Experimental methods for measurement of phase equilibria at high pressures

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Abstract - This paper describes in chronological order the development of selected vapour-liquid equilibrium measuring techniques that have been devised by the author and his associates over a period of some 20 years. These include a description of an apparatus that can be used to simultaneously determine equilibrium phase compositions and densities, a description of equilibrium cells fabricated from synthetic sapphire crystals and a high pressure visual apparatus that is based on a hydraulically loaded pyrex cylinder. Example data are used to illustrate some of the uses for each method. The use of a charged coupled device for the accurate electronic detection of menisci and column lengths is described to illustrate the trend toward automation in vapour-liquid equilibrium measurements.

INTRODUCTION

A review of the literature on the observation of phase behaviour and the measurement of thermodynamic properties of gases and liquids reveals that an astonishing variety of equipment and methods has been developed. In view of the number of variables and the range of conditions over which measurements must be made, it can readily be appreciated why so many techniques have been used. This paper describes several experimental techniques which have been developed by the author and his associates during some 20 years of studying fluid phase equilibrium. Each technique embodies some novel feature which was introduced to solve a particular practical problem.

SIMULTANEOUS PHASE COMPOSITION AND DENSITY

The desirability of knowing the equilibrium phase densities as well as the equilibrium phase compositions for an equilibrium mixture is well known. For example, phase density data can be used to calculate component fugacities and the data are an intrinsic part of enthalpy and entropy departure calculations. In spite of these advantages, however, data on equilibrium phase compositions have seldom been obtained simultaneously with density data. Thus, the practical problem is one of devising a scheme to simultaneously measure equilibrium phase compositions and in-situ phase densities. The refractive index was chosen as the means for accomplishing this because refractive index is a property which is closely related to density and it can be measured conveniently and accurately. The relationship used here is

$$R_{LL} = M/\rho \, n^2 - 1/n^2 + 2 = \text{constant} \tag{1}$$

where R_{LL} is the Lorentz-Lorenz refractivity, n is the refractive index, ρ is the fluid density and M is its molecular weight. For mixtures, the refractivity is calculated using a molal average mixing rule

$$(R_{LL})_m = \Sigma x_i (R_{LL})_i \tag{2}$$

where $(R_{LL})_m$ is the molar refractivity of the mixture and $(R_{LL})_i$ is the molar refractivity and x_i the mole fraction of each pure component i in the mixture. Thus a knowledge of the fluid composition makes it possible to calculate M and $(R_{LL})_m$ and with the measured refractive index the density may readily be calculated from equation (1).

Development of methods

The optical system. Traditionally, refractive index has been measured using a spectrometer which can be used to determine the minimum angle through which a beam of monochromatic light is deviated by a prism-shaped sample of fluid. However, two disadvantages of this optical system are evident. Firstly, two pressure-sealed windows would be required to confine the fluid in the cell body and secondly, the trial and error procedure necessary to find the minimum deviation angle is time consuming. In order to eliminate these two difficulties, a new optical system was developed. This system makes use of only one pressure sealed window and the determination of the

minimum deviation angle does not require a trial and error procedure. The new system is represented schematically in Fig.1. Here, a mirrored reflecting surface is mounted inside the cell and one window is mounted in the cell wall as shown. From Snell's law, it follows that $n_3 = n_1 \sin \gamma / \sin \alpha$, where n_1 is the refractive index of air, α is the prism angle, γ is the minimum deviation angle and n_3 is the refractive index of the fluid under investigation. The angle γ is automatically the minimum deviation angle and thus the measurement requires no trial and error.

Experimental system. The equilibrium cell incorporated many of the features common in most similar equipment, however this cell incorporated the means for measuring the refractive indices of the equilibrium phases and thus embodied several unique features.
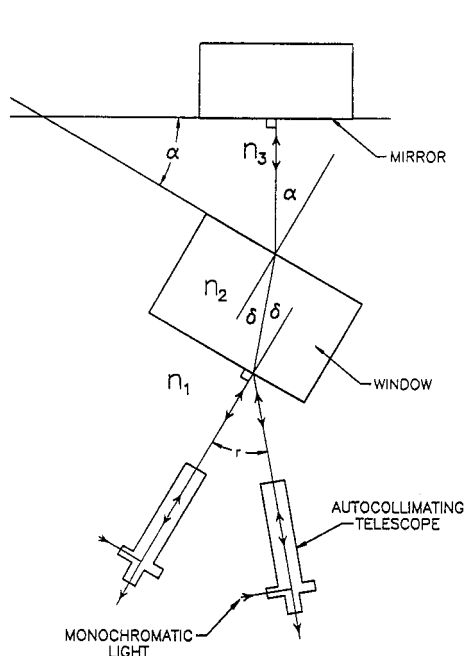

Fig. 1. Schematic representation of the angle measurement involved in determining the refractive index.
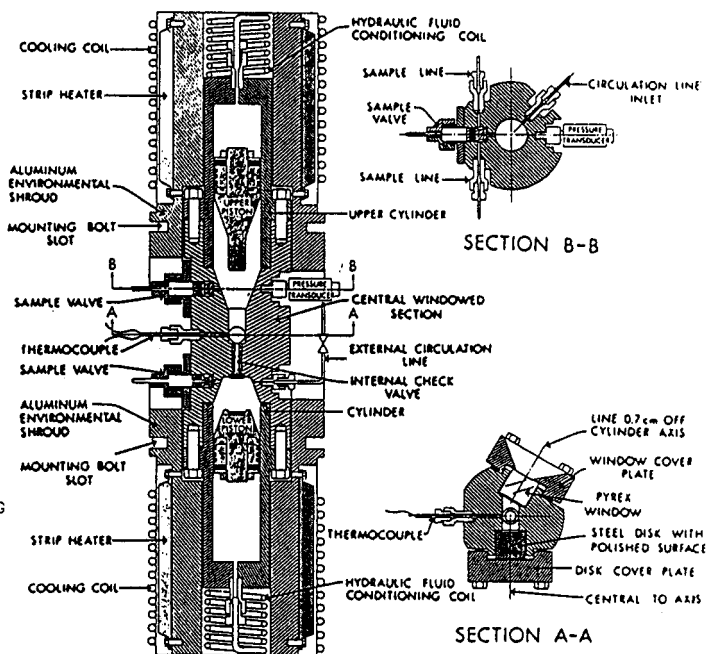
Fig. 2. Details of equilibrium cell design. (See ref. 1 for details).

The essential features of the cell design are shown in Fig. 2. The cell proper consisted of three parts, two cylinder-piston end sections and a central windowed section. The function of the pistons was to isolate the cell contents from the hydraulic fluid, to provide a means for varying the cell volume and to provide a mechanism for bringing the meniscus of either of the two equilibrium phases within view of the window.

The horizontal section A-A shows how the window, an optical quality pyrex glass disc and a stainless steel mirror formed the boundaries of a 30° prism of fluid. A second horizontal section B-B shows the details of one of the sampling valves and the outlet of the circulation line used for achieving equilibrium. The sampling valves are internally mounted micrometering valves with provision made for flushing and evacuating the low pressure sample lines. The circulation system consists of an internal check valve in the central section and an external stainless steel line with a shut-off valve.

The equilibrium cell is mounted above a precision rotary table which carries an autocollimating telescope and a He-Ne laser. The laser provided monochromatic light at a wavelength of 6328Å. The measured angles had a repeatability of ±4 seconds and the refractometer had an overall possible error of ±6x10^{-5} in the refractive index and a range from 1.0 to 1.7.

Operational procedure. The two pistons in the cell are hydraulically driven by a motorized dual cylinder pump with an opposed transmission. This feature allowed the pistons to move up or down individually or simultaneously, i.e. in a variable volume (pressure) or constant volume (pressure) mode. Thus it is possible to bring each equilibrium phase in view of the window as required.

After the cell is charged with the desired feed, mixing and equilibration are achieved by running the pistons up and down. On the upstroke, the internal check valve closes and the fluids are forced through the external circulation line and sprayed into the upper cylinder. On the downstroke the valve in the circulation line is closed and the fluids pass through the check valve.

An unexpected benefit from the use of the refractive index technique was that the point when equilibrium had been achieved was obvious. In a non-equilibrium situation, with composition and hence changing density the optical line was blurred and wobbly. At equilibrium, the line was extremely sharp and stable. The refractive index was determined by moving the phase into the prism and measuring the angle *γ* (Fig.1) on the rotary table. Samples of liquid and vapour are expanded to a pressure of 0.2 atm through the micrometering valve into an evacuated chamber connected to the gas chromatograph sampling valve.

Example performance. The measuring equipment described above has been used to study the behaviour of a large number of binary hydrocarbon and hydrocarbon + non-hydrocarbon systems. The behaviour of the carbon dioxide + n-butane system is chosen to illustrate the effectiveness of the technique. Measurements were made on the refractive indices of carbon dioxide and n-butane and on the equilibrium vapours and liquids of their mixtures at 310.95 K over a range of pressures. Molal refractivities were calculated from pure component values using the molal average mixing rule described previously. Typical results for this system are shown graphically in Fig. 3 where they are seen to compare very favourably with results obtained for the same system using more traditional means.

SAPPHIRE CELL TECHNOLOGY

Many severe demands are made on the performance of phase behaviour equipment. Some of the main features are the ability to withstand a wide range of pressure and temperature, the ability to visually or instrumentally observe the appearance or disappearance of the meniscus between phases, the ability to sample each phase present at equilibrium, the ability to achieve equilibrium in a reasonable period of time and the ability to observe the relative amount of each phase present or to deal with the limiting case of the dew point or bubble point.
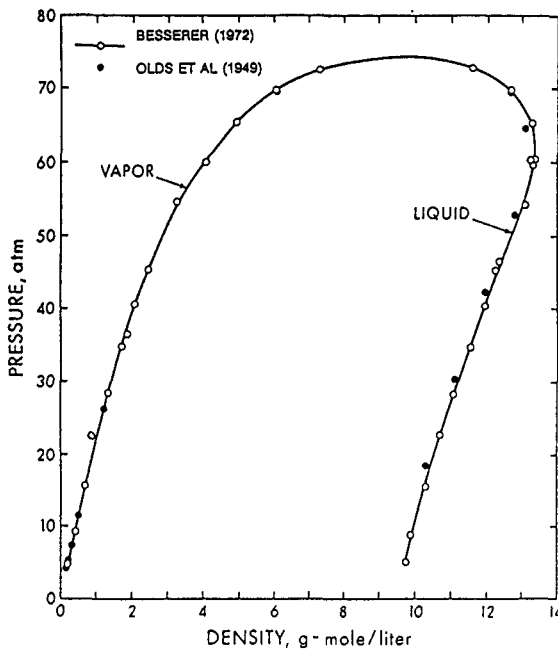

Fig. 3. Pressure-equilibrium phase density diagram for the n-butane-carbon dioxide binary system at 310.95 K.
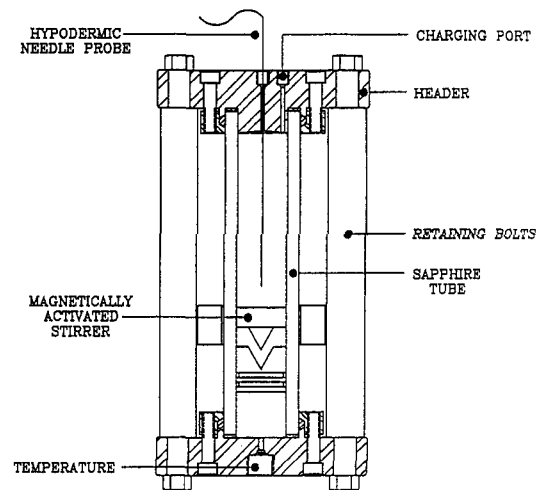

Fig. 4. Schematic diagram of sapphire equilibrium cell.

In studying the behaviour of hydrocarbon + non-hydrocarbon mixtures containing non-hydrocarbons such as carbon dioxide and hydrogen sulfide, one is faced with the problem created by reaction between hydrogen sulfide and mercury which is typically used as the confining fluid in an equilibrium cell. Thus, the practical problem to be addressed in this case is how to design a visual, variable volume cell that could be used effectively with mercury and mixtures containing hydrogen sulfide.

A clue to the solution of this problem was found while working on another phase equilibrium study. In this study it was necessary to observe the interface between bitumen and water phases as they were displaced sequentially from the steel equilibrium cell. A small thin-walled sapphire tube grown as a single crystal was used as the sight glass. This proved to be very successful even at pressures to 20 MPa. This experience led to the conclusion that it should be possible to construct the body of an equilibrium cell entirely from synthetic sapphire. This material would be completely transparent, would have a strength in the same order of magnitude as steel and could be shaped in the form of a cylinder with the advantage of a circular cross section. This would replace the rectangular cross section found in typical steel plate - pyrex window cells.
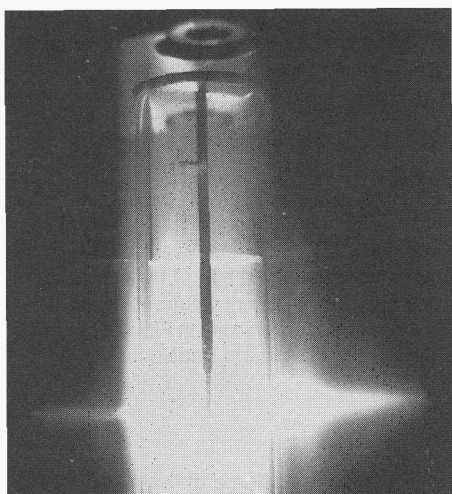
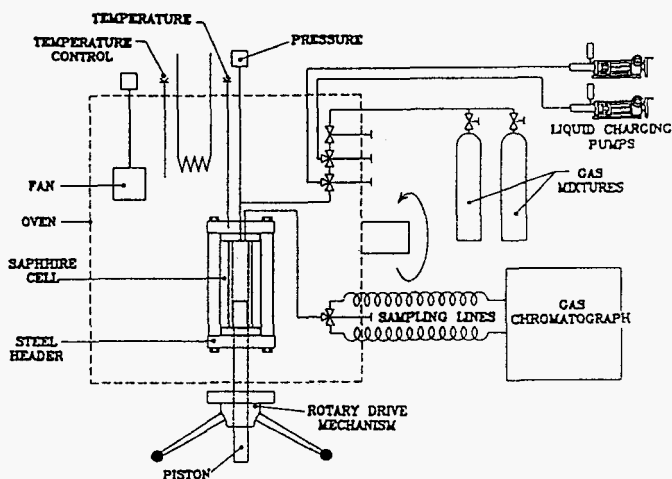Fig. 5.   Two-phase vapor liquid equilibrium in a sapphire cell at 6.62 MPa and 216 K.

Fig. 6.   Variable volume equilibrium cell cut from sapphire crystal. (See ref. 4 for details).

The first attempt at using the sapphire tube technology was designed to study the phase behaviour of mixtures of hydrogen sulfide, carbon dioxide and methane. Mercury could not be used and complete visibility of the cell contents was essential. A schematic illustration of the cell design is shown in Fig. 4. The sapphire tube was 1.9 cm O.D., 12.3 cm long and had a 0.32 cm wall. It had a working pressure of 20 MPa. The shaped teflon coated mild steel piece was used to achieve equilibrium by the vertical reciprocating motion of the permanent magnet. The V-notch was used to observe very small volumes of a liquid phase. Fig. 5 is an illustration of the visibility achieved using this cell for a two-phase mixture at a temperature of 216 K and a pressure 6.62 MPa. The second version of a cell based on the sapphire cylinder concept is illustrated schematically in Fig. 6. This cell was also mercury-free and a variable volume feature was provided by a steel plunger driven by a rotary ball-screw mechanism. The cell was 3.81 cm O.D., 15.24 cm long and had a 0.64 cm wall. The cell has been used to carry out phase behaviour studies on binary, ternary, quaternary and other multicomponent systems exhibiting vapour-liquid, vapour-liquid-liquid and vapour-liquid-solid equilibrium. Fig. 7 and 8 illustrate typical observations made.

HYDRAULICALLY LOADED TRANSPARENT CELL

The sapphire cell concept had many advantages and it helped to resolve many of the difficulties that had been encountered when studying multi-phase behaviour with mercury in cells of irregular cross-section. However, there is a physical limit to the size of single sapphire crystals that can be produced synthetically and this in turn imposes a limit on the capacity of cylinders that can be cut from them. It was our belief that when a combination of capacity and costs were considered the effective upper pressure limit was 20 to 30 Mpa. Thus the practical problem to be addressed was how to design a visual, variable volume cell that could accommodate larger fluid volumes and would withstand working pressures in the order of 80 to 100 Mpa.
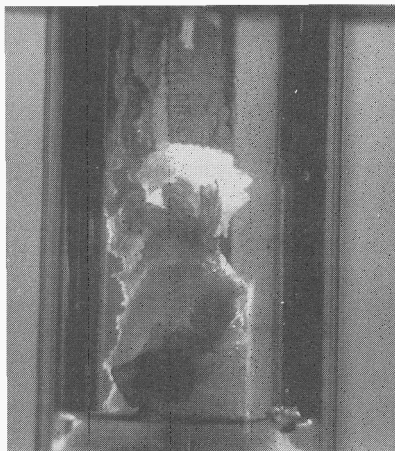

Fig. 7.   Hydrate formation in sapphire equilibrium cell.

Fig. 8.   Near-critical condition for the methane + n-butane binary system in sapphire equilibrium cell.

The solution involved the use of a hydraulically overburdened pyrex cylinder. The cylinder was housed within an outer steel shell such that the internal fluid pressure was always balanced by an external pressure applied hydraulically. Full visibility of the cell contents was provided by diametrically opposed slots cut in the steel shell. These slots were sealed from the outside environment by tempered borosilicate glass plates held in place by steel cover plates. The hydraulic balancing fluid (usually water) was connected in parallel with the sample pressurizing fluid (usually mercury) through a positive displacement pump.

In this cell, the pyrex cylinder is about 20 cm long and has an internal diameter of 3.175 cm and a wall thickness of 1.27 cm. It can be operated with the pressurizing fluid acting as the sample confining fluid or with a floating piston as illustrated in Fig. 9 and 10. The cell is designed to operate at pressures to 90 MPa and has been used extensively at temperatures between 223 and 473 K. A cut-away view of the cell is shown in Fig. 9. This clearly shows the location of the pyrex cylinder within the steel housing, the position of the tempered pyrex glass windows in the outer shell, the configuration of the end caps and the sealing arrangement at the ends of glass cylinder where the hydraulic fluid and test fluid are separated from each other.

In studying the behaviour of naturally occurring hydrocarbon and related mixtures the experimentalist often encounters situations where the amount of liquid present is at levels of 1% or less by volume. Thus a practical problem that must be addressed is how to make accurate measurements of these liquid volumes. The hydraulically loaded pyrex cell described above helps resolve this problem because a variety of configurations may be used for the floating piston. As an example, it may be cut in the form of a truncated cone. This greatly enhances the accuracy of measurement when very small volumes of liquid are present, such as in the retrograde dewpoint region of a multicomponent system. Fig. 10 illustrates both a standard floating piston and a floating piston cut in the form of a truncated cone. An example of observations which are possible through the use of the truncated piston are illustrated in Fig. 11 for a case where two immiscible liquids are in equilibrium with vapour. This shows the piston and the menisci between the vapour and two immiscible liquid phases in a multicomponent gas condensate system at a temperature of 283 K and at a pressure of 19.2 MPa.
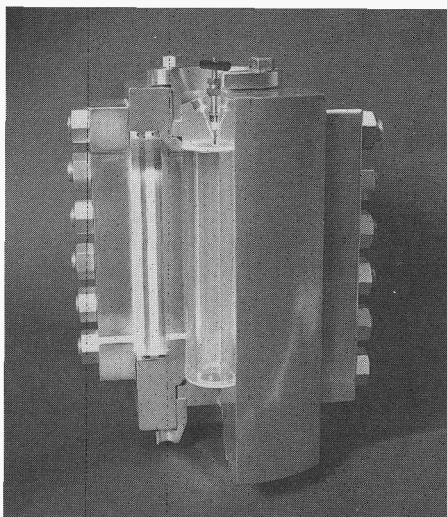

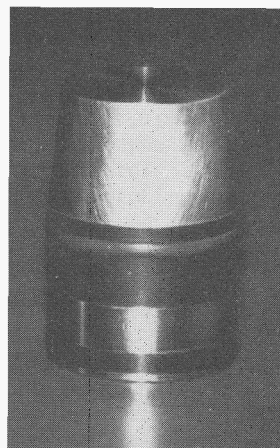Fig. 9. Cut-away view of hydraulically loaded pyrex equilibrium cell.

Fig. 10. Floating pistons used in hydraulically loaded cell.

INTERFACE DETECTION

Much of the equipment described above depends on the ability of an operator to detect and measure the relative location of an interface between phases. These measurements, are used to calculate phase volumes. Since the measurements are invariably made in the vertical direction, a cathetometer is typically the instrument used for the observations. In many ways the cathetometer is well suited for the task and it can yield accurate results. However, a number of drawbacks are: (a) The operator is exposed to the hazards of a cell failure unless elaborate and usually inconvenient precautions are taken, (b) there may be errors associated with parallax, (c) an element of human error exists in taking the readings, (d) there may be errors associated with the non-standard conversion of cathetometer readings to volumes, and (e) data acquisition is discrete rather than continuous.

This list serves to illustrate the fact that some very real practical problems exist with respect to the accurate observation and determination of equilibrium phase volumes.

We have recently addressed the above problems through the design and development of an imaging system based on the use of charged coupled devices (CCD) for the accurate electronic measurement of column lengths and fluid volumes. This represents an innovative method for the digital detection of an interface by differentiating areas of dissimilar light intensity. The physical arrangement of the primary elements required for the CCD Imaging System is shown schematically in Fig. 12. In practice, the front light may be supplemented by a rear light source. Fig. 12 illustrates the nature of the image and the light intensity profile that appears on the PC screen. The point where the solid light intensity line crosses the vertical dashed line represents the location of any point within the cell where a measurable change in light intensity occurs. This includes the ends of a piston, the top and bottom of a meniscus, the ends of the cell, etc.
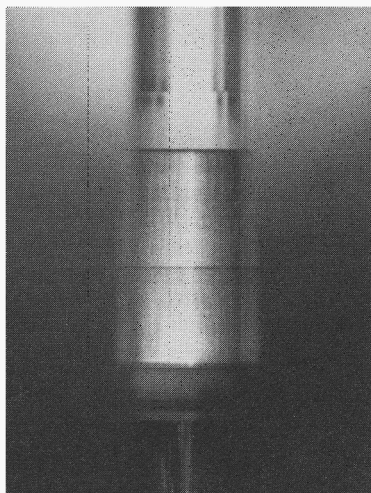

Fig. 11. Three phase equilibrium in a multi-component system at 283 K and 19.2 MPa.
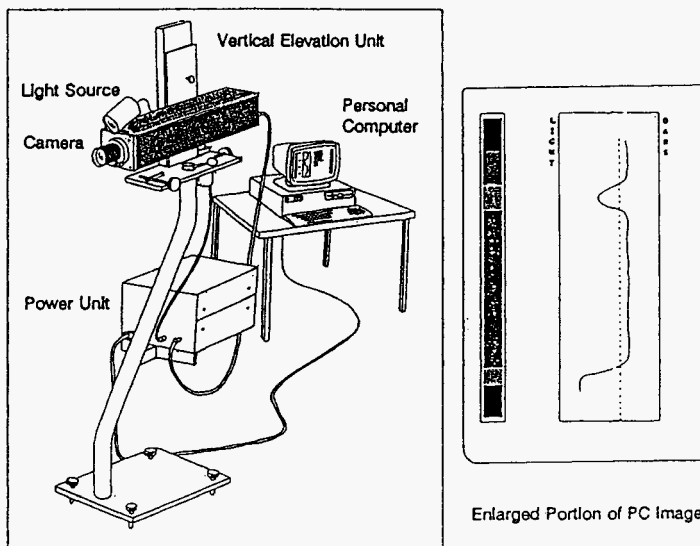

Enlarged Portion of PC Image

Fig. 12. Physical arrangement of components for charged coupled device imaging system.

This electronic measuring system effectively addresses all of the problems listed above which are inherent in the manually operated cathetometer system. The accuracy of linear measurements is at least comparable to cathetometer readings. The linear resolution is 0.0127 cm which corresponds to a volumetric accuracy of approximately ± 0.01 cm^3 in the hydraulically loaded pyrex cell described earlier.

SUMMARY

Fluid property experimentalists everywhere are involved in an on-going quest for improvement in their methods. This paper has presented some of the advances that have occurred over a period of approximately 20 years as a result of the efforts of a group of workers originally located at the University of Alberta and later in the laboratories of DB Robinson Research Ltd. Advances in the future will perhaps be more on the automation of experiments using existing equilibrium cell technology rather than on the development of original technology. The development of the CCD Imaging System is a step in that direction.

Acknowledgement

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