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Simultaneous Vapor−Liquid−Liquid Equilibria and Phase Molar Densities of a Quaternary System of Propane + Pentane + Octane + Water

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This paper presents a new procedure to measure simultaneously equilibrium phase compositions and phase densities of multicomponent fluid mixtures. This is accomplished using a uniquely designed pressure/volume/temperature-vapor/liquid/liquid equilibrium apparatus (*PVT*-VLLE) connected to a modified sampling system for gas chromatographic analysis (GC) at high pressures and temperatures. The data reported in this paper include (1) three-phase equilibrium compositions and pressures of hexane + water and (2) three-phase equilibrium compositions and phase molar densities for a quaternary system of propane + pentane + octane + water. The equilibrium compositions and three-phase equilibrium pressures for hexane and water compare well with the published data of Tsonopolous and Wilson, which are considered as a calibration test to validate our procedure. Thus we conclude that this methodology is suitable for determining volumetric and phase equilibria properties of multiphase systems.

Introduction

Aqueous-hydrocarbon systems frequently occur in the petroleum industry either in steam flooding for enhanced oil recovery or in downstream separation processes. Phase equilibrium in these systems is complex and usually involves three or more equilibria phases (Reid and Robinson, 1981). In steam flooding processes, steam is injected through an injector well to displace oil within the reservoir to a producer well. In this process, heat and mass transfer cause multiphase separations including a vapor phase, a hydrocarbon-rich liquid phase, and an aqueous phase.

Numerous investigators have studied the phase behavior of hydrocarbons + water and CO_2 + hydrocarbon systems. Among these are Panagiotopolous and Reid (1986), Orr and Silva (1983), and Yaws *et al*. (1993). Among the most recent theoretical developments, Eubank *et al*. (1994, 1995) were successful in predicting the phase behavior of complex + water and hydrocarbon systems using new minimization procedures with the powerful mixing rules of Wong and Sandler (1992). Shinta and Firoozabadi (1995) used an association model coupled to the Peng−Robinson EOS and were successful in predicting three-phase equilibria compositions of multicomponent mixtures.

Because the equipment needed to measure high-pressure, high-temperature, three-phase equilibria is complex, experimental data are expensive and scarce.

Materials

The *PVT*-VLLE system was charged with the propane + pentane + octane + water mixture prepared gravimetrically using a Mettler PM #600 Delta range electronic balance (accuracy ±0.01 g). All hydrocarbons used were from Aldrich Chemical Co. with 99+% purity. The water content was less than 0.005%, and the evaporation residue less than 0.0003%. The water used was degassed and deionized.

Description of the Experimental *PVT*-VLLE Apparatus

We assembled a mercury-free Ruska *PVT* Model 2370 to a Hewlett Packard 5880 gas chromatograph (GC) and a specially designed sampling system capable of measuring the compositions of all equilibrium phases on-line at high pressures and temperatures. The significance of this experimental setup is a superior on-line sampling for compositional analysis and for accurate phase volume measurements. This is possible because a negligible volume (0.1 μL to 0.5 μL) is withdrawn and sent to the GC for compositional analysis. Since the volumes used for analysis represent less than one in 10^7 of the sample volume, the mass withdrawn for analysis is negligible, and the equilibrium of the system is essentially undisturbed. We refer to this as a *PVT*-VLLE (vapor/liquid/liquid equilibrium) apparatus.

Figure 1 shows a schematic of the *PVT* system which consists of two cells: a pump cell (PC) and float piston cell (FPC). These cells are interconnected with high-pressure steel tubing. The volume in both cells can be changed separately by computer-controlled stepping motors. The pump cell can be used as a blind cell for single-phase analysis or with a sapphire, see-through tube to identify interfaces in multiphase analysis. The volume in the pump cell (PC) is a function of the piston position. Both cells are vertically mounted in the temperature-controlled region of an air bath. By careful control of the two positive displacement pumps, the sample mobility can be achieved at constant temperature, pressure, and volume. The volumes depend upon the dimensions of the cylinders, piston position, temperature, pressure, reference points, and magnet volume. The internal volumes for both cells and interconnecting tubing have been calibrated, including pressure and temperature correction coefficients (Ruska M2370, 1990). At standard conditions, the full volume of the pump cell is 358.85 ± 0.01 cm^3 and the volume of the FPC is 609.09 ± 0.01 cm^3. Phase volumes can be measured by placing the phase boundary at a reference point in the sapphire window; the estimated accuracy of these measurements is ±0.01 cm^3. The sample mixing in both cells is accomplished by stirring a magnetic coupling. An interior ring magnet, which acts as a mobile baffle, is moved by an exterior magnet traversing along the outer wall of the cell.

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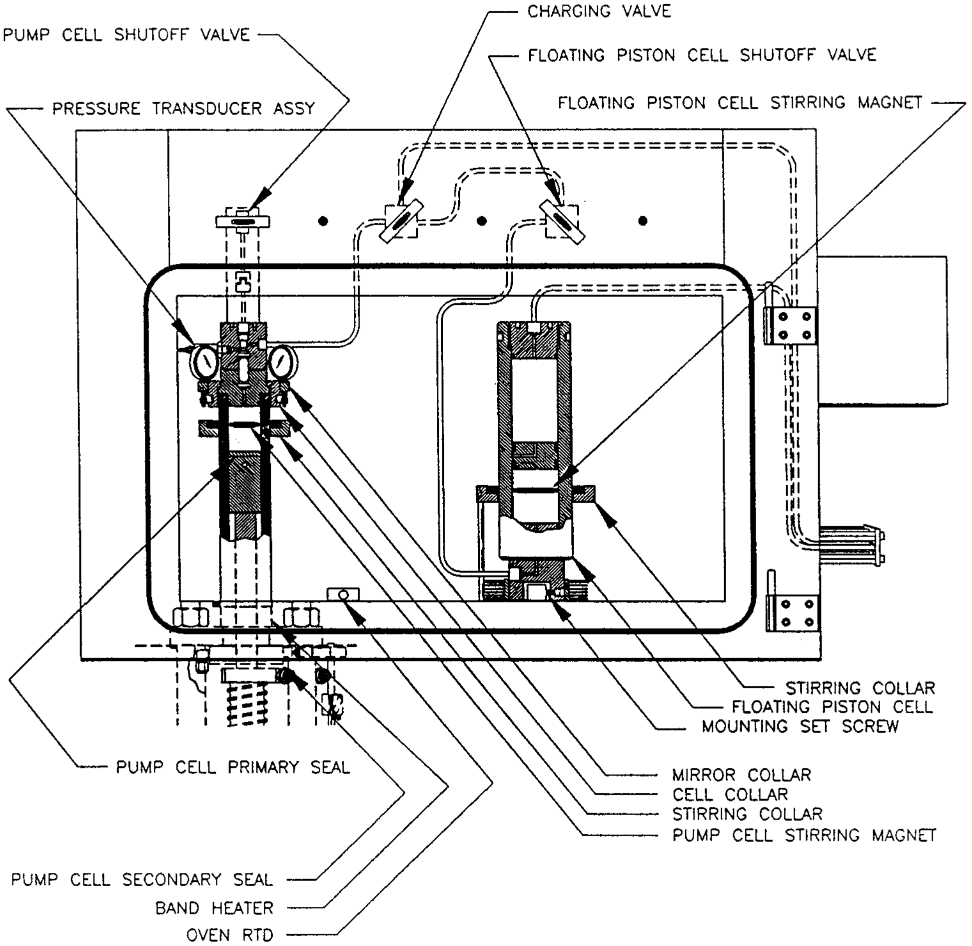

Figure 1. Schematics of the *PVT* system.

The pressure is measured automatically by a temperature-compensated strain gauge transducer. The transducer is located in the pump-cell top assembly, below the valve seat, so measurements are valid whether the valve is closed or open. Two resistance element heaters are located within the air bath and are controlled by a dedicated channel dual PID (Proportional, Integral, Derivative) process control unit. The temperature is measured using three RTDs (resistance temperature detectors) that send feedback signals to the control unit.

The temperatures in these experiments are considered accurate to ±0.2 K, whereas the pressures are accurate to 0.005 MPa. These uncertainties were taken from the manufacturer of the equipment and confirmed from earlier calibration tests.

Upgraded Sampling System

We incorporated an upgraded sampling system to a Hewlett Packard 5880 gas chromatograph (GC). This sampling device has four-port sampling valves and four-port and six-port switching valves with digital valve interfaces and relays. The valves are air actuated and have a maximum working pressure of 27 MPa. These valves can be operated with the gas chromatograph terminal key strokes. Figure 2 shows the sampling loop consisting of three sampling valves that have been incorporated between the two cells of the *PVT* system. Each of these valves is connected to a switching valve for back-flushing and to separate columns for various phase composition analyses. The gas chromatograph uses three digitally-operated valves for injection of very small fluid volumes (0.1 μL to 0.5 μL) and for back-flushing to eliminate column contamination.

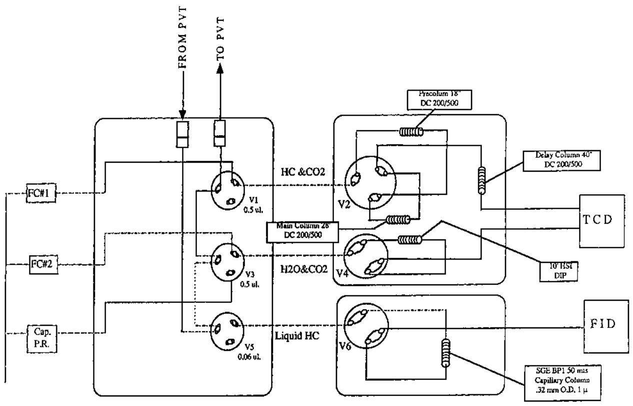

Figure 2. Upgraded gas chromatograph sampling loop.

Measurement of Phase Compositions

During this portion of the experiment, the valve at the top of piston cell is open. The oven is heated to the desired temperature and the fluids are allowed to expand and vaporize until equilibrium is achieved. The liquid phases are at the bottom of the pump cell, and the rest of the volume is occupied by the vapor phase. The fluid within the sampling loop is vapor and is analyzed for composition. After the vapor phase analysis, the piston of the pump cell is moved upward and the float piston cell is moved up simultaneously by removing hydraulic oil. Both pistons are set to move at the same volumetric speed so that the overall volume of the system is constant and equilibrium is maintained. The process of fluid movement continues until the liquid phase reaches the sampling loop and can

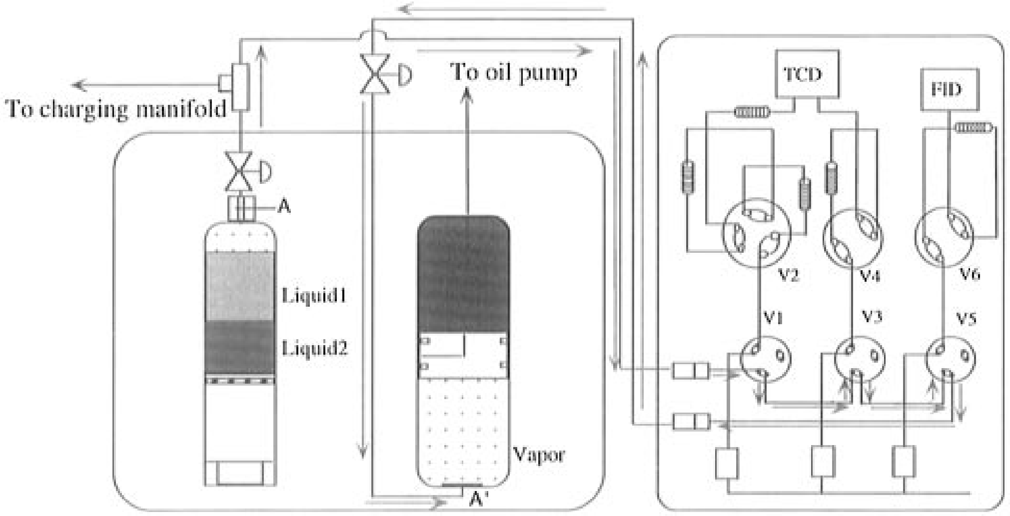

Figure 3. Integrated experimental setup.

Table 1. Equilibrium Phase Compositions and Molar Phase Volumes for the Hexane (1) + Water (2) System

/MPa	T/K	y_1	x_1	w_1	v_v/cm^3·mol^{-1}	v_o/cm^3·mol^{-1}	v_a/cm^3·mol^{-1}
0.343	373.11	0.6672	0.9866	6.157×10^{-6}	11859.15	148.72	18.81
0.612	394.22	0.5997	0.984	1.848×10^{-5}	5391.17	152.99	19.13
1.267	423.11	0.4745	0.9674	3.108×10^{-5}	2294.59	160.62	19.66
2.252	449.88	0.4283	0.9342	1.159×10^{-4}	984.17	167.71	20.26
2.956	463.67	0.4042	0.9069	1.883×10^{-4}	574.19	169.03	20.62

be sampled for compositional analysis. For this procedure to be successful, one must optimize the amount of mixture charged in the cell to ensure that the volumes of the equilibrium phases are larger than the dead volume and small enough to cover a wide range of pressures and temperatures with a single load. This dead volume includes the reference mark in the sapphire see-through window to the sampling valves of the GC and return tubing to the base of the float piston cell (≈35 cm^3). Figure 3 sketches the connections between the GC and the *PVT* system where this dead volume is enclosed between points A and A′.

The chromatographic techniques used were the ASTM (1989) simulation distillation (SIMDIS) procedures and those of McAuliffe (1966) for the determination of hydrocarbon solubility in water. The experimental technique has been validated by reproducing experimental compositions and three-phase equilibrium pressures of binary systems of water + alkanes from the literature. (Tsonopolous and Wilson, 1983; Heidman et al., 1985; Rahman and Barrufet, 1995; Rahman, 1995; Beladi, 1995).

All compositions reported in this work are the average of three measurements, and the reproducibility of these is better than 0.03%.

Evaluation of Phase Fractions from Three-Phase Equilibria Systems

Binary Systems. Applying the phase rule of Gibbs to a nonreacting binary system that exhibits three-phase equilibria provides only one degree of freedom.

$$F = C - \phi + 2 \tag{1}$$

where C is the number of components and ϕ is the number of equilibrium phases. Thus a binary system exhibits a unique three-phase equilibrium pressure at a fixed temperature. The compositions of these phases are likewise fixed.

The material balance equation relating overall (or feed) compositions to phase compositions and molar phase fractions (i.e. vapor, hydrocarbon-rich, and aqueous) is

$$z_i = x_i f_o + y_i f_v + w_i f_a \qquad i = 1, ..., n_c \tag{2}$$

where z_i, x_i, y_i, and w_i are the experimentally measured feed, hydrocarbon-rich, vapor, and aqueous molar phase compositions, respectively, and f_o, f_v, and f_a are the molar fractions of feed in the hydrocarbon-rich phase, the vapor phase, and the aqueous phase, respectively.

Although phase compositions and phase volumes can be measured using our *PVT*-VLLE equipment with a binary system exhibiting three-phase equilibria, it is not possible to evaluate molar phase volumes because the equations resulting from solving the material balance equations (2) are linearly dependent (Barrufet and Liu, 1995). However, we estimated molar phase densities by assuming, since the solubility of hydrocarbons in the aqueous phase is very low, that the aqueous phase has a density very close to saturated liquid water. We estimated this density at the experimental pressures and temperatures using Kell's equation (1975). This independent estimate allows the calculation of the vapor and the hydrocarbon-rich density. The steam tables could be used to determine the saturated water density more precisely, but we used Kell's correlation because of its simplicity. For the range applied, this equation provides densities within 0.2% of the steam tables. Once this is estimated, the aqueous phase fraction is calculated as

$$f_a = \frac{V_a}{v_a n_t} \tag{3}$$

where V_a is the aqueous volume (cm^3), n_t is the total number of moles loaded in the system, and v_a is the molar volume of the aqueous phase. Once f_a is fixed; f_o and f_v can be obtained from the two material balance equations (eq 2). With the phase fractions and the measured volumes, one can determine the molar volumes of the hydrocarbon-rich and the vapor phases. Table 1 shows the

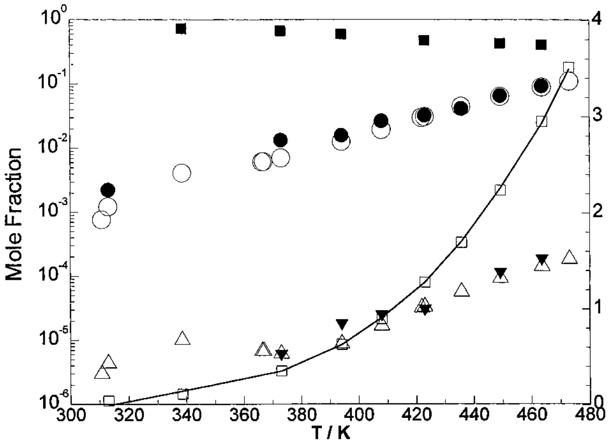

Figure 4. Phase equilibrium compositions for hexane (1) + water (2): (solid symbols) this work; (open symbols) Tsonopolous and Wilson (1983); (■) (1) in vapor phase, (○/●) (2) in hydrocarbon-rich phase; (△/▼) (1) in aqueous phase; (□) three-phase equilibrium pressures.

equilibrium phase compositions and the estimated phase densities for hexane + water at five different temperatures.

Figure 4 shows the measured phase equilibrium compositions for this system along with published data of Tsonopolous and Wilson (1983). They did not report the vapor compositions. The three-phase equilibrium pressures agreed within ±0.005 MPa. Figure 4 also shows the three-phase equilibrium pressure line. For hexane + water, Tsonopolous and Wilson (1983) estimate this pressure from the following equation based upon a fit from their experimental data. Measured pressures are within ±0.005 MPa of the values predicted by this equation.

$$\ln(P_3^{\sigma}/\mathrm{MPa}) = 9.8127 - \frac{4047.70}{(T/\mathrm{K})} \qquad (4)$$

Notice that at low temperatures there is substantial scatter, particularly in the hydrocarbon-rich phase.

Multicomponent Systems. A three-component mixture exhibiting three-phase equilibria provides a system of three equations with three unknowns (eq 2) and a unique solution for the phase fractions. Thus, one may verify the material balance, although this is not enough to assess the experimental uncertainty. The minimum number of components that should be used to estimate experimental uncertainties in this type of experiments is four. If the experiments were error free, one could select any three equations to solve a linear system of equations and solve for the phase fractions. A quaternary system provides four different combinations of equations, which will likely provide different values for the phase fractions even with carefully prepared experiments. Therefore, the reported phase fractions are optimized using least-squares error techniques.

Since all compositions are measured, one could also use eq 2 for consistency tests. Any one of the compositions (x_i, y_i, w_i) can be *recalculated* as a function of the remaining variables. For example, the hydrocarbon-rich compositions can be reevaluated from eq 2 as

$$x_i^c = \frac{z_i^e - y_i^e f_v - w_i^e f_a}{f_o} \qquad i = 1, ..., n_c \qquad (5)$$

Similar expressions are found for the vapor and aqueous compositions. Here superscript "e" is for experimental and "c" for recalculated. If no errors were present, this would be a trivial exercise with recalculated values identical to measured values. However, due to experimental uncertainties, these compositions could differ from the measured ones. We analyzed all the compositions and allowed them to change within an uncertainty that would satisfy all the material balance constraints. The largest uncertainty obtained in the mole fractions was ±0.0004. This indicates that the consistency checks for all components (x_i^c, y_i^c, w_i^c) indicated by eq 5 are satisfied within a tolerance of 10^{-8}.

We measured phase equilibria compositions and volumes for this quaternary system at six different temperatures and pressures. Since the sampling is infinitesimal, several measurements can be done at various temperatures and pressures without the need of reevaluating the overall composition after sampling.

Table 2. Equilibrium Phase Compositions and Phase Densities for the 12.92% (Mole Basis) Propane (1) + 5.44% Pentane + 5.67% Octane (3) + 75.97% Water (4) System

phase	x_1	x_2	x_3	x_4	ρ/g·cm^{-3}
		$P = 0.7377$ MPa, $T = 313$ K			
vapor	0.950 57	0.045 51	0.002 93	0.000 98	0.0127
hydrocarbon	0.517 56	0.233 64	0.245 7	0.003 09	0.5996
aqueous	2.0922×10^{-4}	4.8629×10^{-6}	4.80510×10^{-8}	0.999 79	0.9928
		$P = 1.186$ MPa, $T = 338$ K			
vapor	0.926 54	0.054 35	7.0×10^{-6}	0.019 1	0.0203
hydrocarbon	0.504 32	0.236 13	0.250 41	0.009 14	0.5835
aqueous	1.83×10^{-5}	1.1×10^{-6}	1.76×10^{-9}	0.999 98	0.9806
		$P = 2.034$ MPa, $T = 373$ K			
vapor	0.906 89	0.050 8	0.013 54	0.028 77	0.0412
hydrocarbon	0.472 58	0.249 53	0.266 33	0.011 56	0.5548
aqueous	1.87×10^{-4}	2.15×10^{-6}	1.84×10^{-8}	0.999 81	0.9593
		$P = 2.633$ MPa, $T = 393$ K			
vapor	0.759 64	0.072 39	0.033 55	0.134 42	0.0547
hydrocarbon	0.457 63	0.243 86	0.263 04	0.035 47	0.5437
aqueous	2.225×10^{-4}	2.9939×10^{-6}	9.2342×10^{-9}	0.999 78	0.9424
		$P = 3.93$ MPa, $T = 423$ K			
vapor	0.692 82	0.115 26	0.037 13	0.154 8	0.0816
hydrocarbon	0.427 16	0.237 22	0.273 87	0.061 76	0.5113
aqueous	9.20×10^{-4}	1.07×10^{-6}	1.80×10^{-7}	0.999 08	0.9187
		$P = 5.15$ MPa, $T = 448$ K			
vapor	0.685 19	0.117 29	0.042 93	0.154 59	0.1065
hydrocarbon	0.377 24	0.232 17	0.279 38	0.111 21	0.4838
aqueous	1.76×10^{-3}	7.692×10^{-4}	4.4×10^{-6}	0.997 47	0.8965

To determine phase densities, we coupled the material balance equations (eq 2) with the volumetric measurements from the *PVT*-VLLE apparatus.

The total cell volume is evaluated as

$$V_\mathrm{t} = V_\mathrm{a} + V_\mathrm{v} + V_\mathrm{o} \tag{6}$$

where the subscripts in the volumes indicate the phase: aqueous (a), vapor (v), and hydrocarbon-rich (o). The apparent total molar volume is related to the phase molar volumes as follows:

$$\frac{V_\mathrm{t}}{n_\mathrm{t}} = f_\mathrm{a}v_\mathrm{a} + f_\mathrm{v}v_\mathrm{v} + f_\mathrm{o}v_\mathrm{o} \tag{7}$$

where n_t is the total number of moles loaded to the system and the phase fractions are obtained from eq 2. The molar volumes are obtained from the following relations:

$$= \frac{V_\mathrm{a}}{n_\mathrm{a}} = \frac{V_\mathrm{a}}{f_\mathrm{a}n_\mathrm{t}}, \qquad v_\mathrm{v} = \frac{V_\mathrm{v}}{n_\mathrm{v}} = \frac{V_\mathrm{v}}{f_\mathrm{v}n_\mathrm{t}}, \qquad v_\mathrm{o} = \frac{V_\mathrm{o}}{n_\mathrm{o}} = \frac{V_\mathrm{o}}{f_\mathrm{o}n_\mathrm{t}} \tag{8}$$

and the mass densities are obtained as

$$(\rho_\mathrm{a}/\mathrm{g\ cm^{-3}}) = \frac{(M_\mathrm{wa}/\mathrm{g\ mol^{-1}})}{(v_\mathrm{a}/\mathrm{cm^3\ mol^{-1}})} = \frac{\sum_{i=1}^{n_\mathrm{c}} w_\mathrm{i}M_\mathrm{wi}}{v_\mathrm{a}} \tag{9}$$

where M_wi is the molecular weight of species "i". Analogous expressions hold for the vapor and the hydrocarbon-rich density.

Table 2 shows the phase compositions for this system along with the phase densities.

Conclusions

We described a new procedure to measure phase equilibria and volumetric data using a uniquely designed apparatus. Three-phase equilibrium phase compositions and phase density data have been reported for two different systems. One is reported as calibration data, and it compares well with the literature values. On the basis of this, we conclude that our data are of enough engineering accuracy. The second system analyzed is a quaternary from which no data have been previously published. The importance of having at least four components in the mixture is that one can estimate the experimental uncertainties in the experiments.

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