

Semiquantitative control of hydrogen fugacity in rapid-quench hydrothermal vessels

ROBERT K. POPP, KATHRYN L. NAGY, AND ANDREW HAJASH, JR.

Department of Geology
Texas A&M University
College Station, Texas 77843

Abstract

A method is described by which the hydrogen fugacity within cold-seal hydrothermal vessels can be controlled roughly using mixtures of argon and methane as the pressure medium. The procedure consists of charging the vessel with a known pressure of methane prior to final pressurizing and heating. Methane pressures were varied between 14,500 psi and 0.25 psi using a diaphragm-type compressor, two inexpensive gas regulators, and commercially available methane-argon gas mixtures. In calibration experiments carried out at 650°C and 1 kbar total pressure, hydrogen fugacities (as measured by the Ag + AgCl hydrogen sensor technique) ranging continuously from that of the graphite-methane buffer down to nearly that of the hematite-magnetite-H₂O buffer were achieved.

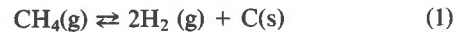
Introduction

The use of rapid-quench hydrothermal vessels (Wellman, 1970) has proven to be a valuable experimental technique for studies in which standard quench times may affect the nature of the experimental charge; e.g., in the case of the fluid phase that has equilibrated with a mineral assemblage at elevated pressure and temperature. Shortly after the technique was developed, it was discovered that use of water as the pressure medium resulted in quite severe temperature gradients for certain bomb configurations, but that use of argon as a substitute for water greatly reduced the gradients (Rudert et al., 1976). More recently, Luddington (1978) and Charles and Vidale (1982) have devised bomb configurations in which a small inclination of the hot end results in reasonable gradients, even when water is used. Although a water-pressured system is less expensive and easier to use, a gas-pressured system provides much more flexibility in terms of controlling fugacities of various gas species within the pressure vessels.

This study was undertaken primarily to develop a technique for approximate control of f_{H_2} within rapid-quench vessels during experiments that involve the Ag-AgCl acid buffer. The use of the Ag-AgCl buffer assemblage as a hydrogen sensor is a reliable method for the relative measurement of f_{H_2} in experimental charges (e.g., Chou and Eugster, 1976; Chou, 1978, 1979, 1980; Frantz and Popp, 1979; Burton et al., 1982). Because the technique is very sensitive to variations in f_{H_2} , exchange of H₂ between the charge and pressure medium can often complicate interpretation of run results. Unless the reaction rate of the charge is rapid enough to generate or consume hydrogen faster than the rate of H₂ exchange

with the pressure medium through the capsule walls, the f_{H_2} of the pressure medium rather than that of the charge may actually be recorded by the sensor. Only if the f_{H_2} within the vessels can be independently varied to values both greater than and less than that of the charge, can true equilibrium between the sensor and the charge be demonstrated.

The technique described herein uses mixtures of argon and methane as the pressure medium, with the initial pressure of methane at room temperature varying between 100% and approximately 0.002% of the total pressure. The fugacity of H₂ in the gas mixture at elevated pressure and temperature is controlled by the equilibrium



$$K_2 = \frac{f_{H_2}^2}{f_{CH_4}} \quad (2)$$

where $P_{CH_4} + P_{H_2} + P_{Ar} \cong P_{Total}$.

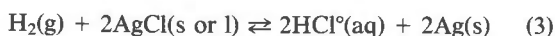
Experimental techniques

All runs were carried out in the same bomb-furnace assembly at 650°C and a total pressure of 1 kbar. The rapid-quench vessel used was essentially identical to that depicted by Frantz and Popp (1979). The bomb and cooling extension (both 12" × 1¼" O.D. × ¼" I.D.) were constructed from non-heat-treated Rene 41 alloy. The temperature gradient within the bomb was determined previously at pressure using internal thermocouples. The temperatures reported are considered accurate to within ±4°C over a 1" capsule.

Pressure was generated by an Aminco model 46-14060 vertical, single end, air-operated diaphragm-type com-

pressor. Pressure was measured on a 30,000 psi High Pressure bourdon tube gauge that was calibrated against a 50,000 psi Heise bourdon tube gauge. The Heise gauge was factory calibrated and set to read 0.0 psi at atmospheric pressure.

Measurement of the relative differences in f_{H_2} of the pressure medium was accomplished by means of the hydrogen sensor technique (Chou 1978; 1979; Chou and Eugster, 1976). The technique relies on the assemblage $Ag + AgCl + \text{solution (H}_2\text{O-HCl mixtures)}$, sealed in a small Pt capsule and contained within the medium for which f_{H_2} is to be measured. Diffusion of hydrogen through the Pt wall of the capsule occurs until f_{H_2} values of the medium and the capsule are equal. Within the capsule, the activity of the associated aqueous HCl° species is fixed by the equilibrium relation



$$K_{eq} = \frac{a_{HCl^\circ}^2}{f_{H_2}} = \frac{(m_{HCl^\circ}^2)(\gamma_{HCl^\circ}^2)}{f_{H_2}} \quad (4)$$

Equation (4) assumes that Ag and AgCl are pure phases. Thus, the concentration of HCl° in the Pt capsule at temperature and pressure is directly related to f_{H_2} of the medium in which the capsule is contained, provided that γ_{HCl° is assumed to be a function of P and T only, and is independent of solution composition over the composition range of interest. This assumption is reasonable, based on a rather large body of data (Chou, 1978; Frantz and Popp, 1979; Popp and Frantz, 1979, 1980; Burton et al., 1982). From values of m_{HCl} measured in the sensor capsules after quench, fugacities of H_2 at the P - T conditions of the runs can be calculated if a number of assumptions are made (Chou, 1978). However, for the purposes of this study it is more convenient to compare m_{HCl} values directly to those measured for standard experimental buffer assemblages (e.g., HM, NNO, FMQ, C- CH_4) and thereby avoid possible problems inherent in the required assumptions.

The technique for construction of the sensor capsules, run procedures, and analytical techniques and errors have been discussed in detail (Chou, 1978; Frantz and Popp, 1979; Burton et al., 1982) and have been reiterated several times (Popp and Frantz, 1979, 1980; Boctor et al., 1980). For the purposes of this study, it will be sufficient to note that m_{HCl° values have standard errors of less than 5% of the concentrations reported.

Because the small Pt sensor capsules occasionally stuck at the hot end of the bomb when it was inverted during quench, the sensor was placed inside a large (4.75 mm O.D.) Au capsule that had been welded at one end only. This configuration assured that the sensors fell completely to the cool end of the vessel. A small graphite rod was also placed in the large Au capsule in order to assure the presence of excess carbon in the pressure medium.

Control of f_{H_2} of the pressure medium was accomplished by (1) charging the vessel with a predetermined pressure of methane (hereafter referred to as the "nominal" pressure of methane (nominal P_{CH_4})); (2) pumping argon into the vessel to raise the pressure to 1 kbar at room temperature; and (3) raising the temperature to that which was desired, 650°C. Nominal pressures of methane ranging from 14,500 to 0.25 psi were achieved using either the compressor or gas regulators and cylinders of three commercially available gases: pure argon, pure methane, and a mixture of 95% argon-5% methane. To achieve nominal P_{CH_4} greater than that contained in the pure methane cylinder (approximately 2000 psi), pure methane was pumped to the desired value using the compressor while pressure was monitored on the bourdon tube gauge. To achieve nominal P_{CH_4} equal to or lower than approximately 2000 psi, methane or the methane-argon mixture was loaded directly from the cylinder to the vessel by means of a capillary tube connecting the cylinder to the pressure line. For such cases, P_{CH_4} was monitored by either a high-pressure regulator (2000 psi capacity, 50 psi divisions) or a two-stage regulator (100 psi capacity, 2 psi divisions), depending upon the desired value of P_{CH_4} . In this manner nominal pressures of methane ranging from 14,500 psi down to 0.25 psi (*i.e.*, 5 psig of 95% argon-5% methane) were achieved.

The standard procedure was to first flush the vessel with argon and bleed to atmospheric pressure before charging with methane. In all cases, after charging with methane, the vessel was closed off and the compressor and/or pressure line were well flushed with argon before final pressurizing to 1 kbar. To prevent a surge of methane from the vessel into the line, the line was pumped to approximately 1 kbar before the vessels were reopened. During heating, gas was occasionally bled from the vessel to maintain total pressure at 1 kbar; it is assumed that the gases were well mixed so that bleeding did not alter the proportions of argon and methane.

Results

Results of runs are plotted in Figures 1 and 2. The duration of all runs plotted in Figure 2 was 3 days.

Inherent f_{H_2} of pressure vessels

The oxygen fugacity imposed by Rene-41 pressure vessels is generally considered to be near that of the NNO solid buffer. If water is used as the pressure medium, equilibria in the H-O system define the fugacities of H_2 and H_2O for a given temperature and total pressure (Eugster and Skippen, 1967). Diffusion of hydrogen through the walls of a capsule contained within the bomb will occur until f_{H_2} in the capsule is equal to that of the pressure medium. If the fluid in the capsule is also defined by the H-O system, f_{O_2} and f_{H_2O} in the capsule will be the same as that of the pressure medium. In an argon-

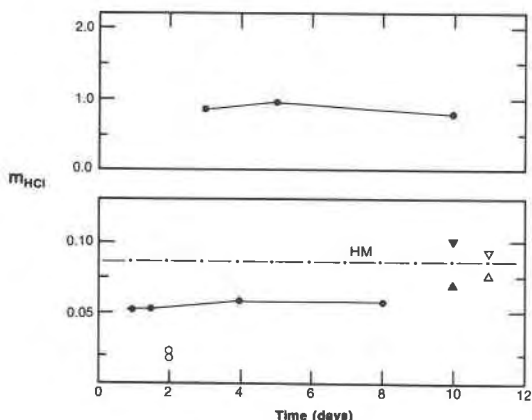


Fig. 1. Variation of HCl concentration from hydrogen sensors as a function of run time at 650°C and 1 kbar. Lower diagram, pure argon pressure medium. Open circles 2500 psi cylinder, solid circles 1800 psi cylinder; triangles represent reversals of HM oxygen buffer, solid symbols this study, open symbols Chou and Frantz (1977); Dot-dashed line is center of HM reversal bracket which is not time dependent. Upper diagram, nominal $P_{CH_4} = 50$ psi (see text).

pressured system, however, water vapor will be present only as a likely minor impurity in the argon and will also form by reaction of O_2 in the vessel with H_2 lost from the capsule. The resulting fugacities of H_2O and H_2 are thus considerably lower, i.e.,

$$K_w = \left(\frac{f_{H_2O}}{f_{H_2} f_{O_2}^{1/2}} \right)_{O-H} = \left(\frac{f_{H_2O}}{f'_{H_2} f'_{O_2}{}^{1/2}} \right)_{O-H-Ar}$$

$$f_{O_2} = f'_{O_2} \text{ and } f_{H_2O} > f'_{H_2O}$$

$$\therefore f_{H_2} > f'_{H_2}$$

Equilibration of H_2 between the argon pressure medium and a sample capsule will, therefore, raise the f_{O_2} in an O-H vapor in the capsule relative to that of a water-pressured system.

Concentrations of HCl in sensor capsules equilibrated with a pure argon pressure medium are shown in the lower portion of Figure 1. Solid and open circles indicate values obtained using two different argon cylinders, the solid circles from a well-used cylinder (~1800 psi tank pressure), the open circles from a new cylinder (~2500 psi tank pressure). The variation from tank to tank might be related to change in the oxide coating in the pressure vessel with time, but is most probably related to differences in impurities in the argon. Both cylinders were AIRCO "High Purity, oil-free" argon with maximum impurities of 10 ppm O_2 , 30 ppm N_2 and 10 ppm H_2O . There is no significant variation of HCl concentration with time. Several runs made using three other bomb-furnace assemblies indicate that HCl concentration can vary by approximately 0.07 m from bomb to bomb.

Shown for comparison are reversal values obtained for

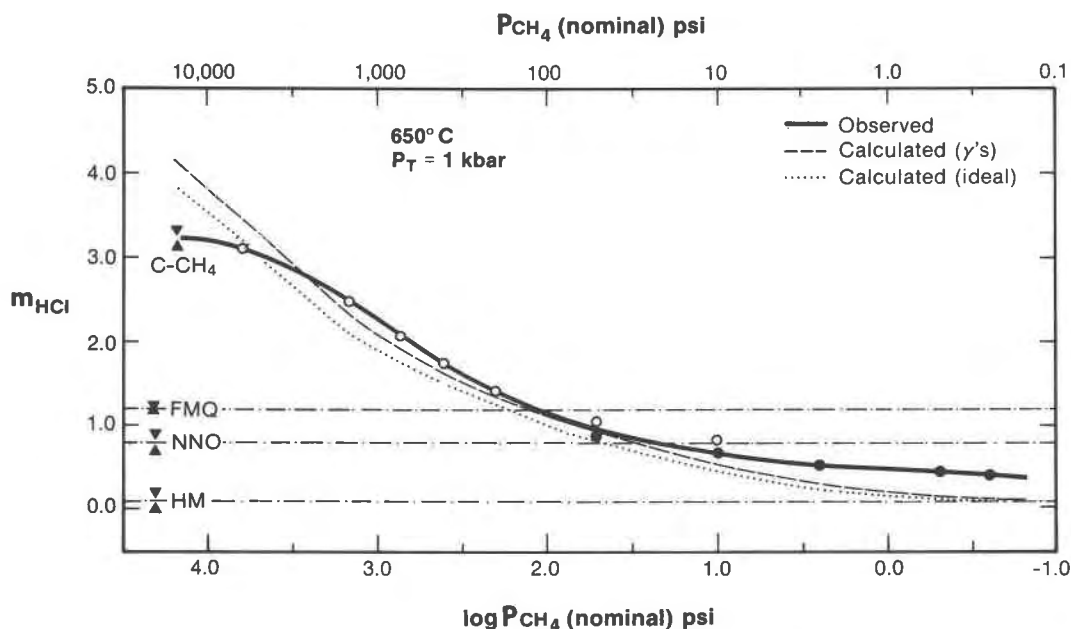


Fig. 2. Variation of HCl concentrations from sensors as a function of nominal P_{CH_4} . Open circles, P_{CH_4} achieved with pure methane; solid circles, P_{CH_4} achieved with 5% methane-95% argon mixture. Triangles represent values of HCl obtained from solid buffer assemblages; concentrations are represented by apices of triangles which indicate direction of change. Dashed line and dotted line were calculated as described in text. Dot-dash lines indicate m_{HCl} values for standard buffer assemblages.

the HM solid buffer (see below). The exchange of H_2 between the capsules and the pressure medium thus results in an f_{H_2} within the capsules that is slightly more oxidizing than the HM oxygen buffer at 650°C and 1 kbar. Chou (1978) observed two significantly different f_{H_2} values between those of the NNO and MnO–Mn₃O₄ oxygen buffers for two different internally heated vessels pressured with argon at 4 kbar in the 600–800°C range.

Solid oxygen buffer calibrations

Sensor capsules were used to define values of m_{HCl} that result from hydrogen fugacities defined by four of the standard experimental buffers: HM, NNO, FMQ, C-CH₄. The results are shown as triangles in Figure 2. Reversals were obtained by approaching the final concentration from both higher and lower initial concentrations, as indicated by the orientation of the symbols. The value for the C-CH₄ buffer represents a nominal P_{CH_4} pressure of 14,500 psi and therefore can be plotted with respect to both $\log P_{CH_4}$ and m_{HCl} in Figure 2. Because the remaining three buffers do not involve methane, their locations with respect to the P_{CH_4} axis in Figure 2 are meaningless and their values are shown as dot-dashed lines at constant m_{HCl} .

Effect of nominal P_{CH_4}

Variation of m_{HCl} as a function of nominal methane pressure is shown as circles in Figure 2. Open circles indicate values obtained using pure methane; solid circles indicate those obtained using the 5% methane mixture. It should be noted that the reported values have been approached from only one direction, that is, from either higher or lower initial values. However, run times were the same as for the buffer calibration runs (triangles in Figure 2) which have been strictly reversed. The tightly constrained reversal brackets for the buffered runs suggest that either side of a reversal is an adequate measure of the true value.

The variation of m_{HCl} with time for nominal $P_{CH_4} = 50$ psi is shown in the upper portion of Figure 1.

Several factors could complicate the technique. Precipitation of carbon on capsule walls, particularly at high nominal P_{CH_4} , can inhibit diffusion of H_2 (D.A. Hewitt, pers. comm.). Loss of hydrogen by diffusion through the bomb, as well as incomplete or sluggish mixing of Ar–H₂–CH₄ gases in the vessel may cause f_{H_2} to vary with time. The effect of these factors is difficult to evaluate, but the variation of m_{HCl} with time, (Fig. 1) and with nominal P_{CH_4} (Fig. 2) shows no obvious irregularities that can be attributed to these factors.

Theoretical considerations

The technique described here is intended to be empirical in that values of hydrogen fugacity in the argon-methane pressure medium (as inferred from m_{HCl}) can be compared directly to those of the standard oxygen buffer

assemblages. However, the variation of m_{HCl} as a function of nominal P_{CH_4} can be calculated theoretically if some simplifying assumptions are made.

The standard approach is to solve a series of mass-action and mass-balance equations involving the gaseous species present (Eugster, and Skippen, 1967). In the C–H system, two independent equations are required, equation (2) and a mass-balance equation relating the pressures of H_2 and CH_4 . Because the actual pressures of H_2 and CH_4 are unknown at elevated temperature and pressure, the following assumption was made:

$$P_{CH_4}(\text{nominal}) = P_{CH_4}(T,P) + \frac{1}{2} P_{H_2}(T,P). \quad (5)$$

Equation (5) assumes that (a) dissociation of one molecule of methane at elevated temperature and pressure produces two molecules of hydrogen, and that the resulting pressure increase is equal to the increase in the total number of molecules and (b) the amount of the H_2 lost or gained by the capsule is negligible relative to the total amount of H_2 in the vessel. It is important to note that the nominal pressure of methane loaded into the vessel at room temperature is not the same as the partial pressure of methane in the vessel at run conditions. Substitution of the pressure–fugacity expression into equation (5) results in

$$P_{CH_4}(\text{nominal}) = \frac{f_{CH_4}}{\gamma_{CH_4}}(T,P) + \frac{f_{H_2}}{2\gamma_{H_2}}(T,P) \quad (6)$$

The fugacities of H_2 and CH_4 can thus be calculated by simultaneous solution of equations (2) and (6), using an equilibrium constant for equation (2) obtained from Robie et al. (1978) corrected to 1 kbar total pressure. Two series of calculations were carried out, one in which the fugacity coefficients for both gases were assumed to be unity, and the other in which fugacity coefficients of pure methane (Ryzhenko and Volkov, 1971) and pure hydrogen (Shaw

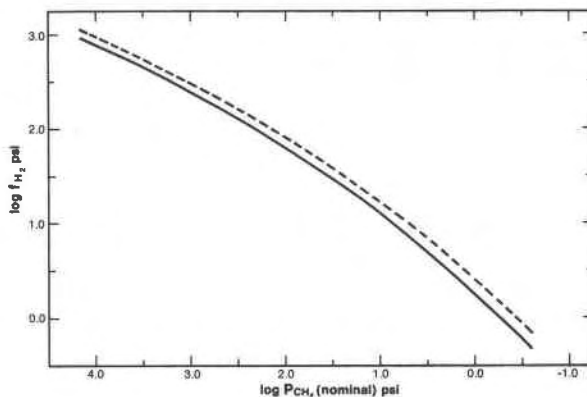


Fig. 3. Calculated variation of f_{H_2} as a function of nominal P_{CH_4} as 650°C, 1 kbar. Solid line, unity activity coefficients of gases; dashed line, activity coefficients for pure gases. See text for discussion.

and Wones, 1964) at 650°C and 1 kbar were used. The results of the calculations are plotted in Figure 3.

Given the calculated values of f_{H_2} , the expected variation of m_{HCl} can be calculated, provided that the equilibrium constant for equation (4) is known. A value of K_4 at 650° and 1 kbar was obtained from the measured m_{HCl} (Fig. 2), and a calculated f_{H_2} for the NNO buffer. The NNO buffer was selected because the f_{O_2} of the assemblage is well calibrated (Huebner and Sato, 1970; Huebner, 1971). The value of f_{H_2} for NNO was calculated as described by Eugster and Skippen (1967), using the value of f_{O_2} for NNO obtained from Huebner (1971), the dissociation constant of H_2O from Robie et al. (1978), and fugacity coefficients of H_2O and H_2 from Burnham et al. (1969) and Shaw and Wones (1964), respectively. The relation between the calculated f_{H_2} values and the predicted value of m_{HCl} is then described by

$$K_4 = \frac{(m_{HCl}^*)^2 (\gamma_{HCl}^*)^2}{f_{H_2}^*} = \frac{(m_{HCl})^2 (\gamma_{HCl})^2}{f_{H_2}}$$

or,

$$m_{HCl} = m_{HCl}^* \sqrt{\frac{f_{H_2}}{f_{H_2}^*}},$$

where it is assumed the activity coefficient ratio is unity, m_{HCl}^* is the concentration of HCl predicted for a given P_{CH_4} , m_{HCl}^* is the empirical concentration of HCl measured for the NNO buffer, $f_{H_2}^*$ is the calculated hydrogen fugacity for the NNO buffer and f_{H_2} is the calculated hydrogen fugacity for the given P_{CH_4} (nominal).

The calculated variation of m_{HCl} is shown in Figure 2. The dashed line is for the model that included activity coefficients, the dotted line for the ideal model. Considering the uncertainties that the mixing properties of Ar–H₂–CH₄ gases might introduce in equations (5) and (6), the agreement between the calculated and observed HCl concentrations is reasonable, particularly in the mid-range of the data.

Discussion

Mixtures of argon and methane can be utilized to control the hydrogen fugacity within hydrothermal vessels in a semiquantitative manner. Values of f_{H_2} (as inferred from m_{HCl}) can be varied continuously from that of the C–CH₄ buffer to nearly that of HM. The values are essentially independent of time for runs up to 10 days in length. Values are reproducible and insensitive to small changes in nominal P_{CH_4} . The observed variation is in reasonable agreement with that predicted from a simple theoretical model.

Because of slow reaction rates of the C–CH₄ buffer at temperatures $\leq 650^\circ\text{C}$ (Chou, 1980), application of the technique at lower temperatures may be limited, but a

series of lower-temperature calibration experiments are required to verify this possibility.

The method is not intended to replace the "Shaw-bomb" technique (Shaw, 1967; Hewitt, 1977; Gunter et al., 1979) in which hydrogen pressure within the vessels can be continuously monitored and regulated. In addition to the application discussed in the introduction, other applications include (a) extending the life of solid buffer assemblages by fixing f_{H_2} of the pressure medium near that of the buffer, and (b) making large volume synthesis runs at selected hydrogen fugacities. An important feature is that f_{H_2} can be continuously varied as opposed to the discrete steps attained by use of the standard solid buffers. Because f_{H_2} of a pure argon pressure medium is quite low (near that of HM, Fig. 1), the technique might be used routinely to extend the life of buffer assemblages during experiments.

Semiquantitative control of f_{H_2} might also be achieved by simply charging the argon pressure medium with hydrogen gas at room temperature rather than with methane. As shown in Figure 3, variation in nominal P_{CH_4} of nearly five orders of magnitude corresponds to a variation of approximately three orders of magnitude in f_{H_2} . Because nominal gas pressures are measured by gas regulators over most of the range, the methane technique provides the advantage of decreased sensitivity to variations in nominal pressure. Experiments using Ar–H₂ mixtures have not been attempted.

The data presented here are intended to demonstrate the technique and the range of hydrogen fugacities that can be achieved. Because measurements have been made in a single bomb and at a single temperature and total pressure, this study is not to be considered a universal calibration.

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