2. THE MYSTERY OF ORE-FORMING ENVIRONMENTS: WHICH PARAMETERS TO RESOLVE?

2.1 Redox Conditions

My initial objective at the Geophysical Lab in 1956 was how better to resolve the conditions where hydrothermal deposits must have formed. Progress on the physical environment was moving ahead following the various criteria mentioned above but, for the chemical environment, we were struggling. Aqueous and general physical chemists were focused very dominantly on temperatures between 25 and 60°C and rarely considered higher temperatures or pressures above 1 bar. A common and fruitful geochemical approach was to generate Eh-pH diagrams for each ore type as demonstrated by *Prof. Bob Garrels* (*e.g.*, Garrels and Christ, 1965) and his graduate students at Harvard. Nevertheless, those diagrams were not so useful for many ore types because of poor resolution of both pH and Eh for higher temperatures and pressures. Spirited discussions of ore-forming redox environments ensued with *Paul Barton* of the U.S. Geological Survey who pointed out that if we disagreed that there was double the possibility that one of us might be correct. However, *Paul* and I soon concluded that there was a more direct redox parameter for aqueous environments, one that was clearly superior to Eh for conditions much above 100°C. We asked ourselves why we should not use either oxygen pressure or better, fugacity (Lewis, 1901) or its corresponding thermodynamic activity, a_i (Tunell, 1984). Interrelationships among these parameters can be appreciated readily by the following functions.
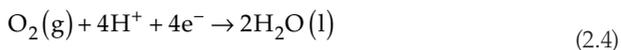
The redox state of a hydrothermal solution was obviously described at least at equilibrium by the reaction:

$$2H_2O(1) \rightarrow 2H_2(g) + O_2(g) \tag{2.1}$$
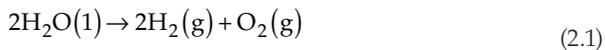
where at equilibrium:

$$K_T = \left(a^2_{H_2(g)} \times a_{O_2(g)} \right) \Big/ a^2_{H_2(l)} \tag{2.2}$$

with half-cells in coexisting, equilibrated aqueous solutions of

$$1/2H_2(g) \rightarrow H^+ + e^- \tag{2.3}$$

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(1) \tag{2.4}$$

which can be evaluated with the Nernst equation at a temperature, T, by

$$E_R = E^0 - \frac{RT}{nF} \ln \left[a_{H^+} \Big/ a^{0,5}_{H_2(g)} \right] \tag{2.5}$$

to which Eh is related by:

$$Eh = E_R \qquad (2.6)$$

Consequently, Eh is a function of both a_{H^+} and a_{H_2} (or alternatively, a_{O_2}) giving it a dual dependence on the two parametres, acidity and redox state. In contrast, at equilibrium a_{O_2} (g) or a_{O_2} (aq) are independent variables indicating exactly the redox state and they are often directly measurable under many different conditions (Chou, 1987; Heubner, 1987). Diagrams intended to circumscribe the environmental conditions of hydrothermal deposition would be better designed by adopting the variable "log a_{O_2}" as the ordinate rather than Eh. Isothermal stability boundaries at constant redox state on an Eh-pH diagram have an inclined slope set by the RT/nF factor of the Nernst equation but those on log a_{O_2} – pH figures are often orthogonal (for example, see Fig. 3.6). In 1961, *Gunnar Kullerud* and I published probably the first such diagrams for hydrothermal environments that used log P_{O_2} (Barnes and Kullerud, 1961). *Gunnar*, after action in the Norwegian Underground during World War II, devised methods for evaluating sulphide phase equilibria and became noted for his lab's publications from the Carnegie Institution Geophysical Laboratory. Our applications, emanating from Fe-S phase relations, were to hydrothermal iron-containing systems and useful to 250 °C. They included a treatment of acidity at elevated temperatures and with that addition they carried more conviction than earlier diagrams for several reasons. About two decades later, a neat comparison of the Eh – pH and Log a_{O_2} – pH diagrams was published by Henley *et al.* (1984). Remarkably, both of these diagrams continue to be used commonly by today's geochemists.

2.2 Acidity

Similar to the Eh problems at high temperatures, there continued to be to an inadequate evaluation of the acidity function under such conditions. For redox-acidity diagrams to be applied to high temperatures, a problem was that the abscissa, pH, was poorly resolved due to a dearth of precise measurements. By 1960, there had been published only very rare determinations of acidity in aqueous solutions at high temperatures and pressures and these stemmed only from comparatively simple experimental lab systems. The application of those acidity measurements to ore solutions was at best problematical. As with the Eh discussion with *Paul Barton*, the resolution of the acidity problem came again from interaction with a visiting colleague. *James Ellis*, from the Department of Scientific and Industrial

Figure 2.1   Prof. Dr. Ulrich Franck, University of Karlsrhue, 2004.

Research of New Zealand, visited the Geophysical Laboratory and gave a seminar on his geothermal research progress. Afterward, he remarked on problems with resolving the acidity of hydrothermal solutions and explained that answers were forthcoming from studies underway at the Oak Ridge National Laboratory. There *Ulrich Franck* (Fig 2.1) explained that he had used aqueous electrical conductances to evaluate ionisation constants most crucially for water and also for solutions of HCl, KCl, and KOH, to about 800 °C at pressures extending above 2 kilobars. I wrote to *Dr. Franck* and his response to my letter and his reprints opened a life-long friendship. His initial results were all published in German (Franck, 1956a, b, and c) in a journal then not so often used by geochemists (*Zeitschrift Physicalische Chemie*) so remained underappreciated by Earth scientists. His work was soon reputed to be of Nobel Prize calibre and under consideration for that award (Nobel Symposium, 1981). Those were the key data necessary at the time for evaluating acidity in hydrothermal systems. They were the ionisation constants for water, and for solutions of the alkali chlorides and hydroxides. Without those, it was impossible to calculate the pH of the principal solutions of many hydrothermal systems. Only a few measurements of K_w that had been published by 1970 and they deserved confirmation. Recognising that critical need, for his doctoral thesis *Jim Fisher* used conductance measurements in our lab to provide additional values along the liquid–vapour P-T curve to 350 °C (Fisher and Barnes, 1972). We were especially pleased with his results. For three years, he wrestled with problems of producing ultrapure water and with failure of 10 of our 12 expensive, custom-fabricated, sintered sapphire insulators. *Jim's* faith in our designs and endurance were remarkable before, eventually, an electrode performed. His persistence was rewarded with the needed data obtained finally in only two months. Since then, there have been many more such experimental measurements and the results are compiled in Figure 2.2.
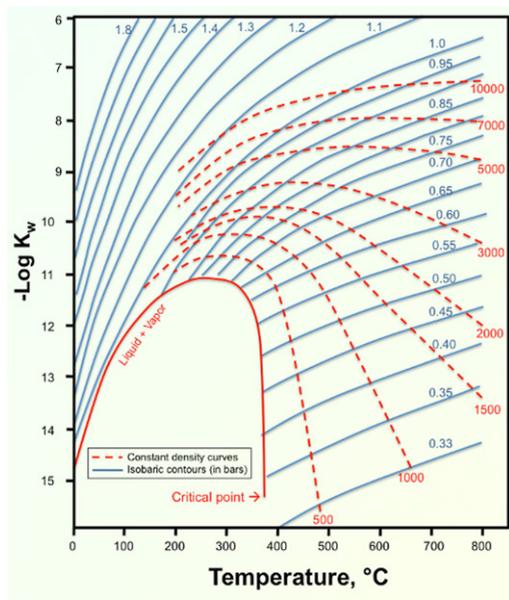

Figure 2.2 The ionisation constant of water (modified from Seward and Barnes, 1997; data from Marshall and Franck, 1981). The critical point is at 373.99 °K, 220.64 bars and a water density of 0.322 g/cc.

The range in pH for specific pressures and temperatures can be determined from pertinent K_w's from Figure 2.2 where:

$$K_w = a_{H^+} a_{OH^-} \qquad (2.7)$$

By assuming that the limits to the activities of a_{H^+} and a_{OH^-} are each roughly 10 (which bracket the range of pH), then the minimum pH is temperature – *independent* and is always:

$$pH_{min} = -\log a_{H^+_{max}} = -1 \qquad (2.8)$$

and the maximum pH at $a_{OH^-} \sim 10$ varies with K_w:

$$pH_{max} = (-\log a_{H^+_{min}}) = (\log a_{H^-_{max}} - \log {}_{Kw}) = (1 - \log {}_{Kw}) \qquad (2.9)$$

so that at 25 °C, where $K_w = 10^{-14}$ then the maximum pH is about 15. Neutrality at all temperatures remains at:

$$pH_n = (-\tfrac{1}{2} \log K_w) \qquad (3.0)$$

With my colleagues, we further examined the utility of these constants for thermodynamic implications initially with *Gary Ernst* of the Carnegie Institution Geophysical Laboratory (Barnes and Ernst, 1963) and a little later with *Hal Helgeson* and *Jim Ellis* we compiled and published the available ionisation constants needed for calculating the pH for hydrothermal conditions (Barnes *et al.,*1966; Barnes and Ellis, 1967). These were the critical constants that everyone used at that time as the preferred parameters for constructing log a_{O_2} – pH diagrams to demarcate the environments that generated the common Fe-containing, hydrothermal deposits up to 250 °C (Barnes and Kullerud, 1961).

2.3 Nature of the Fluids

We could analyse the behaviour of hydrothermal solutions in ore-forming processes only if we had reliable data for their volumetric and thermal states. In the 1950s and 60s, geochemists were appalled that physical chemists did not have available tables of both volumetric and thermodynamic properties of water and of halide and sulphate solutions to high temperatures and pressures. We needed that information for thermodynamic calculations ideally to about 1,000 °C and 10 kilobars, most crucially for water and for saline solutions. Consequently, volumetric data for conditions up to geologically useful temperatures and pressures were starting to be developed. Early examples were by *George Kennedy* and geochemical colleagues at Harvard for H_2O (Kennedy, 1957) and NaCl-H_2O (Sourirajan and Kennedy, 1962). Furthermore, the data for water were extended by *Wayne Burnham* (Fig. 2.3) and his students at Penn State (Burnham *et al.*, 1969) beyond the Steam Tables (Bain, 1964).

Figure 2.3 Wayne Burnham at the 1999 Goldschmidt Conference, Cambridge Massachusetts.

Although *Wayne* was a genius for reaction vessel design and operation, the experiments in his lab were commonly tests of the crews's endurance. The internally heated reaction vessels, when operated at the important upper levels of temperatures and pressures, were near their design limits and required for operation the devotion of a full time mechanic, a post-doctoral fellow, us his collaborators, and *Wayne*. Runs were assembled in an internally heated reaction vessel, which was then enclosed by a ¼ inch thick steel canopy that was mobile on roller skates, and finally heated to the intended run conditions. An experiment continued as long as possible commonly ending by equipment failure, usually due to burning out of the heaters or, more emphatically, by failure of pressure seals. The vessels were mounted vertically so that end seals and ther-mocouples, when ejected, would travel down-ward with no hazard, or upward, sometimes through the steel shield, and into the masonry ceiling. Innocents in the overlying rooms had to be reassured that their floor was a safe shield from *Wayne's* experiments even though the boom was disconcerting. To obtain the most complete results, a run would continue as long as the system would remain intact, typically for several tens of hours during which tending was required.

The products of the volumetric measurements were thermodynamic P-V-T data, permitting calculations of hydrothermal solution behaviour: specific volumes, Gibbs free energies, enthalpies, entropies and fugacities. Since 1970, there have been published very many compilations of these parameters, including the additional, especially geochemically important components KCl, $CaCl_2$, and CO_2; see for examples Naumov *et al.* (1974) and the current Thermodynamics of Geothermal Fluids, edited by Stefánson *et al.* (2013). We can be proud of the predominance of geochemists over physical chemists among the laboratories that were generating reliable hydrothermal data. Our compulsion to develop a quantitative understanding of hydrothermal processes was the initiative to obtain data on how much and which metals could be transported in nature to produce valuable mineral concentrations.

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