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**FINAL REPORT
SUBMITTED TO
THE DEPARTMENT OF ENERGY**

by

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for

**Electrochemical Determination of the Gibbs Free Energies
of Rock-Forming Minerals**

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Abstract

This grant provided support for a series of measurements of thermodynamic data for rock-forming minerals using an electrochemical approach. The relative accuracy of electrochemical measurements and the fact that this technique is the only one that directly measures the Gibbs energy of a phase as a function of temperature makes data obtained in this manner ideal for many types of geochemical calculations. A laboratory for these measurements was completed, and data were acquired on a series of metal - oxide buffers. Data were obtained with precisions of approximately ± 20 J/mole O_2 at a single temperature, and fitted precisions of ± 50 J/mole O_2 . Tests of the accuracy of these data were completed by running relative to air, to air through an intermediate gas stage, and relative to a solid buffer, and temperatures were calibrated relative to a primary standard obtained from NIST. These tests suggested that precision of currently available electrochemical studies may not reflect the accuracy of these measurements. The chemical potential of oxygen measured at any given temperature for all solid buffers tested appears to be a direct function of the voltage across the electrolyte containing the solid sample. Further tests of this effect, and recalibration of most or all of these reactions are needed if truly accurate data for these basic reactions are to be available.

Preliminary to a planned electrochemical measurements on pyroxenes, a thermodynamic model of the system diopside - enstatite was derived. These results suggest that the activity/composition relations derived from solvus data are strongly dependent on the thermodynamic formulation chosen. This appears to be especially true for ordered intermediate compositions like diopside. In the future, this may be tested by direct measurements on the analogue system $CaCoSi_2O_6$ - $Co_2Si_2O_6$.

Executive Summary

Two years of funding were provided by DOE/BES for electrochemical determination of the Gibbs-Free energies of important mineral and oxide-buffer systems. A number of significant conclusions and results were obtained under the sponsorship of this grant. These include:

- An electrochemical laboratory was designed, built and tested using two designs for solid-electrolytes, which yielded results as precise, or more precise, than those previously obtained for buffers of geologic interest.
- Intercomparison between results for the same buffer measured using different experimental apparatus reveal the presence of significant differences between these results.
- An experimental configuration was designed and tested which eliminates errors caused by polarization of the samples and allow results to be obtained in which accuracy is closer to measured precision.
- An abstract describing these results was presented at the Geological Society of America meeting (Bhattacharyya and Anovitz, 1993), and a paper describing them is in progress.
- A method for the equilibrium synthesis of reduced iron glasses, superior to techniques developed previously, was developed, tested and applied. A suite of glasses across the enstatite - ferrosilite and diopside - hedenbergite joins was synthesized.
- The glasses were shown to make excellent starting materials for synthesis of pyroxenes (and probably other iron-silicates), and the orthopyroxene glasses were crystallized.

- Thermodynamic analysis of the enstatite - diopside join showed that the activities derived from different assumed mixing models can be very model dependent. A new model was derived and fitted in which the parameters obtained are reasonable, and the fit to the experimental data excellent, but the derived activities of diopside are significantly different from those obtained by other fitting methods. This implies that direct measurement of activities in many of these systems may be critical to both our theoretical knowledge of a/X relations and our applications of such data to “real-world” geological problems. An abstract discussing these results was presented at the 1990 Geological Society of America annual meeting (Anovitz, 1990). A paper was submitted to the American Mineralogist. The paper has been revised following both reviewers suggestions and my post-review ideas. This paper requires only minor revisions before re-submittal.

A number of problems with current electrolyte techniques were identified during this study, and several important future research directions defined. These include:

- Temperature measurement for temperatures below 850°C can be improved by using an RTD rather than a thermocouple. RTD's are both more precise and more stable than thermocouples, but are limited to maximum temperatures of 850°C.
- The polarization of the solid buffers and it's effect on the accuracy of the available thermodynamic data for these systems can be measured more accurately using the two-electrolyte approach and adding a mass-flow controller capable of regulating much lower flow rates than the current design for carbon-monoxide. This will allow voltages nearer to zero to be attained across the sample-containing electrolyte.
- The current polarization results suggest that the currently available data for the oxide buffers are precise, but not accurate. It is possible that no experiment in which one polarizable solid buffer is

measured relative to another is usable or correctable. These data are critical to a wide range of thermodynamic applications, and several should be redone.

- Lower temperature electrolytes are available from CSIRO. These have a lower temperature limit of 500°C, rather than the 700°C for the electrolytes currently employed. In our work on C-O-H-N gases it is imperative that the oxygen fugacities of several buffers, most importantly nickel - bunsenite and Co - CoO be known accurately and precisely in this temperature range. These electrolytes and the two-electrolyte method will provide these data.

- The applicability of the solid-electrolyte method to silicates remains to be proven. The methods developed here reverse the oxygen fugacity for any reaction at a given temperature. While slow equilibration may yield reversal brackets less closed than those observed here, significant accuracy should be obtainable. Future work will examine mixing properties of orthopyroxenes, critical to geothermobarometric applications, and cobalt analogues of the diopside - enstatite join to directly measure mixing properties in an ordered-intermediate system.

Introduction

The measurement or derivation of the thermodynamic properties of minerals and other materials is a problem of primary importance to all physical chemical problems in geology, as well as in materials science and other fields. Without such data we can neither quantitatively analyze nor predict the conditions under which phase assemblages will be stable.

Three types of data are needed for such calculations: the entropy of a phase as a function of temperature, the volume of a phase as a function of pressure and temperature, and the Gibbs energy or enthalpy of that phase at a given pressure and temperature to serve as a starting point. Unfortunately, the accuracy with which this last type of data can be obtained is typically far lower than that with which the first two are known. Values derived from experimental reversals or solution calorimetry typically have uncertainties of one to several kJ, which creates large uncertainties in sensitive reactions.

The electrochemical method, while not suitable for all materials, offers a partial solution to this problem, with precisions typically 1 to 2 orders of magnitude better than those obtained by other methods. A number of important systems can be studied using solid electrolytes. Stabilized zirconia electrolytes permit analysis of oxide buffers, crucial both as reference points for experiments such as the C-O-H-N fluid project currently funded by DOE/BES, and to understanding oxidation/reduction processes in the crust and upper mantle, over a range of oxygen fugacities from somewhat below iron - wustite to atmosphere. Analysis of the Gibbs end-member and mixing properties of the silicates of these oxides, especially iron-silicates, is also possible, and will yield data crucial to geothermobarometry and our understanding of many geological processes. The potential range on utility of these electrolytes has yet to be fully explored. In addition, the applicability of other solid-electrolytes, such as the beta-aluminas, to geological materials is virtually unknown. While there remain some questions about the relationship between precision and accuracy for these measurements, as there remains for all types of experiments, this potential improvement is well worth exploiting.

This report summarizes the results of two years of my research on this problem, funded by DOE/BES. It will discuss some of the details of the equipment built for this work, insights gained into the proper procedures for these sensitive measurements, and results obtained. This last will cover three facets of the work. The first is an electrochemical measurement of the Gibbs free energy as a function of temperature of several important oxide buffers. These data will be used for an evaluation of some of the uncertainties in these measurements, and how we believe these can be avoided or corrected for. The second facet deals with our work on the synthesis of pyroxenes for future electrochemical measurements, and the third is an evaluation of activity/composition relations on the join diopside-enstatite, which was undertaken as a preliminary task in an electrochemical study and re-evaluation of mixing properties for quadrilateral pyroxenes.

Theory of Operation

Solid-state electrochemical cells are a well-known tool for the acquisition of Gibbs free energies and mixing properties of silicate and oxide phases (see Hagenmuller and van Gool, 1979; Subbarao, 1980; Holmes et al., 1986 for reviews). These electrolytes are ion specific, and within a known temperature range allow only ionic conduction. The most commonly used electrolyte materials, calcia-stabilized and yttria-stabilized zirconia, allows conductance of O²⁻ ions, and therefore measure the difference in oxygen fugacity across the cell between a reference buffer and an experimental buffering assemblage of unknown oxygen fugacity. The voltage (electromotive force or emf) measured across the cell is a direct function of this difference. For instance, much of the data on which the Gibbs energy of ilmenite derived by Anovitz et al. (1985) was based was determined by emf measurements. These experiments (Taylor and Schmalzreid, 1964; Levitskii et al., 1970, 1972; Merritt and Turnbull, 1974) were performed by placing all of the solid phases in the reaction:

on one side of the electrolyte, and a known reference buffer assemblage on the other as:

where M is an electrically conductive lead. The Nernst equation relates the emf measured by such a cell to the fO₂ differences between the electrodes, and may be written for this cell as:

$$\ln fO_2 (A) = \frac{4FE}{RT} + \ln fO_2 (B) \quad (3)$$

where F is Faraday's constant and E is the cell emf, and the 4 is obtained from the fact that four charge units are transferred across the cell per O₂. If the oxygen fugacity of the reference buffer and the Gibbs energies of Fe and TiO₂ are known, these data then yield the Gibbs energy of the unknown phase (ilmenite) as:

$$\ln fO_2(a) = (2/RT)[\Delta G_{f,T}^0(Fe) + \Delta G_{f,T}^0(TiO_2) - \Delta G_{f,T}^0(ilm)] \quad (4)$$

This approach may be modified, further increasing the utility of the technique, by substituting a phase containing a known amount of solid-solution for one of the end-member phases in the assemblage constituting the unknown electrode. If a solid-solution, for instance Fe_xMn_(1-x)TiO₃, is introduced into one of the phases, the resultant change in emf yields a direct measure of the Gibbs energy of mixing of the phase in question. Examples of the use of the emf technique to obtain mixing properties of rock-forming minerals from the literature include the data of Li and Cao (1982) on the join FeTiO₃ - MgTiO₃, that of O'Neill et al. (1989) on FeTiO₃ - MnTiO₃, of Mattioli et al. (1987), on MgAl₂O₄ - Fe₃O₄ spinels, Nell and Wood (1989, 1991) and Nell et al. (1989) on Fe₃O₄ - FeCr₂O₄ - MgCr₂O₄ - FeAl₂O₄ spinels, Siefert and O'Neill (1987) on Ni₂SiO₄ - Mg₂SiO₄ and Co₂SiO₄ - Mg₂SiO₄ olivines, and that of Sharma et al. (1987) on FeSiO₃ - MgSiO₃ orthopyroxenes.

In order to obtain accurate data using this approach several experimental constraints must be met (Arculus, pers. comm.). These include:

- 1) accurate quantification of the purity and structure state of the electrode materials,
- 2) minimization of electrode/electrolyte and emf lead/electrode reactions,
- 3) non-polarization of reference buffers (Worrell, 1976),

4) precise thermocouple and emf measurements,

5) monitoring of barometric pressure when an air reference electrode is in use.

All of these requirements can be met, and useful results can be obtained from this technique provided that sufficient care is taken in the construction of the laboratory experiment and the characterization of both starting materials and run products.

Description of Laboratory Built for this Project

The first requirement which had to be met for this project was to design and construct a laboratory suitable for the measurements. This included the furnaces, their internal geometries, temperature controllers, measurement devices, gas flow, vacuum chilled water systems, and pressure and humidity monitors.

Two emf furnace systems were built for the laboratory. An additional gas flow furnace was built for synthesis purposes. The furnaces for both emf systems are non-inductively wound, and water cooled using a self-contained heat exchange system tied to, but otherwise isolated from, the building chilled water system. Digitally controlled, DC furnace controllers, which limit AC noise and control thermal cycling to less than 0.5°C (generally less than 0.1°C), were built "in-house". A heat pipe was inserted into each furnace to limit thermal gradients. Tests on the furnace/heat pipe assembly suggest that this configuration yields a thermal gradient of less than 0.1°C over several inches. The controllers are in turn tied to the same computer system which monitors the experiment, vacuum and atmospheric pressures, and humidity. Complex temperature cycles can easily be programmed in if desired. Each of the two furnaces utilizes a different experimental geometry. As this was one of the important results of the research, these will be described below under experimental procedures.

The electronics in the lab consist of several parts: computer interface, analog measurement and control interface, temperature control units, vacuum valve control units, and remote sensing heads. All were built "in-house". The computer interface is a 16 bit bi-directional bus with

transfer rates of about 200 kilobytes per second. It uses passively terminated high speed CMOS logic, which permits cable lengths of about 30 meters, and plugs into an IBM PC compatible computer.

The analog measurement and control circuit has a 20 bit differential A/D converter with an ± 10 volt input range, providing a 10 microvolt resolution. There is a 16 input differential multiplexer on the inputs, permitting the A/D to measure the thermocouples, emf, and pressure. A conversion rate of 20 times a minute was selected to maximize noise rejection and minimize nonlinearities. There are three 16 bit D/A converters to provide computer controlled analog signals. They are loaded 16 bits wide to minimize spike noise. The signals are fed to the temperature controller, providing a set point resolution of 0.025°C for a 1700°C range. In addition, on the gas-mixing furnace and the second electrochemical furnace, signals are fed to two mass flow controllers which require 0 to 5 volt programming. There is also a 16-bit-wide digital port for switching optically isolated triacs, which control valves and other equipment.

The temperature controllers are of two power capabilities: 2000 watt and 7000 watt. The 2000 watt controller provides DC voltage to power nichrome wire furnaces. The DC voltage is generated by rectifying the line voltage and then using a 50 kHz pulse width modulated power switcher to adjust average voltage out followed by an inductor-capacitor filter. The 7000 watt controller is the same except that a transformer is first used to cut the voltage in half, because the molybdenum disilicide furnace only requires 70 volts. DC voltage was chosen over AC because the noise from AC might interfere with the emf readings. On the molybdenum disilicide furnace, using DC prevents vibrational stress on the elements, and the effect of DC healing currents helps to maintain electrical connections.

There are two types of remote sensing heads: emf and thermocouple. The emf sensing head uses a differential amplifier with 10^{12} ohms impedance, 4 microvolt input noise, and 2 microvolt input offset. Differential was chosen so that the signal could be measured as close as possible to the reaction cell with a continuous run of wire. Because platinum is used in the emf leads from the cell, only platinum wire is used to carry the emf signal to minimize unwanted thermocouple

junction effects, and the outer leads are grounded at their feedthrough points and voltages measured relative to this. Remote thermocouple and emf sensing heads are used to minimize platinum wire run costs. Each thermocouple head has a temperature controlled reference thermocouple to provide junction correction. The voltage is amplified and nulled so that 0°C is zero volts and 1700°C is 10 volts.

The vacuum/gas system in Furnace 1 (Figure 1) consists of two main parts, the upper vacuum chamber, which includes the inner part of the cell, and the lower vacuum chamber, which includes the outer part of the cell. Furnace 2 (Figure 2) has a single vacuum/Ar gas system for the inside of the upper electrolyte. Both parts of the system are independently controllable through a valving and gas system not shown, and can be sealed and disconnected from that system when desirable. The lower vacuum chamber controls the atmosphere around the unknown buffer. A diffusion pump is available on the vacuum line, but has generally been found unnecessary. Where atmosphere, or other gases near atmospheric pressure are to be used as a reference, a high-precision pressure transducer (Sensotec Inc.) is used to directly and accurately monitor the pressure of the reference gas. The current pressure is recorded each time the experimental conditions are logged. An additional modification allows relative humidity to be monitored and recorded as well.

Two sets of electrical connections were provided. Except for the Pt/Rh legs of the thermocouples, all were composed of Pt wire and direct Pt/Pt contacts to avoid thermocouple effects. The first, connected directly to the tube thermocouple, exits directly from this vacuum chamber to air via a Cajon fitting, with the top sealed with high vacuum epoxy. The second, used for the outer lead, is first grounded to the vacuum head and then passed through a feedthrough to the air. This has several advantages. The design helps prevent short circuits by keeping tighter control of the position of the outer lead. Wiring past the grounding point can be semi-permanent, allowing surer connections, and the arrangement allows for easier assembly of the cell. Grounding the outer lead also provides a fixed reference zero for the measurement.

While electrical feedthroughs are available commercially, those which allow direct passage of the platinum wire are both expensive and only available in a limited number of configurations. An electrical feedthrough was designed which can be made "in-house" quite cheaply as follows. Pt wire 1 mm in diameter is first epoxied inside a piece of high purity alumina tubing. High vacuum epoxy is used to limit outgassing. The ceramic is then epoxied inside a piece of drilled brass rod, which is of the right diameter to make a tight seal in a standard Cajon Ultratorr fitting which has been Ag soldered or welded into a hole drilled in a blank vacuum flange. The ceramic serves to insulate the Pt wire from the brass rod, and the brass both supports the ceramic and allows a good seal to be made with the Cajon fitting. In addition, if at any time the feedthrough should fail, it can be easily removed by reheating the solder and cheaply replaced. If desired the Pt wire can be replaced with Alloy No. 11 thermocouple Pt-leg extension wire (available from Omega Engineering). As long as both ends are at the same temperature there will be no thermocouple junction effects (which should be very small in any case). Where it is desirable to ground the circuit at this point the heavy gauge Pt wire can be placed through a smaller diameter Cajon fitting and connected to the fitting with electrically conductive epoxy.

The upper vacuum chamber controls the vacuum/gas atmosphere in the inside of the cell, and requires a feedthrough for the inner lead wire, which is placed in the top of the chamber. The connection between the inner face of the electrolyte and the inner lead is maintained by pressure from a steel weight drilled to the correct diameter to fit over the thermocouple ceramic. Once the wires have exited the ceramic they are insulated from the weight by a short piece of smaller diameter high purity alumina ceramic, and are connected directly to the feedthrough.

Several different types of electrolytes are available. These differ both in design and in composition. The "plugs-in" type, manufactured by Ceramic Oxide Fabricators (SIRO₂), in which a plug of zirconia electrolyte is eutectically welded into the end of an alumina tube, is advantageous in several respects. Alumina is less brittle than doped zirconia, and thus these electrolytes are less fragile than those composed totally of electrolyte material. In addition, as only the end of the tube contains the electrolyte, oxygen diffusion across other parts of the tube, where the gases may be at

Figure 1. Single Cell Design

other temperatures or oxygen fugacities, is minimized. Sato (pers. comm., 1988) notes, however, that the SiO_2 electrolytes often contain small amounts of iron. This is sufficient to render them unusable for unbuffered, highly sensitive experiments (such as intrinsic oxygen fugacity work), but is too small to affect the buffered experiments described here. O'Neill et al. (1988) examined results from both SiO_2 electrolytes and those composed solely of doped zirconia (manufactured by Cerac, Nippon Chemical Ceramic Co. and Coors) in order to ascertain whether significant differences are observed. This yielded no observable differences. O'Neill et al. (1988) notes that these electrolytes have an effective maximum usable temperature of 1300 - 1400 K, above which electronic conduction effects become significant. Because the heat pipe in our system limits the upper temperature to 1100°C, temperatures above 1050°C were not investigated. In addition, temperatures below the 700°C limit of the standard electrolytes were not examined. In the future, additional tests can be conducted to see if reasonable results can be obtained using scandia-doped zirconia electrolytes. These electrolytes, available from Ceramic Oxide Fabricators, are purported to work at temperatures as low as 500°C. Such an extension of the minimum temperature of these experiments would be very useful, as many geologic applications require knowledge of a/X relations at temperatures below 700°C.

Experimental Procedures

One of the most important results of this work was the new methodology for solid electrochemistry that was developed. It was shown that, unless correct procedures are adopted, highly precise but inaccurate results will be obtained, and many of the calibrations for standard buffers currently relied on for a number of geological applications are probably erroneous.

Two different cell designs were adopted for these experiments: a one-cell and a two-cell design. Originally it was assumed that this would allow a maximum of experimental flexibility and cross checking of results on the same reaction obtained by different methods. In fact, it was comparisons between these results which led to a clearer understanding of the source of the

problem: the effects of electrical polarization of the cell. The basic one-cell design is shown in figure 1. This was a re-design of the vacuum head originally built for this furnace. This newer design is smaller, cheaper, and much easier to use, and can largely be fabricated from "off-the-shelf" components with minor machining. The figure has been somewhat simplified, and all proportions are schematic. This system was designed to: a) allow complete control of the gas/vacuum atmosphere on both sides of the cell, b) minimize electrical difficulties such as short circuits or poor feedthrough connections, and c) achieve maximum flexibility in the experimental design. All steel parts of the system are constructed of non-magnetic 304 stainless steel to avoid induced currents. Because a vacuum may be applied to both sides of the cell, and the cell then flushed with argon, this configuration can be used either for measurements against air or for comparing the oxygen fugacities of two solid buffers.

A typical experiment in this apparatus, e.g. measurement of the oxygen fugacity of the Ni - NiO buffer vs. air, is performed in the following manner. The equipment is first assembled without a sample, and run over the temperature range of interest, usually 700 - 1000°C, with air on both sides of the cell to ensure that no residual emfs are present and/or to bake out contaminants. If this blank run does not yield values lower than 0.0001 V (0.1 mV) the electrolyte is not used. The equipment is then reassembled with the sample held in a quartz glass tube against the outside of the electrolyte in the lower vacuum chamber by a glass rod and a crushable alumina spacer. An insulated steel weight is placed on top of the inner lead ceramic to assure that a good connection is achieved, and the inner lead is attached to the inside of the electrical feedthrough. The vacuum line is then attached to the lower chamber, evacuated to 10 mTorr and flushed with Ar. In this case no vacuum system is attached to the upper chamber, as air is the reference electrode. The pump/Ar flush procedure is repeated at least three times to remove as much air as possible from the environment of the sample, and the assembly is then heated to 150°C and left overnight to release any adsorbed water. Next, the sample chamber is pumped and flushed three additional times, sealed under Ar at atmospheric pressure, and heated to the first run temperature in two or three steps to limit strains due to transient temperature gradients. Automatic logging of results and run

conditions is begun at this time, with measurements of all conditions every 15 minutes. (Originally data were logged every 5 minutes, but this proved excessive and unnecessary.) Results and conditions were also recorded in a log book by hand at regular intervals to check progress toward equilibrium. Once equilibrium is attained, temperature is run through the 700 - 1000°C temperature range in both the up and down temperature directions at 50°C intervals, and at 25°C intervals in at least one direction. The bi-directional method allows reversals to be obtained, as the equilibrium is reached from starting emfs both above and below the final value. While this has usually simply repeated the same result for the oxides, it may be a more important method in dealing with materials such as silicates, which react much more slowly.

In cases where the sample is to be run against a solid reference buffer, the sample may be placed either inside or outside the electrolyte. There are two alternatives for mounting the material inside the electrolyte. The simplest approach is to place the sample in the bottom of the electrolyte tube. This has several disadvantages. First, a coil of wire must be added to assure connection between the inner face of the electrolyte and the inner lead, thus making the inner connection far less certain. Secondly, reactions may occur between the sample and the electrolyte material which may change the properties of both, and iron from the sample may be lost to the Pt lead wire. In addition, the difficulty of removing such samples severely limits the life of a given electrolyte. An alternative method was used by Mattioli and Wood (1987). The sample is either pressed into a pellet or contained in an unsealed small diameter Au or Ag tube and placed in a notch cut in the thermocouple ceramic. Because the volume of Ar gas in the upper vacuum chamber is small once the chamber is sealed, the fO_2 of the gas quickly equilibrates with that of the sample, allowing a direct measurement without placing the sample in contact with the electrolyte. In our experiments only the first method was used because of the difficulty of fitting the enclosed sample into the small internal diameter of the electrolyte, and because experiments with a similar arrangement in the much larger outer chamber were very slow to equilibrate. Experience first in the laboratory of Dr. R.J. Arculus (then Univ. of Michigan), and subsequently in my own laboratory, suggests that the second method is also more sensitive to the experimental procedure than the first. The purity of the

Ar gas used to flush and backfill the system, for instance, appears to be of importance. In order to reduce contaminants, Ar in my laboratory was run through both oxygen and organics scrubbers before entering the system to insure that it acts as nearly as possible as an inert medium.

When air is the reference electrode, the sample is placed in the outer chamber, and the inner chamber is left open to the air. The sample may either be placed in the chamber and allowed to equilibrate with the Ar atmosphere in the chamber, or placed in contact with the end of the electrolyte. A number of experiments with the first alternative showed that equilibrium was difficult or impossible to achieve, and therefore the second was adopted. Contact is achieved and maintained by filling most of the tube with a quartz glass filler rod. The sample is placed in a quartz glass tube with one end sealed, which is slid over the end of the electrolyte. A crushable alumina disk slightly too thick for the remaining space is placed on the end of the glass filler rod, and the electrolyte/sample assembly slid into place. This provides the slight pressure needed to hold the sample in contact with the electrolyte during the experiment.

The second system uses a two-cell arrangement (Figure 2). In this design the two electrolytes are placed "nose-to-nose" in a tube inside the furnace, which is sealed at both ends and contains a CO/CO₂ gas mixture. The first electrolyte measures the oxygen fugacity of the gas mixture relative to air, and the second the oxygen fugacity of the unknown buffer relative to the gas. Only a single vacuum chamber is necessary in this design. Sato (1972; Sato et al., 1973) has shown that for intrinsic oxygen fugacity (IOF) work it is necessary to maintain the emf of the cell as close to zero as possible to avoid altering the IOF of the sample. Such a delicate experiment requires a two-cell arrangement in which one cell measures the emf of the sample relative to a mixed furnace gas, and the other measures the emf of the furnace gas relative to air. Because assemblages such as the metal /metal oxide pairs are far better buffered than an IOF experiment (even when solid-solutions for ilmenite are included) it is less critical that the emf be very small. However, this design allows the oxygen fugacity of the unknown assemblage to be measured directly relative to air without the added uncertainty of the reference buffer. It also allows the oxygen fugacity of the gas mixture relative to the unknown assemblage to be minimized to avoid

Fig. 2

electrical polarization or loss of buffering capacity. The limited size of the vacuum system is also a benefit, as vacuum problems are one of the recurring difficulties in these measurements.

In this second furnace a typical experiment, for instance the Ni - NiO buffer discussed previously, is run as follows. The electrolyte is first checked for residual voltages, with air in all three chambers. A small air flow is needed into the lower electrolyte in order to prevent the formation of a slightly fO_2 reduced, thermally stable air pocket at its upper end. Pure oxygen could also be used for this purpose. Once a zero voltage is achieved, and both electrolytes read the same value, CO_2 is introduced into the central chamber. The flow rate is initially set at 200 cc/min, the highest rate available, to flush air out of the system, but once a stable result is achieved the flow rate is gradually reduced. If the emfs of the electrolytes do not drop significantly, there are no significant leaks in the gas system. This is monitored overnight. The furnace is then cooled and the sample, along with small Pt wire for improved conductivity, is introduced into the upper electrolyte. Next, the inner lead and its ceramic are reinserted, the insulated steel weight is placed on top of the inner lead ceramic, the inner lead is attached to the inside of the electrical feedthrough, and the vacuum system is attached. The pump/Ar flush procedure described above is then performed for the inside of the upper electrolyte, and the sample heated to the first run temperature. A CO_2 or CO_2/CO gas mixture is chosen to minimize the voltages of the electrolytes and the experiment is run and monitored in a manner similar to that already described.

Initial comparisons between results from these two methods were disturbing. They did not agree, and the differences were larger than those allowed by the very high precisions achieved in both approaches (Fig 3). Because the voltage across the cell in each of these experiments is different, this suggested that electrical polarization of the sample and/or the standard (for solid references buffers) was responsible. O'Neill (1988) has recommended the use of the Cu/Cu₂O buffer as a reference in electrochemical experiments because of its low polarizability, but the effect of this phenomenon on that calibration or on measurements made relative to it, has never been determined.

Figure 3: Comparison (F1-F2) between results obtained on the Ni-NiO buffer in furnace 1 (directly relative to air) and furnace 2 (relative to air through a CO_2 intermediate step)

Tare et al. (1980) defined electrical polarization as: "non-ohmic behavior ... due to the slowness of one or more of the several kinetic steps occurring at an interface or in the bulk phase". This can effect the final result by adding or subtracting voltage to the measured value as:

$$E_{st} = \eta + i\Omega \quad (5)$$

where E_{st} is the steady state or measured voltage across the cell, i and Ω are the cell current and resistance, respectively, and η is the overvoltage. This equation indicates that, if the current in the cell is small, the steady state voltage can be a combination of two effects. The first, given here as the product of a current and resistance, is the true, Nernstian voltage sought in the experiment. The second is an overvoltage due to these kinetic effects, which causes a distinct offset of the measured from the true voltage.

Worrell and Iskoe (1973) suggested that overvoltages in the metal oxide reactions were related to the diffusivity of oxygen in the metal particles, and offered the following equation to quantify their observations.

$$\eta = i \frac{RT}{F} \left[\frac{\Delta X}{2FAC_oD_o} \right] \quad (6)$$

where I is the current, R the gas constant, T the absolute temperature, F is Faraday's constant, ΔX is the diffusion distance in the metal particle, C_o is the saturation solubility of oxygen in the metal, and D_o is the diffusivity of oxygen in the metal. As the diffusivity is a function of temperature, the overvoltage should also vary with T , and this has been observed in my experiments.

Equation (6) is extremely important because it suggests how to correct for electrical polarization. Overvoltage is a function of current. If there is no current, there is no overvoltage. In his IOF experiments, Sato (1972) noted that a zero voltage experiment was needed to avoid altering the state of the unbuffered samples. This same approach can be adopted here. If we either adjust the gas mixture until a zero volt reading is obtained across the upper electrolyte in furnace 2, or do a series of experiments at different gas ratios at constant temperature, and interpolate to zero volts, the true voltage relative to air can be obtained.

Figure 4: Voltage of the Ni-NiO buffer relative to air in furnace 2 as a function of that part of the total voltage across the electrolyte which is across the cell containing the unknown solid buffer.

Figure (4) shows some of my results for an experiment of this type on the Cu-Cu₂O buffer at 900°C. The X axis shows the voltage across the upper electrolyte in furnace 2, and the Y axis shows the total emf relative to air. A distinct and significant effect is observed. As the Cu/Cu₂O buffer is the primary reference used by O'Neill for a number of measurements of the emfs of the oxide buffers, and as it itself (as well as those buffers) is subject to this effect, this means that all of the oxide buffer references obtained in this manner contain significant, non-random errors whose scale is beyond that of the uncertainties quoted. It also means that results from two solid-buffer experiments are likely to be difficult or impossible to correct for this effect and only zero-voltage experiments relative to gas-buffers (non-polarizable) should be used.

My experiments did suffer, however, from the fact that results near zero volts were hard to achieve for some buffers using a CO/CO₂ gas and the flow-control equipment described above. Unfortunately, if Worrell and Iskoe (1973) are right and this is a diffusion-dependent effect, the mechanisms are likely to change as the sign of the voltage changes and one cannot project across zero. This problem is easily corrected, however, by adding an additional gas-flow controller for CO with a 20x smaller maximum flow rate (0 - 10cc/min).

Temperature calibration also proved to be a correctable, if fairly small, source of error. All temperature measurements were made using Pt/Pt10%Rh thermocouples. While thermocouple-grade wire purchased commercially is usually of high quality (most experimenters use it without further testing), calibrations are necessary to achieve higher accuracy. O'Neill (cf. O'Neill, 1988) calibrated his thermocouples by performing a DTA experiment while melting a small piece of Au wire directly on the thermocouple bead. Unfortunately, this requires that the bead then be cut off and a new one welded for the actual experiment. In addition, McAdie et al. (1972) noted that Au is an uncertain temperature reference point, and that calibrations using it may be off by 5 - 10°C. Anovitz et al. (1987) described the difficulties encountered performing temperature calibrations for accurate thermodynamic measurements, and I therefore adopted an alternative method of thermocouple calibration. A primary standard thermocouple was purchased from the U.S. Department of Commerce, National Institute of Standards and Technology (formerly National

Bureau of Standards). This thermocouple was calibrated from 32 to 2000°F relative to IPTS - 68 (NIST test 243116 C). Because repeated heating may affect the calibration of a thermocouple, this primary standard was used to calibrate several secondary standards in 10°C intervals over the temperature range 450 - 1050°C. The primary standard was then set aside and the secondary standards used to calibrate the thermocouples used for the experiments.

Figure (5) shows the voltage recorded from the NIST primary standard thermocouple at a single temperature setpoint. The variation is due to noise and the fact that, at a given temperature, the measurement variation is ± 1 microvolt. As there are 4 - 5 microvolts per degree C for this type of thermocouple, this range yields a temperature uncertainty of slightly less than 0.5 degrees for the standard.

Imprecision in the fitted equation used to calculate T from the thermocouple emf is an additional source of error (Figure 6). The temperature in figure 6 was calculated from the equation provided by NIST with the standard, and the Y axis shows the difference between this temperature and that calculated with an equation fitted to standard tables and used in our temperature measurements. Thus the inaccuracy in our thermocouple calibration is at least ± 2 °C from this effect, but can be improved by correcting our temperatures using these data and the equation provided by NIST.

Finally, each individual thermocouple, even from the same batch of wire may have it's own calibration uncertainty. Figure (7) shows the results from calibration of some of our secondary standards. This shows that there is an additional 1 - 2 degree uncertainty in thermocouples from the same batch of wire, but once calibrated each can be corrected and temperatures traced to the reference. Similar calibration runs can then be done for the experimental thermocouples relative to the secondary standards. This suggests that the uncertainty in an uncalibrated Pt/Pt10%Rh thermocouple is approximately $\pm 5^\circ\text{C}$. This calibration procedure will improve the situation, but as the calibration provided is only good to $\pm 1^\circ\text{C}$, the final calibrated temperature is probably no better than $\pm 1 - 2^\circ\text{C}$.

Figure 5: Voltage recorded from the NIST primary standard thermocouple at $401 \pm 1^\circ\text{C}$. At any given temperature the uncertainty is approximately ± 2.5 microvolts

Figure 6: Difference between measured and standard temperature for the NIST primary standard.

Figure 7: Calibration of a secondary standard. Temperature relative to the NIST primary standard as a function of temperature. Solid diamonds are the primary standard, open squares a secondary standard.

Experimental Results

Two years of funding was received from the Department of Energy for work in my laboratory. This yielded the following results. The laboratory was designed, built and tested, and made to yield high quality data. Experiments were performed on a number of oxide buffers including nickel - bunsenite, copper - cuprite, cuprite - tennorite and iron - wüstite. These runs yielded highly precise results, which suggest that there may be larger uncertainties in accepted data for these buffers than is currently recognized. A method was devised for "equilibrium" reduction of iron-bearing silicate glasses as starting materials, and synthesis of orthopyroxenes along the join enstatite - ferrosilite is nearly complete. Clinopyroxene glasses on the join diopside - hedenbergite have also been prepared, but not yet crystallized. Available experimental data on the join diopside - enstatite have been re-examined and modeled in light of the observation that current solution models suggest that diopside, and by extension other ordered intermediate compounds, is metastable with respect to, in this case, a subcalcic diopside and wollastonite.

Oxide Buffers

The first reactions to be investigated for this project, and those which led to the above insights concerning experimental procedures, were the oxide buffer reactions:

Originally, these were planned as test reactions, to be compared with the results of O'Neill (1987, 1988) to calibrate the equipment. Initial results, however, yielded very precise results which differed somewhat from those of O'Neill. These are important reference buffers. At the time they were believed necessary as future reference buffers in solid-electrolyte runs. A careful set of

experiments was initiated to test their calibration. As discussed above, each reaction was studied relative to air across a single electrolyte, relative to air in two steps with a CO_2/CO gas intermediate, and relative to other solid buffers.

The oxide buffer reactions studied here, especially nickel - bunsenite, are also critical for our ongoing effort to measure the mixing properties of C-O-H-N gases. In one part of these experiments the activity of water is buffered by controlling both the hydrogen and oxygen fugacities, the later using a solid oxide buffer. The resultant a/X properties of water-bearing joins are only as accurate as the thermodynamic properties of this buffer.

Initial results were both interesting and encouraging. Very precise results were obtained from the single electrolyte experiments. Figure 8 shows the measured chemical potential of oxygen as a function of temperature for the Ni-NiO buffer measured relative to air in furnace 1. The data points fall in a nearly straight line. Several hundred data points are shown on this figure, the precision of which is much smaller than the size of the points plotted. This reaction has also been reversed by performing experiments starting from both higher and lower temperatures. The actual precision of these data can be seen by looking at data for a single temperature. Figure 9 shows data obtained on this buffer at a single set point temperature. The temperature in the tube varied slightly during the experiment from 1122.1 to 1122.7 K. At any given temperature in this range the chemical potential varies from the average by only ± 25 joules. This is an extremely precise result, at least 1 to 2 orders of magnitude better than those obtained by any other approach. Figure (8) shows the data for this reaction.

While the precision of these data is very good, accuracy is more difficult to evaluate. Another electrochemical study of these buffers was published by O'Neill (1988). Figure 10 compares my data to his from 1000 to 1300 K. Although ± 1 kJ in each of our experiments (half the measured difference) is still a small uncertainty relative to most other experimental techniques, the difference is consistent and significantly larger than the fitted precision.

As noted above, both polarization and temperature uncertainties may play a role in the observed differences between my results and those of O'Neill (1988). Figure 11 shows the

Figure 8: Measured chemical potential of oxygen as a function of temperature for the Ni-NiO buffer in furnace 1 relative to air.

Figure 9: Data for the Ni - NiO reaction at a single setpoint.

Figure 10: Chemical potential difference between my results (Furnace 1) and those of O'Neill (1988) for the Ni-NiO buffer.

Figure 11: Temperature difference necessary to account for the difference between my results and those of O'Neill (1988).

temperature differences necessary to compensate for the differences in the chemical potential. The temperature difference varies from 10° to 14°C, and increases at higher temperatures. If this is the sole source of the differences it is not unreasonable, as $\pm 5^\circ$ to $\pm 10^\circ$ temperature uncertainties are commonly assumed in most experiments, but given our known temperature uncertainties it is unlikely that this is the complete explanation.

Data were obtained in this manner for all of the buffers listed above. These experiments yielded, from the single electrolyte design relative to air:

$$\text{for Ni-NiO: } \mu_{\text{O}_2} = -472639 + 190.075 T - 2.10227 T \ln T (\pm 50 \text{ J, T K}) \quad (11)$$

$$\text{for Cu-Cu}_2\text{O: } \mu_{\text{O}_2} = -352011 + 261.578 T - 14.3584 T \ln T (\pm 20 \text{ J, T K}) \quad (12)$$

and from the two electrolyte design:

$$\text{for Ni-NiO: } \mu_{\text{O}_2} = -504238 + 425.409 T - 31.7910 T \ln T (\pm 60 \text{ J, T K}) \quad (13)$$

$$\text{for Cu-Cu}_2\text{O: } \mu_{\text{O}_2} = -389722 + 561.037 T - 52.4281 T \ln T (\pm 98 \text{ J, T K}) \quad (14)$$

$$\text{for CuO-Cu}_2\text{O: } \mu_{\text{O}_2} = -284341 + 321.545 T - 16.5191 T \ln T (\pm 128 \text{ J, T K}) \quad (15)$$

$$\text{for Fe-''FeO'': } \mu_{\text{O}_2} = -504845 - 65.2270 T + 24.9260 T \ln T (\pm 36 \text{ J, T K}) \quad (16)$$

Each of these differs, slightly but consistently from the data of O'Neill and results in the single electrolyte runs are different from those in the two-electrolyte runs at a similar scale. As noted above, it was the differences between these sets of experiments, and others run in the single electrolyte furnace comparing two solid buffers, which led to the direct measurements of the effects of cell emf on the measured total emf obtained. Data have been obtained in this manner for both the Ni-NiO and Cu-Cu₂O reactions, and a paper describing these results is in progress.

Pyroxene Synthesis

The second goal of this project was to measure the Gibbs Free Energies of orthopyroxenes using the solid-electrolyte method. While analysis of the polarization effects, and derivation of a technique to overcome them prevented direct measurements from being obtained on these materials, a great deal of work was completed on the synthesis of orthopyroxenes for this project.

The first step in this synthesis was to obtain suitable starting materials for crystallization. These can be either oxide mixtures or glasses. Oxide mixtures have the disadvantages of being less homogeneous, and of not containing iron in the correct oxidation state, as stoichiometric FeO does not exist. Most syntheses of iron-bearing silicates thus are currently being completed using glasses which are made by melting and reducing the initial oxide mixtures. These glasses have the additional advantage of being very reactive. They are usually made (cf. Bohlen and Boettcher, 1981) by melting the oxides in capped graphite crucibles. This approach, however, has two disadvantages. First, it is inherently a disequilibrium experiment. Because the oxygen fugacity of graphite is within the stability field of iron metal, experiments which are run too long, or at too high a temperature, yield metallic iron "balls" in a silicate glass, rather than a homogeneous iron-silicate glass. Secondly, because most of the reduction occurs when the material is in the liquid phase, oxygen exchange becomes difficult, because the oxygen must diffuse through the melt to equilibrate with the surrounding reduced atmosphere.

It would be advantageous, therefore, to devise a technique in which divalent iron is stable at temperature, so that the experiment is time independent and can be run as long as needed to assure complete reduction to Fe^{2+} without formation of iron metal, and in which the reduction can be done while the material is still a powder. Such a technique was devised during these experiments. The first step was to choose a crucible material. Molybdenum metal is stable at oxygen fugacities slightly above those at which iron oxidizes to wüstite, and there is little solid solution between Mo metal and Fe oxide. The gas mixing furnace can therefore be used to put a molybdenum crucible containing an iron-silicate oxide powder mixture under conditions where the molybdenum will remain a metal and ferric iron will reduce to ferrous iron but not iron metal. After a suitable time for reduction (6 - 12 hours), the temperature can then be raised above the melting point, and then cooled to form a glass ($\pm$ quench crystals).

The first difficulty with this technique was obtaining the Mo crucibles. Mo metal is very hard, and local machinists were not equipped to machine it. We therefore fabricated a press in which Mo sheet (0.005") can be pressed into small crucibles that look like high-sided bottle caps.

If the sides are made too high, the bottom may split out of the crucible, but otherwise good results are obtained. After fabricating the crucibles, we devised the rest of the procedure while at the same time testing the gas mixing furnace, and prepared glasses for all of the orthopyroxene and clinopyroxene compositions described below. In some cases quench crystals were formed, but all "glasses" were thoroughly crushed and ground in an agate mortar and a SPEX mill to assure homogeneity.

Having prepared the starting materials, the next step was to crystallize the orthopyroxenes. This proved more difficult to do than expected. I had originally proposed to carry on this stage of the work in the laboratory of Dr. Ganguly at the University of Arizona. Unfortunately, despite his initial promise of cooperation, it proved impossible to obtain the necessary experimental time. Arrangements were then made for the student working on this project, Mr. Samir Bhattacharyya, to spend a month in the laboratory of Dr. Steve Bohlen, USGS Menlo Park, to perform this work. In this relatively short time all of the orthopyroxenes were crystallized. Examination with the electron microprobe on Mr. Bhattacharyya's return suggested that a few percent inhomogeneity remains in the samples. A final run at higher temperatures will therefore improve the quality of the synthetic materials which are otherwise ready for electrochemical measurement.

Pyroxene a/X relations

In preparation for a reevaluation of quadrilateral pyroxene activity/composition data, which will be necessary on completion of the binary electrochemical experiments, I reexamined the a/X relationships on the diopside - enstatite join. Examination of available models shows that all predict that end-member diopside is metastable with respect to wollastonite and a sub-calcic diopside as a necessary condition of the Margules model applied to the $\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$ portion of the $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{Ca}_2\text{Si}_2\text{O}_6$ join (Figure 12). Available experimental data suggest that this is unreasonable, because at high temperatures the deviation from end-member composition of a diopside synthesized or otherwise formed "on-composition" should be significant. A reevaluation

Figure 12: Theoretical DG/X curves for the wollastonite - diopside - enstatite join.

A: Model treating clino- and orthopyroxenes as separate solutions on the diopside - enstatite subjoin. Dots show the Gibbs energies of stable and fictive end-member phases, light lines connect stable mineral pairs. The chemical potential of diopside in a clinopyroxene on the solvus is significantly different from end-member diopside. Diopside is metastable with respect to a subcalcic diopside and wollastonite.

B: Model treating the entire wollastonite - enstatite join in which diopside remains stable. Two methods of treating the wollastonite - diopside half of the join are shown. Curve 1 approximates reality. The curve bends steeply away from diopside, and little excess Ca is predicted. Curve 2 predicts fictive phase equilibria for this half of the join, but is easier to fit with standard models. As only half of the curve is used to fit real data this model is less flexible for a given number of parameters than that shown in part A.

of phase equilibria along this join was therefore undertaken involving both examination of the stabilities of the various $\text{Mg}_2\text{Si}_2\text{O}_6$ polymorphs and reformulation of the solvus model.

Evaluation of the stabilities of the $\text{Mg}_2\text{Si}_2\text{O}_6$ polymorphs shows that a great deal of uncertainty remains. Discrepant experimental data on the low-clinoenstatite ($\text{P}2_1/\text{c}$) to orthoenstatite (Pbca) transition cannot be reconciled by any possible reaction curvature, and a preferred data set cannot be identified. Similarly, several sets of experimental data suggest stability fields for $\text{C}2/\text{c}$ clinoenstatite, but two such fields may exist, one at high and one at low pressures. The relationship between these two fields remains uncertain. The orthoenstatite - protoenstatite (Pbcn) transition is somewhat better known. If only half-reversals are considered the experiments are consistent with a transition located between

$$T\ (^{\circ}\text{C}) = 975 + 0.0500\ P\ (\text{bars}) \quad (17)$$

and

$$T\ (^{\circ}\text{C}) = 995 + 0.0425\ P\ (\text{bars}) \quad (18)$$

However, extrapolation of available thermodynamic data suggest that this reaction may not be linear, but may curve to lower pressures at higher temperatures (Figure 13).

In order to use the Margules formulation to model the solvus while retaining end-member diopside as a stable phase, it is necessary to consider the join $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{Ca}_2\text{Si}_2\text{O}_6$. Such a model reproduces the available experiments as well as currently available models below 50 kb and 1773 K, but is mathematically inflexible and yields coefficients which can at best be considered fitting parameters. In addition, the qualitative shape of the $\Delta G/\text{X}$ curve for diopside, and therefore the activity/composition relations suggested by this model, are unusual. The equations for diopside do not reduce to $a = X$ for all compositions as W is reduced to 0. Instead, they suggest that a better estimate for the activity of ordered and nearly pure intermediate is $a = 1$. As the model accurately reproduces the solvus data (figure 14), this analysis suggests that calculated activities for ordered intermediate compounds such as diopside are very model dependent. Direct measurement of the activities of such compounds are needed in order to ascertain the appropriate shape of the $\Delta G/\text{X}$ curves for such materials. As the model presented in this paper both reproduces the solvus and

does not predict that end-member diopside is metastable, however, it is regarded as an improvement over other models currently available in the literature. This paper is currently undergoing post-submission revisions.

The most significant result of this work is the realization that activities derived from mathematical formulations which fit solvus data may or may not yield real activity/composition relations for compositions outside the solvus, even if the solvus is well fit. This appears to be especially true for ordered-intermediate phases such as diopside, and experiment aimed directly at obtaining such data for at least one such phase, (possibly $\text{CaCoSi}_2\text{O}_6$ (cobalt diopside)) is badly needed. Because the a/X relations predicted by the newer formulation are qualitatively different from those in older work, such an experiment should be able to compare the two approaches.

Figure 13: Experimental data constraining the orthoenstatite - protoenstatite transition (Atlas, 1952, Boyd et al., 1964; Kushiro et al., 1968; Anastasiou and Seifert, 1972; Chen and Presnall, 1975). The straight line predicted by the model fits all of the available half reversals. The curved lines are calculated from available thermodynamic data (Table 2), with different estimates of $S^\circ(298)$ from 165.7 J/mol•K to 165.8 J/mol•K for protoenstatite. This also fits most of the experimental data, but predicts a maximum pressure of 7 to 8 kb for the stability of protoenstatite. It is uncertain whether this effect is real or due to extrapolation of the thermodynamic data.

Figure 14: Fit of the model to the diopside - enstatite solvus at 1 bar

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Publications Resulting from this Support

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