crack initiation process would be obtained, together with an explanation of the influence of shot-peening.

To achieve this, chemically polished specimens of fuel tubing batch MLI-801 (0.5 inches long) were shot-peened with a strip of cellulose tape 1 mm wide protecting the area opposite the slot (the region of peak stress when the ring was stressed). These specimens were inserted into a nitrate-iodide bath at 300°C at time zero and after 1, 2, 4, 8, 16 hours, and all were removed when the first specimen showed visual evidence of crack initiation. This took 343 hours, which was considerably longer than the 150 - 190 hours previously observed for chemically polished batch MLI-801 specimens in a low chloride nitrate-iodide bath.

The crack had initiated in the protected area, as expected, on the specimen inserted at 1 hour and not on the specimen inserted first into the bath. Examination of the surfaces of the uncracked specimens in the area protected by tape during shot-peening showed no unusual features (e.g. pits) which might be the initiators of stress cracks. However the specimens inserted at 0 and 2 hours from the start of the experiment showed a few small cracks in the surface oxide film along grain boundaries; the specimen in which the SCC had initiated first showed a much more extensive array of surface cracks which were predominantly
transgranular. The other specimens with shorter exposure times showed no such features.

In the shot-peened areas all specimens showed severely cracked oxide films, together with what appeared to be pits beneath the oxide. The severity of this pitting decreased with exposure time.

These observations suggested that the controlling process in stress-corrosion crack initiation in nitrate-iodide baths is the occurrence of small cracks in the protective oxide film which permit direct access of the halide ions to the metal/oxide interface. Shot-peening appears to damage the surface layers to such an extent that gross cracking of the oxide occurs early in the oxidation and this encourages the formation of pits, rather than cracks. Thus the overall cracking process may be a repeated film formation and fracture cycle, such as has been postulated in many other SCC systems.

If this is the case then any technique which produces a very rough surface on Zircaloy, and thereby causes early and extensive cracking of the oxide film, should lengthen the time to failure in nitrate-iodide melts by increasing the probability of pitting rather than cracking. To test this hypothesis a group of specimens containing duplicate pairs of coarsely abraded (120 grit paper), filed (coarse file) and chemically polished samples from batch MLI-801 were exposed in the same nitrate-iodide bath. Times to failure were 597, 865; 360, 625 and \( \sim 168 \) (< 190) hours respectively. Thus coarse abrasion of the specimen surfaces improves the SCC resistance of Zircaloy in fused nitrate/iodide melts, although apparently not as effectively as shot-peening, for which times to failure have been in the range 1200 - 2500 hours.

(b) In aqueous chloride solutions

Times to failure for smooth split-ring specimens polarized anodically at constant current in 5% sodium chloride solutions decrease with decreasing pH at a given current density. Failures of pre-oxidized specimens coupled to platinum, also occur more rapidly with decreasing pH. No failures have yet been obtained
with preoxidized specimens coupled galvanically to mild steel, stainless steel or nickel, irrespective of pH.

Metallographic and SEM examination of the specimens reported previously (PR-CMa-20) has shown that in many instances the majority of the fracture surface resulted from a pitting type of attack with only a small area of transgranular cracking. It is inferred from acoustical emission studies (section 4.2.2) that this transgranular cracking occurred only in the last few seconds of cracking and that most of the reduction in cross-sectional area occurred by pitting.

4.2.2 Acoustic Emission During Stress-Corrosion Cracking of Zirconium Alloys
- B. Cox

A Dunegan Acoustic Emission apparatus, kindly loaned by Engineering Research Branch has been used to listen to stress-corrosion cracking and liquid metal embrittlement of Zircaloys in a variety of environments. In general two types of acoustic emission have been heard during SCC. The first is a more or less continuous swishing noise requiring gains (≥ 80 dB) to record it, and apparently identical with noises resulting from hydrogen bubble liberation during the cathodic polarization of inert (Pt) electrodes. This feature is ascribed to purely electrochemical processes leading to intergranular attack, or pitting. The second is, discontinuous pulses of large amplitude, which often lead to from several hundred to a thousand counts per individual pulse, and which are separated by quiet periods when no acoustic emission is detectable. These are ascribed to the propagation of transgranular cracks. It may be possible to relate the number and frequency of these pulses to the mean crack velocity during transgranular cracking, and the amplitude (number of counts per pulse) may be related to the energy released as the crack moves in any one step, and thus to the area of freshly exposed surface during each movement. Experiments to correlate these quantities are not yet complete. The characteristics of
cracking in the various environments are described below:

(a) Methanol/hydrochloric acid at 25°C

Double Cantilever Beam (DCB) specimens exposed in methanol/hydrochloric acid solution at room temperature initially gave the continuous type of acoustic emission, which increased in count rate to a maximum and then decreased to a low level after about 30 minutes. At this point discontinuous acoustic emission started and continued for a further 30 - 60 minutes at a steady rate, and then the rate diminished to zero. Further discontinuous emission could be obtained by re-stressing the specimen.

Examination of the DCB specimen showed that the SCC crack had not propagated far (max. ~1 mm), but that much crack branching had occurred particularly near the specimen surfaces. It is thought that the continuous emission may result from some initial intergranular penetration, and that the rapid decrease in discontinuous noise production is due to the limited extent of propagation of the transgranular cracking in the DCB specimen. Further metallographic examination of the specimen is still in progress.

(b) Nitrate/iodide melt at 300°C

CB specimens in a nitrate/iodide bath at 300°C gave only isolated single pulses of acoustic emission from the start of the experiment. Noise immediately on immersing the specimen was ascribed to heating-up effects, and disappeared after ~1 minute. There was then a quiet period of ~5 minutes before the first pulse of noise which could be ascribed to SCC. The frequency of these pulses soon reached a fairly steady rate of about one every two or three minutes, and continued at this rate with very little change. The number of counts per pulse (related to the initial amplitude of the acoustic signal) decreased from about $10^3$ initially to $\sim 10^2$ after 24 hours exposure and to $\sim 10$ counts/pulse during some periods in the second day of exposure. A DCB specimen which was annealed in
vacuum at 800°C for 3 hours before testing showed the same initial behaviour, but the pulse height decreased much more rapidly with exposure time, reaching pulse heights $<10^3$ in about 1 hour. After that point the time interval between pulses increased from ~2 to ~5 minutes and the pulse height returned to ~$10^3$ counts/pulse. A smooth split ring specimen of batch MLI-801 gave no acoustic emission for the first six days' exposure. Discontinuous noise was then observed until failure occurred, but the frequency and pulse height were less regular than for DCB specimens.

These results agree with the conclusions drawn from observations of the interference colours on the fracture surface (PR-CMa-20); that the mean crack velocity changes little as the crack propagates, but that the fraction of the crack front which is moving at any time diminishes with decreasing stress intensity ($K_1$) at the crack tip. The acoustic emission results suggest that individual movements of the crack front are very rapid, and occur at roughly constant intervals of time irrespective of $K_1$, but that the area of fresh surface exposed for each movement of the crack front decreases as $K_1$ decreases. If, as the interference colours show, the incremental forward movement of the crack front is also approximately constant, then this implies a decreasing fraction of the crack front moving during any one pulse. These observations are compatible with a repeated film growth and fracture mechanism for SCC propagation.

(c) In 5% NaCl solution at 25°C

Only continuous acoustic emission was observed in aqueous sodium chloride solutions until the last few seconds before complete failure of split-ring specimens of batch MLI-801, when discontinuous cracking was heard. A visible crack could be seen before the onset of this stage, showing that most of the crack generation and propagation in these solutions is electrochemical in nature. Attempts to determine the potential at which these electrochemical processes had a zero rate were defeated by the appearance of noise due to hydrogen evolution when the specimen was made
cathodic. This noise was indistinguishable from the continuous noise obtained when the specimens were anodic.

Unfortunately, because the potentiostats were occupied with other experiments, it was possible to carry out experiments only at constant current, and the potential, therefore, varied during the test. The rate of acoustic emission was observed to depend on the applied current, as expected, but potentiostatic experiments are needed to establish properly the relation between specimen potential and the rate of electrochemical attack.

(d) Liquid metal embrittlement (LME) in mercury

As expected from visual observations, most of the acoustic emission during the cracking of a DCB specimen in mercury occurred in one large pulse which took only about 0.1 - 0.2 seconds to be recorded. However, a small exponentially decreasing tail of discontinuous acoustic emission lasting up to 10 seconds after this pulse was observed. This suggests that the crack velocity - stress intensity curve has the same shape for LME as for SCC with a rapidly decreasing crack velocity branch occurring at low $K_1$ values. $K_{1LME}$ values for Zircaloy-2 in mercury (i.e. that value of the stress intensity at the crack tip below which no propagation occurs) are very low and difficult to determine accurately from present data. However the value of $K_{1LME}$ is almost certainly < 4 ksi/in.

4.2.3 Transmission Electron Diffraction (TED) Analysis by Computer
- R.A. Ploc and R. Davidson

(a) TED analysis of corrosion products in the H-4 loop

An attempt has been made to check theoretical electron diffraction intensities of the materials suggested by SADSP ($\alpha$ Fe$_2$O$_3$, Cr$_2$O$_3$ and NiCrO$_4$) against the experimentally obtained TED pattern. Since there were no correlations, experimental samples of
αFe₂O₃ and Cr₂O₃ were prepared and subjected to TED; however, again there was no correlation between these patterns and those of deposits from the H-4 loop. As the theoretical data for NiCrO₄ were the least reliable, a sample was prepared but as yet has not been subjected to diffraction.

(b) d-spacings

To facilitate electron diffraction analysis a program was written for the CDC6600 which calculates d-spacings for any crystal system for the planes from (666) to (666). The d-spacings are sorted according to both magnitude and Miller indices.

(c) ZrO₂ films formed in oxygen at 300°C

Since PR-CMa-20, section 4.2.8(d), a further 100 patterns have been plotted but have not been checked against the experimental pattern. Approximately 100 patterns remain to be plotted.

4.2.4 Electron Diffraction of Zirconia Films
- R.A. Ploc and R. Davidson

(a) Technique

Discs of Zr with oxide films, formed in oxygen plasmas or fused salt (shorted), have been polished on one side to give a thin duplex oxide/metal layer. The metal edges were lacquered and the sample placed in a 5% pickling solution to promote metal removal. With the appearance of the first hole the chemical attack was stopped and the sample was found, in the Transmission Electron Microscope (TEM), to display an oxide film protruding from the thinned metal. In this manner it is possible to see orientation relationships between the oxide and the metal as well as to identify the oxide/metal interface in the Scanning Electron Microscope (SEM).
(b) Anodic films formed in phosphoric acid

The results reported in PR-CMa-20, section 4.2.8(i), have been carefully checked. An anodized area which displayed an interference colour equivalent to 775 Å of ZrO$_2$ was replicated, the replica was allowed to curl and pore "shells" were silhouetted in the TEM, see Figure 4.2.4.1. These appeared to have an average length of 1000 Å (i.e. greater than the apparent oxide thickness). If one assumed that the estimated 775 Å of ZrO$_2$ was in a layer below the pores, this would give a total oxide thickness of 1775 Å (barrier layer plus porous layer) which does not seem reasonable from image intensities of the stripped ZrO$_2$ films viewed in transmission.

4.2.5 Convection Currents During Anodic Oxidation
- J.P.S. Pringle

The uniformity of the NH$_4$F-HF stripping procedure for Ta$_2$O$_5$ has been tested by a reanodization method whose validity depends on the uniformity of the oxide film produced by anodic oxidation. Measurements made here using the spectrophotometric method confirm that, under most conditions of formation, the oxide film is of uniform thickness all over the tantalum specimen. In unstirred electrolytes at current densities of 10 ma/cm$^2$, however, the oxide film thickness is not uniform, being thicker at the top of the specimen than at the bottom. Since the applied voltage is the same all over the surface, the increased thickness at the top means that more oxide has been formed per volt applied; from the known kinetics of anodic oxidation, it follows that the effective anodizing temperature is greater. That is, heat generated by the anodic oxidation sets up convection currents in the adjacent electrolyte, so that the environment at the top of the foil is hotter than at the bottom.

This interpretation has been checked in several ways. When a series of rectangular tantalum foils were anodized to various voltages with their long axes vertical, the difference in thickness between top and
bottom increased much more rapidly than the mean thickness. This is as expected, because anodizing to greater thickness releases more heat and allows a longer time for the convection currents to operate. When similar specimens were anodized with the long axis horizontal, the convection currents are expected to flow from the ends towards the middle, so that the thickest oxide should occur in the middle; this was observed. Finally, experiments in which similar specimens were anodized simultaneously in stirred and unstirred electrolytes showed that the mean thickness of the films in the unstirred electrolytes was always greater than those in the stirred electrolyte.

Similar results were obtained on stripping, though the effects were smaller and less reproducible. Once again the thickest oxide was at the top, and presumably convection currents were responsible. The situation was, however, more complex than for anodization, because two conflicting factors were at work. Tests showed that when the NH$_4$F-HF reagent was heated, the stripping rate went up; but as it dissolved more tantalum, the rate went down. The warm stripping solution flowing up the foil surface was that which had already dissolved relatively large amounts of tantalum; the result actually observed was therefore the outcome of the competition between these two effects.

4.2.6 Catalytic Activity of Sputtered Films in H/D Isotopic Exchange Reactions
- N. Ramasubramanian

A flow type catalytic reactor system has been built to study the hydrogen-water vapor reaction catalyzed by sputtered films. A nickel film was sputtered on to the walls of a discharge tube in a mixture of hydrogen and argon and preliminary testing at room temperature was carried out at hydrogen flow rates of 25, 150 and 380 ml/min. No detectable exchange was observed. This was probably due to the large dead space in the discharge tube; the catalyst
area to volume ratio was ~ \( 1 \text{ cm}^2/\text{ml} \), about \( 10^4 \) times less than that in conventional catalysts.

In the next series of experiments, crushed Pyrex glass will be used as the substrate material and subsequent to sputtering the crushed glass packed into a conventional catalytic unit will replace the discharge tube. Arrangements are in progress for setting up a rotating drum type sputtering system inside the Veeco evaporator unit.

The preparation of a catalyst by sputtering offers a number of advantages: control on particle size and crystal orientation, good adhesion to the substrate, variation in composition from a pure metal to an alloy, deliberate introduction of impurities such as hydrogen, oxygen, etc.; the main disadvantage is the limit on surface area. Because nonporous substrates are to be used the volume occupied by the sputtered catalyst may be several times that of the conventional catalysts supported on porous substrates.

4.3 CERAMIC STUDIES

4.3.1 Absorption Band Behaviour in Irradiated and Annealed ThO\(_2\) - B.G. Childs and J.B. Hallett

Measurements of optical absorption, during controlled specimen heating from \(-196^\circ\text{C}\) to \(+240^\circ\text{C}\), were reported previously (PR-CMa-20) for Na- and Y-doped CaF\(_2\). Similar measurements have now been made for pure ThO\(_2\) and for ThO\(_2\) doped with Y\(_2\)O\(_3\) or CaO. The main effects noted were as follows.

**Pure ThO\(_2\)**

A partially reduced crystal showing a large but resolvable \( \gamma \)-band at 240 nm but little other obvious structure, developed a broad absorption maximum at 415 nm and a second maximum at 700 nm following \( ^{60}\text{Co} \) gamma irradiation at \(-196^\circ\text{C}\). Previous results indicate that
these maxima probably comprised two groups of overlapping bands; namely the $\theta$ (384 nm), $\iota$ (406 nm), $K$ (439 nm) and $\lambda'$ (466 nm) bands for the 415 nm maximum and the $\sigma$ (623 nm), $\pi'$ (676 nm), $\pi$ (729 nm), $\rho$ (813 nm) and $\sigma$ (934 nm) for the 700 nm maximum.

On annealing, the $K$ and $\lambda'$ bands largely disappeared between $-180^\circ$ and $-160^\circ$C, resulting in a shift of the first maximum to about 390 nm. The $\theta$ and $\iota$ bands decreased subsequently between $-135^\circ$ and $-120^\circ$C. A further small annealing stage for all four bands was apparent in the range $-80^\circ$C to $-30^\circ$C.

The bands comprising the 700 nm maximum also disappeared in two stages; a principal one between $-180^\circ$C and $-100^\circ$C and a lesser one between $-60^\circ$C and $-10^\circ$.

A second, similarly treated crystal behaved differently on irradiation, developing a small absorption maximum at 560 nm. This apparently comprised the $\lambda'$ (466 nm), $\lambda$ (501 nm), $\mu$ (532 nm), $\nu$ (563 nm) and $\xi$ (592 nm) bands which are the prominent features in the spectra for irradiated doped or impure $\text{ThO}_2$ specimens. The maximum disappeared in three stages; two small ones at $-170^\circ$ to $-100^\circ$ and $-80^\circ$ to $-40^\circ$, respectively, and a major stage at $+120^\circ$ to $210^\circ$C.

$Y_2O_3$-doped $\text{ThO}_2$

Two specimens doped with 0.14 mole % $Y_2O_3$, and annealed in air for 2 h at 1200°C also developed the characteristic and prominent $\lambda'$ - $\xi$ band structure on irradiation at $-196^\circ$C.

In contrast to the behaviour of the second pure specimen, this structure annealed out in a principal stage at $-150^\circ$ to $-120^\circ$C, only a minor fraction of the annealing occurring at higher temperatures.

$\text{CaO}$-doped $\text{ThO}_2$

Two specimens doped with 0.28 mole % $\text{CaO}$ again developed the characteristic band structure on irradiation. The annealing behaviour of this was similar to that for
the $Y_2O_3$-doped specimens except that more structure was apparent at higher temperatures—in particular a small stage at $+70^\circ$ to $100^\circ$C. For one of the specimens the main stage occurred at consistently lower temperatures (-160$^\circ$ to -130$^\circ$).

The above changes, corresponding to the release of electrons and holes from various trapping sites, are obviously complex and specimen dependent. It should be possible to correlate them with features in the thermoluminescence spectra once the correction for the different heating rate in this technique has been established.

One experimental complication which has hitherto interfered with the detection of small absorption changes has been the occurrence of major shifts in the background absorbance at particular temperatures. This problem has been overcome by improving the handling equipment and procedures so that no trace of water vapor can enter the specimen cryostat and subsequently be condensed onto the specimen surfaces.

4.3.2 Thermoluminescence in Pure and Doped ThO$_3$

-P. J. Harvey

Thermoluminescence (TL) measurements have been extended to include the temperature range -196$^\circ$C to room temperature. Pure thoria crystals and crystals doped with CaO, $Y_2O_3$ and Ta$_2O_5$ all in the "reduced" condition have been excited by UV light and the TL measured at an average heating rate of ~10$^\circ$/sec. The results are tabulated below.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Pure</th>
<th>ThO$_2$:CaO</th>
<th>ThO$_2$:Y$_2$O$_3$</th>
<th>ThO$_2$:Ta$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL peak maxima (°C)</td>
<td>-187</td>
<td>-170</td>
<td>-149</td>
<td>-137</td>
</tr>
<tr>
<td></td>
<td>-173</td>
<td>-150</td>
<td>-140</td>
<td>-139</td>
</tr>
<tr>
<td></td>
<td>-173</td>
<td>-154</td>
<td>-135</td>
<td></td>
</tr>
</tbody>
</table>

The peaks of greatest intensity in each case are underlined.
Three observations may be made from the above table.

1. The purest specimen contains the greatest number of peaks.
2. Only the peak at $-137 \pm 3^\circ C$ is common to all 4 types.
3. Although $Ca^{2+}$-doping and $Y^{3+}$-doping introduce new peaks at $-116^\circ C$ and $-94^\circ C$, no new peak is evident in the $ThO_3:Ta_2O_5$ specimens.

A further observation is that both $Ca^{2+}$- and $Y^{3+}$-doping reduce the overall luminescence.

4.3.3 Excitation Energy Dependence of TL Intensity
- P. J. Harvey

By selective excitation using the Baird Atomic spectrofluorimeter a series of experiments was performed varying the wavelength of the xenon source in 5 nm intervals from 220 nm to 300 nm. It appears that maximum TL intensity corresponds to 220 nm excitation indicating a band-to-band transition. It has now become apparent, because of the extreme sensitivity of the TL reader, that more controlled excitation conditions may be achieved using the deuterium source in the Perkin Elmer spectrophotometer. Improvements should result in both resolution and range and the excitation experiments are being repeated.

4.3.4 Exposure Dependence of Glow-Peaks in the 20°C - 380°C Range
- P. J. Harvey

As discussed in PR-CMa-20, TL curves were obtained for specimens in the +20°C to 380°C temperature range. Using UV light as the source of excitation, a series of experiments have been performed on a $Ca^{2+}$-doped specimen measuring individual peak intensity as a function of UV dosage. In addition to the 3 principal peaks previously reported at 85°C, 145°C and 280°C, 2 smaller peaks have been resolved at 185°C and 200°C.
Plots of intensity as a function of UV exposure indicate linear behaviour for the 85°C, 260°C and 285°C peaks, indicative of traps containing a single electron. The behaviour of the 145°C peak is more complex. At exposures below ~200 sec it is linear but at higher doses the peak intensity becomes supralinear.

The 185°C peak appears to be linear but the low intensity makes accurate measurements difficult.

It is proposed to extend these studies to the pure and Y⁺-doped specimens and also to cover the range -196°C to room temperature.

4.3.5 Electron Paramagnetic Resonance in Pure and Yttrium-Doped Crystals of ThO₂
- R. Lang

In PR-CMa-19 it was reported that a complex EPR spectrum consisting of a number of unresolved resonance lines was observed in nominally pure ThO₂ upon subjecting the specimen to heat treatment No. 1 (see PR-CMa-19) and subsequent UV irradiation at 77°K. By studying this spectrum in the (110) plane in yttrium-doped specimens as well as in pure specimens (which had been given the appropriate heat treatment) it was possible to enhance certain resonance lines while virtually eliminating others. In this way the spectrum could be resolved into twenty resonance lines, each of which showed a pronounced angular dependence.

The twenty lines are believed to be due to four different electronic defect centers. Precision measurements of the g-tensors of two of the defect centers were carried out at 77°K by measuring to six significant figures both the resonant magnetic field and the microwave frequency as a function of angular displacement from <100> in the (110) plane.

The g-tensor formally describes the magnetic anisotropy of an electron or hole which is trapped near an impurity atom or at a lattice vacancy. This magnetic anisotropy can be used to determine the
symmetry of the defect center and the directions of its distortions from cubic symmetry.

All non-cubic defect centers observed in pure "reduced" ThO$_2$ are axially distorted along the body diagonal of the cubic unit cell of ThO$_2$. In pure "oxidized" and in yttrium-doped ThO$_2$ there is one center of orthorhombic symmetry which is strongly distorted along <001> and slightly distorted along <110>.

If the nucleus of the impurity atom has a non-zero nuclear spin the EPR spectrum of the defect center is likely to show hyperfine structure. This structure can be used to identify the particular impurity atom. It is believed that two of the observed EPR spectra, one due to an electronic center and one due to a hole center, show hyperfine structure.

The results are being interpreted in terms of particular defect models.

4.4 METAL PHYSICS

4.4.1 Dislocations Generated by Zirconium Hydride Precipitation
- G.J.C. Carpenter and J.F. Watters

Tilting experiments have been performed in the HU-11A electron microscope to prove the character of the dislocations generated by zirconium hydride precipitates in Zircaloy-2. The specimens were quenched from 850°C into water, resulting in hydride particles ~1 μm long. Stereo pairs show that the precipitates are in the form of needles lying parallel to {1010} planes. The associated dislocations have been shown in several cases to possess Burgers vectors of the type $\frac{1}{3}$<1120>. Of the three possible Burgers vectors, one or both of the two at 60° to the habit plane are normally represented while the third (lying in the habit plane) is not observed.
The results of a typical tilting experiment are summarized below.

### TABLE 4.4.1.1

**CHARACTERISTICS OF DISLOCATIONS GENERATED BY ZIRCONIUM HYDRIDE PRECIPITATES**

<table>
<thead>
<tr>
<th>Hydride Habit Plane</th>
<th>Dislocations</th>
<th>( g \cdot b ) for ( g ) as specified</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((1\bar{1}00))</td>
<td>set &quot;A&quot;</td>
<td>( \neq 0 ) ( = 0 ) ( \neq 0 ) ( \neq 0 ) ( = 0 )</td>
<td>( \frac{1}{3}[12\bar{1}0] )</td>
</tr>
<tr>
<td></td>
<td>set &quot;B&quot;</td>
<td>( \neq 0 ) ( \neq 0 ) ( = 0 ) ( = 0 ) ( \neq 0 )</td>
<td>( \frac{1}{3}[\bar{2}1\bar{1}0] )</td>
</tr>
</tbody>
</table>

Stereoscopic pairs and trace analysis indicate that the dislocations lie in pyramidal planes and further experiments will be carried out to deduce these planes more accurately.

#### 4.4.2 Modifications to the Tilt Stage of the Hitachi 200E Microscope

- G. J. C. Carpenter and M. J. Ward (System Materials Branch)

As supplied, the \( \pm 30^\circ \), double-axis tilt stage for the 200 kV Hitachi electron microscope has limited use because it causes severe specimen contamination. A similar problem with the 100 kV Hitachi microscope was eliminated by modifying the tilt stage so that a cold trap, in the form of a disc, was situated near the specimen (M. J. Ward and J. Morralee, to be published). A similar device has now been constructed and fitted to the 200 kV microscope with encouraging results. The drive motors are also being replaced since the present system is too rapid for sensitive tilting experiments. The modifications will enable tilting and dark field experiments to be carried out on a given foil area over extended periods of time without serious contamination.
4.4.3 Preparation of Zr Single Crystals
- G.J.C. Carpenter and S.R. MacEwen

The MRC electron beam zone refiner has been modified so that the original rubber belt drives to the scanning device are eliminated. They have been replaced by a direct gear drive which gives much smoother scanning and permits rates between 0.3 and 3.1 cm/hour.

Using a scan rate of 0.6 cm/hour with the specimen at ~1700°C it has been possible to obtain single crystals of the β-phase up to 9 cm in length. However, these often fail to transform into a single α-grain as the scan proceeds. Recently, a different technique has yielded promising results. The specimen is scanned in the β-phase to give a single β-grain and then the beam is switched off so that the specimen cools fairly rapidly. The resulting fine scale α-structure is relatively unstable and can often be converted into a single crystal by annealing for 50 hours at 845°C. Specimens 3 - 4 cm in length have been prepared in this way.

It is probable that this technique is sensitive to the cooling rate and it is planned to examine this effect by adding helium gas to the vacuum chamber as the beam is switched off. Strain anneal techniques are also being applied to the β-scanned specimens.

4.4.4 Analysis of Stress Relaxation
- S.R. MacEwen

The stress-relaxation test is a powerful tool for determining the deformation parameters of materials. In a relaxation test the total strain in a specimen is kept constant, and any plastic deformation is balanced by elastic deformation. Thus the basic equation describing the rate of stress decay is,

$$\frac{1}{E} \frac{d\sigma}{dt} = \epsilon_p$$

......(1)
where $E$ is Young's modulus. The commonly employed analysis of relaxation data assumes that the plastic strain rate, $\dot{\varepsilon}_p$, results from a single thermally activated process which depends exponentially on stress. The solution to (1) for the stress drop $\Delta \sigma$ as a function of time is then,

$$\Delta \sigma = S \ln (Ct + 1) \quad \ldots \ldots (2)$$

Thus at long times, $t \gg C^{-1}$, a plot of $\Delta \sigma$ vs. $\ln(t)$ becomes linear with slope $S$. Two important deformation parameters, activation volume $V^*$, and an approximate value for strain-rate sensitivity can be found from the relationships,

$$V^* = \frac{kT}{\sigma_0} \quad \ldots \ldots (3a)$$

$$\text{and} \quad n = \frac{S}{\sigma_0} \quad \ldots \ldots (3b)$$

where $\sigma_0$ is the stress at the beginning of relaxation, and $\sigma_0$ is the Taylor factor.

One basic problem in applying such an analysis to experimental data arises from the magnitude of the constant $C$. At low temperatures $C^{-1}$ is of the order of a few seconds, however at elevated temperature it may be as large as one hundred seconds. Thus although a plot of $\Delta \sigma$ vs. $\ln(t)$ may appear linear, a relaxation test done for too short a time will yield erroneous results. Another problem in the use of relaxation data arises from the definition of strain-rate sensitivity. Rigorously

$$n = \frac{d \ln \sigma}{d \ln \dot{\varepsilon}} ,$$

and thus $n$ is given in terms of $V^*$ by $n = kT/\sigma_0 \sigma V^*$, not simply by $3b$ as is often assumed. However plotting stress-relaxation data in the form $\ln (-\dot{\varepsilon})$ vs. $\ln (\sigma)$ allows $n$ to be found directly from the slope. If the assumption that a single rate process depending exponentially on stress is valid, $n^{-1}$ will be linearly dependent on $\sigma$, with a slope given by the $S$ of (1).
If plastic deformation is controlled by a mechanism which does not depend exponentially on stress, or if more than one process is contributing to the total plastic strain, only the analysis for strain-rate sensitivity from the slope of \( \ln (-\dot{\varepsilon}) \) vs. \( \ln (\varepsilon) \) remains valid. The extraction of physical parameters, such as activation volume, will require detailed knowledge of how each of the plastic deformation mechanisms affects the total relaxation curve. For example, if two mechanisms are operative, one with a high stress dependence and one with a low stress dependence, the long time behaviour will be dominated by the one with the weak dependence. Analysis of stress rate (rather than total stress drop) as a function of time and stress for particular regions of the relaxation curve can therefore be used to determine physical parameters.

A computer program has been written to do the following:

1) Take raw data from a stress-relaxation test and using the DMAC curve follower, convert it to stress-time data.

2) Apply the conventional analysis to determine \( S \) at long times. A linear regression analysis is applied to \( \Delta \sigma \) vs. \( \ln(t) \) for any desired portion of the total curve. In particular, \( S \) is found for time greater than (approximately) 180 sec, 220 sec, 260 sec and 300 sec. If the \( S \) values thus found continually increase, either the relaxation test was terminated at too short a time, or the assumption that the plastic strain rate depends exponentially on stress is not valid. A line-printer plot of \( \Delta \sigma \) vs. \( \ln(t) \) is given.

3) Obtain values for \( S \) and \( C \) in the theoretical expression for \( \Delta \sigma \) (eqn. 2) using multiple regression analysis. If a good fit can be obtained for the entire curve \( S \) can be used to calculate activation volume. Thus useful data can be obtained from relaxation curves which do not go to \( t \gg C^{-1} \), a fact not true if the conventional form of analysis is used.
4) Calculate the stress rate as a function of time from the experimental data. Because of the small slope of a typical relaxation curve, geometrical means are not sufficiently accurate to determine $d\sigma/dt$. For this reason $\dot{\sigma}$ is found by first fitting a fifth order polynomial in $\ln(t)$ to the curve of $\sigma$ vs. $t$, and then differentiating. (No physical meaning can be attached to the constants obtained in the curve fitting.) Line printer plots are given for $\ln(-\dot{\sigma})$ vs. $\ln(t)$ and for $\ln(\sigma)$.

5) Calculate the strain-rate sensitivity, $n$, as a function of stress by fitting a fifth order polynomial in $\ln(\sigma)$ to the data of $\ln(-\dot{\sigma})$ vs. $\ln(\sigma)$, and differentiating.

6) Fit a polynomial in stress to the data of $n^{-1}$ vs. $\sigma$. If a linear relationship results the equality of the slope with the value of $S$ obtained from (3) confirms the assumption of a single rate controlling process whose activation energy depends linearly on stress.

4.4.5 Deformation Mechanisms in Ultra Fine Grained Zr-2½% Nb

- S.R. MacEwen, C.J. Simpson* and J. Moerman*

Tensile tests have been made on ultra fine grain specimens (grain size 0.15 μm) (gauge length 1 in., cross section 0.100 in.) at a nominal strain rate of $3.3 \times 10^{-5}$ sec$^{-1}$ over the temperature range 250°C to 500°C. All tests were made in a vacuum of $10^{-5}$ torr. Results for the proportional limit and 0.2% offset are given in Fig. 4.4.5.1. For comparison, data obtained from specimens with a $3 \pm 2$ μm grain size are also shown. Apart from the greatly increased yield stress in the ultra fine grained material below 450°C, the most striking feature of Fig. 4.4.5.1 is the temperature dependence of the flow stress. While the 0.15 μm specimens show a very rapid decrease in flow stress with increasing temperature, the 5 μm specimens show little or no variation other than that expected from the temperature dependence of the shear modulus.

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*Ontario Hydro staff on attachment to Metallurgical Engineering Branch
Figure 4.4.5.1 TEMPERATURE DEPENDENCE OF THE YIELD STRESS
(Strain Rate = $3.3 \times 10^{-5}$ sec$^{-1}$)
The elongation to failure is given in Fig. 4.4.5.2. A marked increase in ductility is seen for temperatures above 400°C and the 190% strain observed at 500°C is approaching superplastic behaviour. (It should be noted that elongation is dependent on specimen geometry and thus a comparison with specimens of different shape than that used for the present tests is not valid.)

After an initial period of rapid work hardening, specimens deformed at temperatures greater than 400°C attained a constant, steady-state, flow stress. The strain rate dependence of the flow stress, as determined from strain-rate change tests, is given in Fig. 4.4.5.3. The strain-rate sensitivity \( n = \frac{\partial \ln \varepsilon}{\partial \ln \dot{\varepsilon}} \) is calculated from the slope to be 0.11.

Stress-relaxation tests at 420°C have been analyzed to give strain-rate sensitivity (see Section 4.4.4). From the slope of \( \ln (-\dot{\varepsilon}) \) vs. \( \ln (\sigma) \) relationship, \( n \) has been found to be 0.12 for stresses near the flow stress, in reasonable agreement with the value found from strain-rate change tests. At lower temperatures, below 400°C, a steady-state flow stress was not attained. For this reason strain-rate sensitivity was found by extrapolating back through the transient to the strain at which the rate change was made, and calculating \( n \) from \( \ln \left( \frac{\sigma_2}{\sigma_1} \right) / \ln \left( \frac{\dot{\varepsilon}_2}{\dot{\varepsilon}_1} \right) \). A value of 0.02 was found at 300°C.

The results indicate that a second deformation mechanism, not operative in 5 \( \mu \)m grain-size specimens, contributes to the plastic strain in ultra fine grain (0.15 \( \mu \)m) Zr-2.5% Nb.

The mechanism is highly temperature and strain-rate dependent, and becomes progressively more important at temperatures above 300°C.
Figure 4.4.5.2 - Elongation To Failure ($\dot{\varepsilon} = 3.3 \times 10^{-6} \text{ sec}^{-1}$)
(grain diameter 0.15 $\mu$)

Figure 4.4.5.3 - Strain-Rate Dependence of Flow Stress (T : 420°C)
4.4.6 **Diffusion in \(\alpha\)-Zr**  
- G.M. Hood and R.J. Schultz

(a) **Self-diffusion** (in conjunction with J.L. Whitton and A.F. Quenneville)

Investigations of vibratory polishing and rotary polishing methods for removing sub-micron sections from Zr diffusion specimens are being made. Results to date have yielded self-diffusion coefficients of about \(10^{-14} \text{ cm}^2 \text{ s}^{-1}\) at 800°C. Technical problems have limited the accuracy of the measurements. It is felt these can be overcome.

(b) **Ti diffusion in \(\alpha\)-Zr**

Measurements of \(^{44}\text{Ti}\) diffusion in single crystals of \(\alpha\)-Zr have been made at 850°C. These show that Ti diffusion in \(\alpha\)-Zr is somewhat faster than Zr self-diffusion.

(c) **Mn diffusion in \(\alpha\)-Zr**

Four measurements of \(^{54}\text{Mn}\) diffusion in single crystals of \(\alpha\)-Zr have been made at 830°C. These have shown that Mn diffusion is about four orders of magnitude faster than Zr self-diffusion.

4.4.7 **Diffusion in Al**  
- G.M. Hood and R.J. Schultz

Low temperature measurements of \(^{64}\text{Cu}\) diffusion in Al single crystals have been made with the intention of studying the intrinsic Arrhenius plot for curvature. Such curvature may help to indicate the presence of competing diffusion mechanisms.

The present results indicate that, because of an apparently high dislocation diffusion contribution to Cu diffusion in Al, some difficulty may be encountered in extending the measurements of intrinsic diffusion over a sufficiently wide range.
4.4.8 Positron Annihilation  
- G.M. Hood and R.J. Schultz (in conjunction with S. Kim and P. Martel, Physics Division)

Positron annihilation on pure Al and some dilute alloys of Al is being studied. The aims are to measure vacancy formation energies in the pure metal and the alloys with a view to obtaining solute-vacancy binding energies.

Initial measurements have shown that improvements to temperature measurements and control are required; these modifications are currently being made.

Estimates of possible effects of radiation damage to the sample from the high intensity positron source indicate that in a period of hours atomic displacements up to a maximum of \(~10^{-8}\) atom fraction might occur. It seems unlikely that there will be any serious effect on the measurements from radiation damage.

4.4.9 Bubble Strengthening of Zr-Alloys  
- E.M. Schulson

It has recently been suggested that Zr-alloys might be strengthened by incorporating inert gas bubbles into the lattice, using \((n,\alpha)\) transmutation schemes. Three questions thus arise:

(a) for a given transmutable alloy of \(\text{Be}^9/\text{Zr}, \text{B}^{10}/\text{Zr}\) or \(\text{Li}^8/\text{Zr}\), are He bubbles likely to nucleate in reasonable times under 'CANDU' operating conditions?

(b) If so, what will be the expected bubble size and number density?

(c) Can this field be expected to reduce the in-reactor creep rate to \(< 10^{-7}/\text{hr}\)?
By applying homogeneous nucleation theory and bubble/dislocation interaction theory, an attempt has been made to answer these questions.

The theoretical calculations are summarized as follows:

(i) For Zr(0.01 - 0.10 wt.%)Be\textsuperscript{9} alloys, nucleation is expected to be complete within 10\textsuperscript{8} sec (< 3 yr); for Zr(50 - 500 ppm)B\textsuperscript{10} and Zr(30 - 300 ppm)Li\textsuperscript{6} alloys, nucleation is expected to occur almost instantaneously.

(ii) For the Be\textsuperscript{9}/Zr alloys, approximately 10\textsuperscript{13} - 10\textsuperscript{16} bubbles/cm\textsuperscript{3} of corresponding radii 50 - 5 Å are expected after 3 yr irradiation, if the diffusion coefficient for He atoms in Zr is within the range 10\textsuperscript{-12} - 10\textsuperscript{-18} cm\textsuperscript{2}/sec. This corresponds to a bubble content of < 0.001 vol.%. For the other alloys, about 10\textsuperscript{18} - 10\textsuperscript{19} bubbles/cm\textsuperscript{3} are expected of ≈ 5 Å radii, corresponding to a bubble content ≈ 0.05 vol.%.

(iii) For the bubble drag mechanism to impede dislocation motion to such an extent that the tensile creep rate is ≪ 10\textsuperscript{-7}/hr, calculations suggest that approximately 2 x 10\textsuperscript{17} bubbles/cm\textsuperscript{3} of ~25 Å radii are required. This corresponds to a bubble content of ~1.2 vol.% and is similar to the requirements for high temperature strengthening with hard particles (eg., T.D. nickel).

Viewed collectively, these considerations indicate that the amount of gas produced in the Be\textsuperscript{9}/Zr alloys is expected to be less than amount required to significantly increase the creep strength of Zr through the bubble-drag mechanism. However, other considerations indicate that if all bubbles nucleate on dislocations, the number produced after ~3 yr irradiation might be sufficient to impart the desired creep strength. In the B\textsuperscript{10}/Zr and Li\textsuperscript{6}/Zr alloys, considerably more bubbles are expected, and so these alloys might offer potentially greater bubble strengthening. To be
effective, however, some bubble coalescence would probably be necessary, and so strengthening would be expected to occur sometime after bubble formation.

A report detailing the calculations has been prepared for publication (AECL-4252).

4.4.10 Ordered Alloys: Zr₃Al-Based Alloys  
- E.M. Schulson

(5) Transmission electron microscopy  
  - (in collaboration with L.M. Howe, Solid State Science Branch)

Further observations have been made of stacking-fault and dislocation features (see Section 1.3.2).

Sections 4.4.10 (1), (2), (3), (4) and (6) are described in an Internal CRNL Report.
4.5 REPORTS, PUBLICATIONS AND LECTURES

4.5.1 REPORTS

AECL-4252 "An Analysis of Bubble Strengthening of Zr-Alloys"
- E.M. Schulson

4.5.2 PUBLICATIONS

Proceedings of the 5th ICMC "A Technique for Studying the Rate Controlling Processes During Metal Oxidation"
- B. Cox

4.5.3 LECTURES

5th International Conference on Metallic Corrosion, Tokyo, 20 - 27 May 1972 "A Technique for Studying the Rate Controlling Processes During Metal Oxidation"
- B. Cox
5. REPORT OF McMaster University

H. G. Thode

5.1 Yields of Tin and Cadmium Isotopes in Fission

- Cherian K. Mathews

With a view to determining the relative yields of tin and cadmium isotopes in the fission of heavy elements, uranium-235 and plutonium-239 samples have been chemically purified and are undergoing irradiation in the McMaster Nuclear Reactor. As nanogram quantities of tin and cadmium thus produced must be analysed in the mass spectrometer, various techniques for the efficient production of the ions of these elements are being explored. The "silica gel" technique (1) using a single filament thermionic source appears promising.

6. REPORT OF THE UNIVERSITY OF WESTERN ONTARIO

6.1 **High Temperature Oxidation Resistant Coatings on Zirconium Alloys**
- C. Roy and B. Casburn

(a) **Interfacial Studies**

These studies are being pursued to demonstrate whether the chemical reactions that take place at the metal coating/ZrO$_2$ film interface during vacuum annealing are the result of the oxide film disproportionating. To elucidate the mechanism, the surface stoichiometry of the oxide film is assessed after heat-treating Ni-coated pre-oxidized samples of Zircaloy-2 in vacuo in order to promote the formation of the intermetallic compounds. Samples which, after vacuum annealing, showed areas on the surface where the Ni-coating is loosely adherent (thus unreacted with the ZrO$_2$ film) are selected because over these areas the coating can easily be peeled off, thus exposing the oxide surface which was not in equilibrium with the vacuum in the chamber.

Preliminary microprobe analyses on the oxide surface, together with X-ray diffraction and electron microscopy studies of the stripped oxide indicate the presence of free zirconium in the oxide film. Greater concentration would appear on the oxide surface rather than in the oxide itself but it is possible that the stripping procedure also removed some of the zirconium particles embedded in the oxide.

To improve our understanding of the phenomenon, similar experiments with Ni-coated pre-oxidized tantalum samples were initiated. Short vacuum anneals at 750°C promoted rapid development of intermetallic phases at the metal coating/oxide film interface. From this it may be inferred that disproportionation is not peculiar to zirconia films but may occur in metal systems on which thick protective oxide film can form.
(b) Oxidation Studies

The effectiveness of the coatings formed on pre-oxidized Zircaloy-2 samples by a combination of processes including plasma spraying was assessed from weight gain measurements during oxidation tests at 550°C followed by metallographic studies of the sectioned sample. As reported in PR-CMa-20, the short-term oxidation resistance of Zircaloy-2 only was improved by these coatings; long-term exposures resulted in the degradation of the overlay and diffusion layers of the coatings. Longitudinal cracks and porosity which developed in the oxide layer have been attributed to thermal expansion mismatch although some of the cracks may be artefacts due to sectioning and grinding stresses. Better success in preparing impervious outer coatings on the pre-oxidized samples would improve the oxidation resistance; therefore we are exploring other methods of coating our samples.
7. REPORT OF UNIVERSITY OF OTTAWA

Dr. B.A. Morrow

7.1 Infrared Spectroscopic Studies of Supported Metal and Metal Oxide Catalysts

An investigation of the adsorption of methylamine and of pyridine on various silica-supported metals has been carried out and some of the results are discussed in this report. A preliminary report involving platinum has already appeared (1).

Following the adsorption of methylamine on palladium, ruthenium and nickel, infrared absorption bands characteristic of a chemisorbed species were observed in the C-H stretching region ($\nu_{\text{C-H}}$, 2900 cm$^{-1}$) and the NH stretching region ($\nu_{\text{NH}}$, 3300 cm$^{-1}$) and no infrared absorptions due to $-\text{C}=\text{N}$ species were detected (Table 1). The absence of a $\nu(\text{C}=\text{N})$ band ($\nu \approx 2100 \text{ cm}^{-1}$) indicates that methylamine does not dehydrogenate on these metals and this behaviour is in marked contrast to that previously reported for methylamine adsorption on platinum where HCN is a suspected reaction product (1). On the remaining noble metals (Table 7.1) the behaviour was similar to that previously reported for platinum, viz. dehydrogenation and the appearance of a $\nu\text{C}=\text{N}$ band in the infrared spectrum. In the case of iridium, methylamine adsorption also produced a strong absorption band at 1594 cm$^{-1}$ which could be attributable to a $\text{C}=\text{N}$ stretching mode or to a deformation vibration of a $\text{NH}_2$ group ($\delta\text{NH}_2$). A similar band near 1590 cm$^{-1}$ appears in the case of platinum only after adding $\text{H}_2$ to the adsorbed methylamine followed by pumping at room temperature for 4 - 6 hours. For both iridium and platinum this band disappears in the presence of $\text{H}_2$ and reappears when the $\text{H}_2$ is pumped away. When $\text{D}_2$ is admitted into the cell, this band disappears and does not reappear even after degassing for 16 hours at room temperature, but it does reappear when the surface is hydrogenated (with $\text{H}_2$) and degassed at 25°C suggesting that this band has its origin in $\delta\text{NH}_2$ rather than $\nu\text{C}=\text{N}$. Further experiments with $\text{CH}_3\text{ND}_2$ and $\text{CD}_3\text{ND}_2$ are planned to verify this point.

Some experiments were also carried out with mixtures of $\text{H}_2$ and $\text{MeNH}_2$ in different proportions to check whether dehydrogenation of $\text{MeNH}_2$ could be suppressed by the presence of excess of $\text{H}_2$ in the reaction mixture. It was observed that dehydrogenation took place even with a 40 fold excess of $\text{H}_2$. 

- 106 -
<table>
<thead>
<tr>
<th>Metal</th>
<th>( \nu(\text{NH}) ) Region</th>
<th>( \nu(\text{CH}) ) Region</th>
<th>( \nu(\text{C=N}) ) Region</th>
<th>Bending Region</th>
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</thead>
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<td>3294 (b) cm(^{-1})</td>
<td>2969 (s) cm(^{-1})</td>
<td>2071 (s) cm(^{-1})</td>
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</tr>
<tr>
<td></td>
<td>3153 (m)</td>
<td>2931 (m)</td>
<td></td>
<td>1594 (s) cm(^{-1})</td>
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<tr>
<td></td>
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<td></td>
<td>1420 (b,sh)</td>
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<td>3282 (w,b)</td>
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<td>3280 (v,w)</td>
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<td></td>
<td></td>
<td>2872 (w)</td>
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<td>-</td>
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<td>2904 (m)</td>
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<tr>
<td></td>
<td></td>
<td>2851 (w)</td>
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*Degassed at 20°C for 2 hours
w = weak
m = medium
s = strong
b = broad
sh = shoulder
Some of the results of the investigation of the adsorption of pyridine on various noble metals at room temperature followed by degassing at 20°C for 14 hours are given in Table 7.2. One interesting result from this work is that an infrared band attributable to the pyridinium ion ($\nu$ 1540 cm$^{-1}$) is only observed for platinum, iridium and rhodium whereas for the other metals all infrared bands can be assigned to physically adsorbed or coordinated pyridine.

When pyridine-$d_5$ is adsorbed on Pt-SiO$_2$, exchange between the H of the Si-OH groups, and D of the deuterated pyridine is observed. This exchange can possibly take place as either: (a) direct exchange between the H of the Si-OH groups and pyridine-$d_5$ or (b) as exchange between the surface hydrogen on the metal and pyridine-$d_5$ with the resulting deuterium exchanging with Si-OH groups being catalyzed by platinum. When pyridine-$d_5$ is adsorbed on to a surface that has been treated with carbon monoxide or on to one which has been degassed at 400°C for 50 hours (to remove the surface hydrogen), very little deuteration of the Si-OH groups takes place. Therefore pyridine-$d_5$ can easily be used to monitor the amount of surface Si-OH groups.

Experiments using O$^{18}$, C$^{13}$O are in progress.

TABLE 7.2

Wavenumbers of the Infrared Bands
Observed After the Adsorption of 10 Torr of
Pyridine (for 1 Hour at 20°C).
Samples Degassed for
14 Hours at 20°C Prior to recording Spectra.

<table>
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<tr>
<th>Pt</th>
<th>Ir</th>
<th>Os</th>
<th>Rh</th>
<th>Ru</th>
<th>Pd</th>
<th>Ni</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(sh)</td>
<td>(m)</td>
<td>(w)</td>
<td>(m)</td>
</tr>
<tr>
<td>1581</td>
<td>1565</td>
<td>1571</td>
<td>1575</td>
<td>1580</td>
<td>-</td>
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</tr>
<tr>
<td>(s)</td>
<td>(s)</td>
<td>(s)</td>
<td>(m)</td>
<td>(w)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1548</td>
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<td>-</td>
<td>1546</td>
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</tr>
<tr>
<td>(w)</td>
<td>(sh)</td>
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<td>(w, sh)</td>
<td></td>
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<td>(s)</td>
<td>(w)</td>
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<tr>
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8. REPORT OF UNIVERSITY OF OTTAWA

Dr. B.L. Conway

Studies on Electrolytic Hydrogen/Deuterium Separation

8.1 Lines of Progress in the Work

As indicated in the previous report, one of the aims of work in the present quarter was to fill in the data on the effect of urea and guanidine at Fe and Hg over a wider range of current densities. This work is in progress but was impeded by some equipment failures. Consequently, the full data required for publication of the proposed paper and for the necessary complete evaluation of additive effects with urea and guanidine has not yet been acquired.

For Hg/Au, measurements of $S_{H/D}$ down to lower current densities of $2 \times 10^{-5}$ a.cm$^{-2}$ at Hg/Au were completed but required extended periods of electrolysis. Although long electrolyses can introduce other difficulties, the results obtained seem to have about the same reproducibility as those reported previously at higher current densities. In order to minimize gas collection times, as small a sample as possible of gas was collected at low pressure and then compressed prior to injection into the chromatograph. This is the best technique for maintaining sensitivity of the chromatographic measurement with small samples.

In the experiments down to low current densities, a large amalgamated Au foil electrode in the form of a roll was employed, having an area of ca. 20 cm$^2$.

8.2 Examination of Effects of Urea and Guanidine on Current-Potential Relations at Hg

The effects of 1M and 5 M urea on the Tafel line for $H_2/HD$ evolution at Hg was studied in the isotope separation cell under the same conditions as those employed in actual H/D separation experiments. Isotopically equilibrated urea was employed, as used in the previous separation experiments.

The Tafel lines with and without additions of urea were, surprisingly, almost superimposable (Fig. 8.2.1) even
Fig. 8.2.1. Effect of 1 M urea and 0.17 M guanidine on Tafel lines for Hg (25°C, 1 N aqueous KOH).
in the 5 M solution, indicating that no fundamentally different behavior in the hydrogen evolution reaction arises at Hg in the presence of urea. The observed effects on $S_{H/D}$ are hence due to subtle differences of kinetic behavior which are only manifested in a differentiating experiment such as the isotope separation.

The unavoidable presence of O$_2$ diffusing from the anode compartment in the single-unit cell as operated in separation experiments is a disadvantage for evaluation of the Tafel line owing to depolarization effects which set in below $10^{-3}$ a.cm$^{-2}$. These investigations will be extended by evaluating the log i vs. V relations in a separate 3-compartment cell where the anode is effectively isolated.

At Fe, the effect of guanidine was investigated at 0.17 M in aqueous 1 N KOH (Fig. 8.2.2). In this case, a lowering of H overpotential was observed in the current-density range $10^{-4} - 10^{-2}$ a.cm$^{-2}$. At Hg, guanidine raises the overpotential (Fig. 8.2.1) by ca. 0.1 V at the 0.17 M concentration. The interaction of guanidine with Hg is an interesting one; it was found accidentally that a mercury electrode left on open circuit in the presence of guanidine developed a grey surface film that took several seconds to be dispersed under cathodic electrolysis conditions. Also, in guanidine solution, Hg breaks up into many droplets that remain stable without coalescence for many hours. This reflects a strong adsorption of the guanidine which presumably lowers the surface tension of the Hg. It is of interest that thiourea has a similar affinity for Hg through the =S function.

Hg in urea solutions does not exhibit any unusual behavior and the Tafel line for H$_2$ evolution is seen (Fig. 8.2.1) to be virtually unaffected by the presence of urea as additive.

Table 8.2.1

<table>
<thead>
<tr>
<th>Current Density a.cm$^{-2}$</th>
<th>$S_{H/D}$ (no additive)</th>
<th>$S_{H/D}$ (0.17 M guanidine)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Mean</td>
</tr>
<tr>
<td>$2 \times 10^{-5}$</td>
<td>4.47</td>
<td>4.45±0.02</td>
</tr>
<tr>
<td>$4 \times 10^{-5}$</td>
<td>3.7</td>
<td>[3.7]</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>4.48</td>
<td>4.34±0.15</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>2.75 3.42 3.27</td>
<td>3.35±0.08</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>4.46 4.80</td>
<td>4.63±0.17</td>
</tr>
<tr>
<td>$1.4 \times 10^{-2}$</td>
<td>4.77 4.48 4.9</td>
<td>4.72±0.24</td>
</tr>
</tbody>
</table>


Fig. 8.2.2. Effect of 0.17 M guanidine on Tafel line for Fe (25°C, 1 N aqueous KOH).
8.3 Solution Properties of Urea in H₂O and D₂O

Following presentation of preliminary data in the previous report, we have completed the evaluation of the solution properties of urea in H₂O and in D₂O (as urea-d). Fig. 8.3.1 shows the partial molar volume of urea in H₂O and D₂O and Fig. 8.3.2 the partial molar compressibility \( \varphi_{K,s} \). The data in H₂O in Fig. 8.3.1 are those of Stokes[1], based on a recent publication, and the data indicated by points are from our own measurements with predeuterated urea in D₂O. Both sets of data for \( \varphi_Y \) and \( \varphi_{K,s} \) are plotted on the "aqua-molality" scale, i.e. as a concentration scale based on number of moles of solute in H₂O or D₂O per 55.5 moles of solvent in both cases. The isotope effect in the partial molar volume of urea at infinite dilution is 0.21 ml mole\(^{-1}\) which is just outside the limit of error in extrapolated \( \varphi_Y \) data which is ca. 0.1 ml mole\(^{-1}\) by the method employed (differential buoyancy balance with large floats). The isotopic effect in the volume is substantially smaller than that of H or D in water itself referred to in the previous report and measured in this laboratory[2]. The values were \( \varphi_D/H_2O \) (i.e. D in H₂O) = 18.08 and \( \varphi_H/D_2O \) (i.e. H in D₂O) = 18.63. The isotopic effect in compressibility of urea is larger (Fig. 8.3.2) and amounts to 1.17 x 10\(^{-4}\) ml mole\(^{-1}\) bar\(^{-1}\) at 25°C. For comparison the values for D in H₂O are 8.24 x 10\(^{-4}\) and H in D₂O 8.69 x 10\(^{-4}\) ml mole\(^{-1}\) bar\(^{-1}\). The behavior of urea is similar to that of small ions, e.g. Na\(^+\), Li\(^+\), since the compressibility in comparison with that of the pure solvent is lowered and the effect is greater in D₂O than H₂O. The effect of urea is thus a structure-breaking one and the effects are analogous to electrostriction caused by the small ions[2]. The compressibility is always a more sensitive indicator of solute-solvent interaction effects than is the partial molal volume.

The results of Fig. 8.3.2 can be interpreted in a general way as indicating that urea enters into stronger binding (through H-bonds) with water molecules than do water molecules amongst themselves. Hence, in the double-layer, electrochemical discharge of a proton from water to give H₂ will arise in strong urea solutions from water molecules that are in a different condition from those in ordinary water solutions in the absence of urea. The binding of HOD (or D₂O) to urea will similarly be different and give rise to an isotopic difference of states of HOD and H₂O in the presence of urea which can be different from that existing in ordinary water (H₂O/HOD) solution. This is a basis for considering the origin of the enhancement of separation factor in the presence of urea (and also probably guanidine). The possibility of direct discharge from H and D urea species as the "proton" source in the double-layer requires investigation. In this case, urea would act as a
UREA-\textsubscript{d} in D\textsubscript{2}O and UREA-\textsubscript{h} in H\textsubscript{2}O

$\phi_v(D_2O) = 44.45$

$b_v = -0.05$

$\phi_v(H_2O) = 44.24$

$b_v = 0.135$

isotope Effect

0.21 ml mol\textsuperscript{-1}

Fig. 8.3.1. Partial molar volumes of urea in H\textsubscript{2}O and D\textsubscript{2}O as a function of concentration (aqua-molality) 25°C ($b_v$ = empirical slope of the $\phi_v$ - concentration line). Data for H\textsubscript{2}O from Stokes\textsuperscript{1}.
Fig. 8.3.2. Partial molar compressibility of urea in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ as a function of aqua-molality ($25^\circ\text{C}$). $\phi_{KS}^0$ values are derived by extrapolation of $\phi_{K,S}$ to zero concentration.
"mediator" in the \( \text{H}_2 \) evolution reaction in much the same way as quinoline and quinoline alkaloids do (3) at the Hg electrode. This would have to be investigated in a non-aqueous solvent having electrochemically inactive protons.

References


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