Improved apparatus and procedures for the measurement of solubility of rapidly equilibrating solid–liquid systems to 90 °C

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An improved apparatus for measuring solubilities of solid–liquid systems at temperatures to 90 °C is described. The apparatus has a high capacity (up to 56 samples) and a long term temperature stability of ±3 mK. The design allows the saturated solution to be multiply sampled and microfiltered at the equilibration temperature, making it particularly suited to rapidly equilibrating systems. The reliability of the apparatus and sampling procedures were tested by measuring the solubilities of NaCl, Na2SO4, and Na2CO3 in water. The data obtained showed a routine precision of ±0.05% relative and agreed to within ±0.1% of recommended International Union of Pure and Applied Chemistry values.

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I. INTRODUCTION

The solubilities of solid compounds in liquids are of major technological and scientific importance. Solvents furnish the medium in which most chemical reactions take place; differential solubility relations form the basis of many methods for the isolation, purification, and determination of substances; and solid solubilities underpin many quantitative and qualitative analyses.

Methods for determining the solubilities of solids in liquids vary in accuracy and convenience and in the types of systems to which they are best suited. Solubility determinations for solid–liquid systems have commonly been performed by introducing excess solid solute into a liquid solvent in a scalable container, agitating at constant temperature until equilibrium is reached and then sampling for analysis. Solubilities determined in this way typically have an accuracy of 1% to 10%, depending on the analytical procedure performed on the saturated solution. More accurate solubility measurements require more elaborate procedures. This is especially true for rapidly reequilibrating systems where sampling errors may become significant.

Ideally, an apparatus for the accurate determination of the solubility of a solid in a liquid should have the following features:

(a) The thermal environment should be accurately controlled, as temperature can significantly influence solubility. More importantly, equilibration typically requires hours or days for rapidly equilibrating systems and weeks, months, or even years for systems with slow kinetics.

(b) There should be intimate contact between the solid and liquid phases through constant, slow, and smooth mixing. Vigorous mixing during equilibration can lead to the physical degradation (attrition) of the solid; the solubility is altered if the solid particle size becomes too small or the solid surfaces are under stress.

(c) The apparatus should have a high sample capacity and allow uninterrupted equilibration and sampling, since reliable solubility determinations are in general time consuming and labor intensive.

(d) It should be possible to sample or analyze the saturated solution at the equilibration temperature.

The last point is of critical importance for the accurate measurement of solubilities in rapidly equilibrating systems but is commonly overlooked. Removal of the saturated solution from the thermostated environment during sampling may cause serious errors, especially for determinations at temperatures that differ significantly from ambient. While some designs avoid sampling errors by in situ analysis, they are either not generally applicable or are limited to one-at-a-time measurements. In most solubility determinations, analysis is performed ex situ and sampling errors are ignored or, at best, minimized by controlling the experimental protocol. Such approaches inevitably result in unknown and often unsuspected errors.

Campbell addressed this problem by developing an apparatus whereby solute and solvent are placed in a chamber which is rotated in a thermostated bath until equilibrium is reached. The chamber is then inverted, allowing the saturated solution to filter through a glass wool tube to a receiving chamber. Although this apparatus could be modified to incorporate modern microfiltration, it is not readily adaptable for multiple measurements.

A solubility apparatus which allows a large number of samples to be equilibrated simultaneously has been described by Wesolowski and has been used to measure gibbsite [Al(OH)3] solubilities from 5 to 80 °C. The unit consists of a 45 gal (170 L) thermostated bath, in which is very slowly rotated a rack of disposable plastic syringes containing the solid–liquid mixture. After equilibration, syringes are removed from the thermostated environment for sampling. In this instance the sampling errors are small because gibbsite requires very long periods (months, years) to reach solubility equilibrium.

The equilibrium position is therefore unlikely to be significantly disturbed during the approximately 5 min...
in which the solution is being filtered outside the thermostatic environment.

The present article describes a high-precision solubility apparatus constructed of high quality materials that is loosely based on Wesolowski’s design but incorporates features (a) to (d) above. As built, the apparatus can accommodate up to 56 samples in a bath of 110 l and operates in the temperature range 0 to 90 °C with a long term temperature stability of better than ±3 mK. With appropriate size or materials changes the design is readily adaptable to hold more samples or cover a wider temperature range. Most importantly, the system features a sampling device incorporated within the thermostated environment which allows the saturated solution to be efficiently sampled and microfiltered at the measurement temperature. Modern filtration, along with a more compact bath size (less dangerous at higher temperatures) makes the present apparatus a significant improvement on the Wesolowski design.

The operation of the apparatus and sampling procedures have been tested by measuring the solubility of NaCl, Na2SO4, and Na2CO3 in water at 25 and 65 °C. These salts have been tested by measuring the solubility of NaCl, the Wesolowski design.

II. THE APPARATUS

Solute and liquids for equilibration are contained in presterilized, disposable polypropylene leuer-lock syringe bodies (50 ml, Aldrich Australia). These containers were chosen as they were found to retain their structural integrity up to 90 °C as well as being chemically inert towards most aggressive solutions. Experiments indicated that the plungers supplied with the syringes did not provide a sufficiently tight seal so special pistons (16 mm deep) were machined from polypropylene to the inside diameter of the syringe (30.5 mm) and fitted with a recessed Teflon O-ring. This seal was tested to 90 °C for solution escaping past the piston in both directions. Syringe caps could be machined but a cheaper alternative was to use polypropylene syringe filters (Aldrich) that have had their outlet heat sealed. These filters are designed to screw directly onto the tip of the syringe and provide a reliable seal to 90 °C.

The heart of the apparatus is the cylindrical carousel which houses the sample syringes (Fig. 1). This carousel was formed from seven 40-mm-thick, 900-mm-diam disks made from Delrin (a high density acetyl thermoplastic) fixed to a stainless steel (ss) shaft. Each disk has eight equally spaced protrusions, also made from Delrin, screwed ss to its circumference. These protrusions were machined to fit the inside diameter of the syringe bodies to hold them in place while the carousel rotates. The apparatus has a sample capacity of 56 (seven disks by eight protrusions per disk) but can easily be increased. Narrow slots are cut vertically into the protrusions to allow the escape of bath fluid when the syringes are mounted on them.

The carousel is driven, via two ss toothed wheels and an all ss chain, by a small stepper motor located outside the bath. The stepper motor provides low revolution rates without an elaborate gearing system with no visible jerkiness. A rotation rate of approximately one revolution per 10 min was found to maintain good solid–liquid contact without significant attrition, but can be varied over a wide range.

As it is desirable to be able to view the syringes during operation, the tank (dimensions ~500×500×500 mm, i.e., capacity of ~110 l) was constructed from high density 12 mm toughened glass. A temperature resistant (up to 200 °C) industrial grade silicon sealant (Dow Corning) was used to glue the faces together. For added safety, the exterior of the tank was reinforced with a ss frame, and to reduce evaporative and thermal losses the tank was fitted with a hinged ss lid. High density polycarbonate (e.g., Lexan), which is readily transparent and is rated for use at temperatures up to 130 °C, was originally considered, however glass was ultimately preferred as the material of construction as it is cheaper, more easily fabricated, and less prone to stress cracking at higher temperatures.

To avoid problems associated with differential expansion rates all internal bath components were supported on a ss frame suspended from the top of the tank (Fig. 2). For ease of maintenance, ss supports on the base of the frame allow it and its attachments to stand freely when removed from the bath.

Although the present apparatus has been designed to operate only up to 90 °C it is readily adapted to higher temperatures, e.g., by substituting welded ss for the glass tank, glass syringes for polypropylene, etc. Similarly, the design can be readily adapted to larger or smaller numbers of samples, sample sizes, and so on.

III. EXPERIMENT

A. Temperature control

Since the maintenance of constant temperature is critical for accurate solubility determinations, a thermostatic environment of high stability is required. This has been achieved...
in a manner similar to that employed previously for our elevated temperature isopiestic system. The bath is heated by a ss-encased electrical element (~1 kW) connected to a proportional integral differential (PID) controller of in-house construction. The temperature sensor is a four wire, platinum film resistor (~1 kΩ, Degussa model GR 2141) located towards the end of a thin ss sheath placed centrally inside and near to the bottom of the heating coil (Fig. 2). A ss cooling coil located close to the heating element contains circulating thermostated (~±0.1 °C) liquid maintained approximately 3 °C below the bath temperature. This provides a constant heat sink which minimizes ambient temperature effects. No special precautions were taken to shield the bath from variations (~±6 °C) in ambient conditions, except that 15-mm-thick polystyrene was placed around three sides of the bath, leaving the front face clear for viewing. A fan-cooled electric motor (suitable for continuous operation) is mounted on top of a platform in the rear corner of the bath. This motor drives a shaft which has an end-mounted propeller (50 mm). The propeller shape and pitch were designed to provide a vigorous and pervasive flow downwards over the heating and cooling coils and around the bath with moderate turbulence such that sampling may be executed with minimal splashing (see Sec. III B 2).

Typical temperature performance data at 25 °C (Fig. 3) show that the temperature stability is excellent. Maximum variation in temperature over four days was ±8 mK, with a maximum daily variation of ±6 mK. More importantly from the viewpoint of solubility equilibration, the daily average bath temperature drifted by only ±2 mK over the four days. Longer term measurements suggest that drifts of less than ±3 mK occur over months once all components have “aged.” The source of the diurnal variation in Fig. 3 is unknown, but is believed to be electrical as the temperature runs counter to ambient values and is independent of the bath temperature. Similar but smaller effects have been observed in our somewhat more closely controlled isopiestic baths. Temperature changes were monitored by a thermistor calibrated against a quartz-crystal thermometer (Hewlett Packard Model 2804A), which was itself regularly calibrated in a triple-point apparatus as previously described.

B. Solubility measurement

The procedure for measuring the solubility of rapidly equilibrating solid–liquid systems with the present apparatus involved the following steps.

1. Charging the syringes and equilibration

(a) Approximately 90%-saturated solutions of the salts in water were prepared;
(b) sufficient solid was placed into an inverted, capped, syringe body such that excess solid would remain after saturation;
(c) the polypropylene piston was fitted to the bottom of the syringe, ensuring no solid was trapped between the side of the piston and the syringe body;
(d) the syringe was then inverted, the cap removed and the syringe filled through its outlet with the 90%-saturated solution, ensuring that all air was expelled (no vapor space).

The filled syringe was then recapped and fitted on the carousel in the bath. If less than the maximum number of syringes is used the carousel was balanced, with, for example, syringes containing bath fluid.

Equilibration times vary considerably between systems. The only reliable way of establishing whether equilibrium has been attained is to conduct periodic sampling and analysis. The present apparatus is ideally suited to this purpose.

2. Sampling procedure

The sampling device for the present apparatus is illustrated in Fig. 4. The syringe to be sampled (the “sampling syringe”) is removed from the carousel after it has stopped in the upright position and then placed in the syringe holder. The holder is designed so that the flange at the base of the sampling syringe locks firmly into a recess when twisted 90°.
This operation is performed with the sampling syringe completely submerged and takes approximately 1–2 s. At high temperatures an insulating waterproof glove (Extech ‘‘Cryo-Glove’’) is required. The sampling syringe is left in the sample holder for a period of 5–10 min to settle any solids which may have been disturbed. At this time, rotation of the carousel can be recommenced to continue the equilibration of other samples if desired.

The sampling device handle is then raised and locked into place, which brings the tip of the sampling syringe just above the level of the bath fluid. The sampling syringe cap is then removed, and a syringe filter (45 μm pore size) attached. Note that minimal turbulence in the bath is critical at this stage to ensure no splashing of bath fluid into the sampling syringe when it is uncapped. If necessary the bath stirrer can be turned off and the bath stirrer cap is then left for an appropriate period (5–10 min) for thermal equilibration of the filter and receiving syringe.

An aliquot of the saturated solution is then taken by rotating the handle of the sampling device driving syringe. This forces bath fluid via a polytetrafluoroethylene (PTFE) tube into the base of the sampling syringe, forcing its piston upwards. This pushes the saturated solution through the microfilter into the empty receiving syringe (this is the state of the device as represented in Fig. 4). A ss recess located on the top of the bath accommodates the travel of the receiving syringe plunger, which allows the sampling process to be conducted with the bath lid closed to ensure minimal heat loss. The receiving syringe can then be removed from the bath for subsequent analysis, and the sampling syringe returned to the carousel for further equilibration and sampling if desired. The system is thus ideal for multiple sampling over time with the number of possible sampling operations limited only by the sizes of the syringes and the samples. Note that at no point is the sampling syringe ever removed from the thermostatic environment, ensuring the saturated solution exhibits no significant shift from equilibrium brought about by a change in temperature.

IV. RESULTS

A series of experiments was undertaken at 25 and 65 °C using NaCl, Na₂SO₄, and Na₂CO₃ in water to determine the achievable precision in the solubility measurement. For the measurements at 25 °C, the densities of the saturated solutions were determined using a vibrating tube digital densitometer (Anton Paar, model O2D) thermostated at 25.0 ± 0.01 °C, calibrated with air and water. At 65 °C, densities were taken from the literature. The solid phases were analyzed by x-ray diffractometry (Philips model PW 1049/10 goniometer and a Difftech processing unit) using Co Kα radiation. The solubility measurements as a function of time indicated that equilibrium solubility was reached for all three salts in less than three days.

The results from these experiments are presented in Table I and reveal a routine precision of ±0.05% relative, and where comparison is possible, excellent agreement (typically better than ±0.1%) with the critically assessed solubility values recommended by the International Union of Pure and Applied Chemistry (IUPAC).12

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### TABLE I. Solubility data for NaCl, Na₂SO₄, and Na₂CO₃ in water (numbers in parentheses refer to the standard deviation in the last decimal place quoted).

<table>
<thead>
<tr>
<th>T °C</th>
<th>Solute</th>
<th>Solubility (g/100 g sat. soln.)</th>
<th>Density sat. soln.</th>
<th>Solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Present results (SD)</td>
<td>Literature (Refs. 9, 11, 12)</td>
<td>(g/cm³)⁸</td>
</tr>
<tr>
<td>25.0</td>
<td>NaCl</td>
<td>26.501 (5)</td>
<td>26.46</td>
<td>1.198045</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>21.775 (7)</td>
<td>21.81</td>
<td>1.206614</td>
</tr>
<tr>
<td></td>
<td>Na₂CO₃</td>
<td>22.594 (8)</td>
<td>22.58</td>
<td>1.241707</td>
</tr>
<tr>
<td>65.0</td>
<td>NaCl</td>
<td>27.105 (6)</td>
<td>27.14</td>
<td>1.1730</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>30.916 (8)</td>
<td>30.98</td>
<td>1.2852</td>
</tr>
<tr>
<td></td>
<td>Na₂CO₃</td>
<td>31.413 (9)</td>
<td>31.45</td>
<td>1.3186</td>
</tr>
</tbody>
</table>

⁸Present work at 25 °C; data at 65 °C from Refs. 13 and 14.
invaluable advice and construction of the apparatus, J. Snowball of the Murdoch University Electronics Workshop for the construction of the PID thermostat controller, R. Wigmore, Reynolds Australia, for advice on ss chains, J. D. Lathwell for drawing of the figures, and Dr. P. Sipos for helpful comments.