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ANNUAL PROGRESS REPORT TO THE DEPARTMENT OF ENERGY

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PROJECT DE-FG02-89ER-14080:

DEVELOPMENT OF AN EXPERIMENTAL DATABASE AND THEORIES FOR
PREDICTION OF THERMODYNAMIC PROPERTIES OF AQUEOUS ELECTROLYTES
AND NONELECTROLYTES OF GEOCHEMICAL SIGNIFICANCE AT SUPERCRITICAL
TEMPERATURES AND PRESSURES

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I. Progress in the Experimental Phase

After the usual problems of new apparatus development and the normal amount of malfunction, the experimental part of this project is proceeding at a good pace. Our new method of preparing and storing solutions so that we do not have to do a time consuming analysis after each experiment is up and running. This equipment allows us to do our measurements much more quickly. The H_2S and CO_2 solutions are stored in aluminized mylar bags in PVC pipes with water surrounding the bags at a pressure of several atmospheres. The methane is stored in a one liter autoclave with a sliding teflon piston engaging the sides of the autoclave which separates the standard methane solution from the pressurizing fluid. The solutions are prepared at 100 to 200 atmospheres and do not need to be re-standardized after each experiment.

The new electronics have been installed to keep the amplitude of vibration constant and the stability of the instrument is somewhat improved.

Volumetric measurements have been completed for CH_4 , CO_2 , and H_2S at temperatures from 25°C to 380°C and 2 or 3 pressures at each temperature. We also have some measurements on aqueous ammonia, boric acid, and acetic acid. It is expected that the volumetric measurements will be completed within the next four months.

Some earlier, preliminary measurements on the volumetric properties of carbon dioxide at high temperatures contained an unfortunate numerical error. These results have been revised and the paper has been accepted for publication in the Journal of Chemical Thermodynamics.⁽¹⁾

In the course of exploring the bubble point of aqueous CO₂ solutions at high temperatures, we measured the densities close to the bubble point and these results are being written up for publication. This development allows us to measure the solubility of gases in water at high temperatures fairly easily and with accuracies that not too bad (approximately 10% in Henry's constant) considering the nearness of the critical point.

II. Theoretical Calculations

We have our IBM 6000 model 320 workstation (which was purchased from other funds) set up and the Amber molecular dynamics package is running on it. Preliminary calculations of the free energy of methane in water at room temperature as a function of the model parameters for the methane have been finished. We have been limited in our utilization of this workstation because we only have 8 megabytes of memory and as a result, we are not even able to utilize windows. We have requested permission to buy some additional memory using the present grant funds for this system so that the research can proceed more quickly. Hopefully, permission for this purchase will be received soon.

In preparation for these calculations, the theory and practice of the free energy perturbation calculations was reviewed. In molecular dynamics and Monte Carlo calculations a system does not immediately equilibrate to a change in the Hamiltonian, so that there is a time lag or a configuration number lag in the response of the system. These lags cause errors in free energy calculations. It was realized that the literature estimates for the time-lag errors in this kind of calculation were 10 times too

large. To remedy this situation, two methods of measuring these "time lags" were devised. The first method is based on Onsager's fluctuation regression hypothesis and the measurement of the fluctuations in $dE/d\lambda$. The second method is from a measurement of the hysteresis in slow-growth calculations. Both methods indicate that time lags are between 0.04 and 0.2 ps for typical systems. For time lags showing a single exponential decay, it was shown that the average of the forward and reverse runs provides a very accurate estimate of the free energy for typical experimental curves provided that the system is equilibrated before starting the reverse run. Programming λ in a nonlinear fashion in order to make ΔG a linear function of time is not a generally helpful procedure and is sometimes less accurate than a linear change of λ with time. Using a simple model of the time lags, the free energy perturbation runs can be used to measure the time lags, estimate the errors caused by these time lags, and correct the results for the errors. A generalization of Onsager's fluctuation regression hypothesis allows the calculation of configuration number lags in Monte Carlo runs from the observed fluctuations in $dE/d\lambda$. This paper is in press in the Journal of Physical Chemistry.⁽³⁾

In addition to the time-lag errors in these calculations, there are also hysteresis errors that limit the accuracy of these calculations.

Although it is well known that the free energy perturbation procedure is exact when an infinite sample is used, for finite sample size there is a systematic error resulting in hysteresis for forward and backward simulations. In a second paper, the qualitative behavior of this error was first explored for a

Gaussian distribution, then a 1st order estimate of the error for any distribution was derived. To 1st order the error depends only on the fluctuations in the sample of potential energies, ΔE , and the sample size, n , but not on the magnitude of ΔE .

This 1st order estimate of the sample-size error was used to compare the efficiencies of various computing strategies. It was found that slow-growth, free-energy-perturbation calculations will always have lower errors than window-growth, free-energy-perturbation calculations for the same computing effort. The sample-size hysteresis can be entirely eliminated by going to thermodynamic integration rather than free-energy-perturbation calculations. When ΔE is a very smooth function of the coupling parameter, λ , thermodynamic integration with a relatively small number of windows is the recommended procedure because the time required for equilibration is reduced with a small number of windows.

The results gave a method of estimating sample-size hysteresis during the course of a slow-growth free-energy-perturbation run. This is important because in these calculations time-lag and sample-size hysteresis can cancel, so that separate methods of estimating and correcting for each are needed. When using dynamically modified window procedures, it was recommended that the estimated hysteresis error be kept constant, rather than keeping the magnitude of ΔE constant. Tests on two systems showed a rather small sample-size hysteresis in slow-growth calculations except in the first stages of creating a particle, where both fluctuations and sample-size hysteresis are large. This paper has been accepted for publication in the Journal of Physical Chemistry.⁽⁴⁾

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