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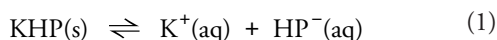
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Equilibrium, Gibbs free energy, enthalpy, entropy, and relationships among them are important thermodynamic concepts in the general chemistry curriculum. Student understanding of these concepts can be enhanced by experiments in which the solubility and solubility product (K_{sp}) are determined as a function of temperature. Experiments involving the determination of solubility and solubility product constant are commonplace in general chemistry labs (1–6). For example, the solubility product of potassium hydrogen tartrate has been determined via titration with sodium hydroxide (1) and the solubility product of Ag_2CrO_4 has been determined by measuring the absorbance of CrO_4^{2-} at 375 nm (3). In the present experiment, students determine the solubility products of potassium hydrogen phthalate (KHP) using flame emission for the determination of potassium in the temperature range 0–65 °C. The students also determine K_{sp} in 0.50 M KCl by titrating HP^- with NaOH(aq) . The value of K_{sp} is shown to be constant since the same numerical value is obtained with and without KCl.

The applicable equations are



$$K_{sp} = [\text{K}^+][\text{HP}^-] \quad (2)$$

$$\Delta_{\text{soln}}G^\circ = -RT\ln(K_{sp}) = \Delta_{\text{soln}}H^\circ - T\Delta_{\text{soln}}S^\circ \quad (3)$$

$$\ln(K_{sp}) = -\frac{\Delta_{\text{soln}}H^\circ}{RT} + \frac{\Delta_{\text{soln}}S^\circ}{R} \quad (4)$$

where $\Delta_{\text{soln}}G^\circ$ is the Gibbs free energy of solution, $\Delta_{\text{soln}}H^\circ$ is the standard molar enthalpy of solution, $\Delta_{\text{soln}}S^\circ$ is the standard molar entropy of solution, T is the temperature, and R is the gas constant. With K_{sp} much greater than the acid dissociation constant ($K_a = 3.9 \times 10^{-6}$), less than 1% HP^- acid dissociation occurs and therefore is ignored. Solubility, K_{sp} , and $\Delta_{\text{soln}}G^\circ$ vary with temperature; however, as the temperature change is small in this experiment ($\Delta T < 65 \text{ K}$), $\Delta_{\text{soln}}H^\circ$ and $\Delta_{\text{soln}}S^\circ$ can be regarded as constant. If the potassium concentration is determined by flame emission analysis, K_{sp} can be calculated using eq 2 since the potassium concentration is equal to the hydrogen phthalate concentration. The Gibbs free energy of solution ($\Delta_{\text{soln}}G^\circ$) is calculated using eq 3. Equation 4 indicates that if K_{sp} is determined as a function

of temperature and if $\Delta_{\text{soln}}H^\circ$ and $\Delta_{\text{soln}}S^\circ$ are constant, a plot of $\ln(K_{sp})$ versus $1/T$ will be linear and the slope will equal $-\Delta_{\text{soln}}H^\circ/R$ and the y intercept will equal $\Delta_{\text{soln}}S^\circ/R$.

It is well known that students in general chemistry do not adequately prepare solutions unless they are given many opportunities to make the solutions on their own (7–9). In this experiment students do the calculations and devise a procedure for the preparation of the KHP concentration standards in a prelab exercise.

Experimental

Materials and Equipment

- Temperature baths
- Natural gas, single-channel flame photometer (one per 24 students, Cole-Parmer)
- 100 μL –1000 μL autopipets
- Volumetric glassware
- Test tubes (>10 mL)
- KHP(s)
- KCl(s)
- 0.10 M NaOH (standardized)
- Gatorade
- Phenolphthalein indicator solution

Procedure

1. KHP standard solutions: Prepare 50 mL of each of the following KHP standard solutions: $7.5 \times 10^{-5} \text{ M}$, $15.0 \times 10^{-5} \text{ M}$, $22.5 \times 10^{-5} \text{ M}$, $30.0 \times 10^{-5} \text{ M}$, and $37.5 \times 10^{-5} \text{ M}$.
2. Dilute Gatorade by a factor of 25.
3. KHP saturated solutions: Prepare six saturated KHP solutions. Place the solutions into the temperature baths. After temperature equilibration, remove 1 mL of clear solution from each KHP saturated solution and dilute by a factor of 2,500.
4. KHP saturated solution with 0.50 M KCl: Remove 1 mL of clear solution from the solution and dilute by a factor of 2,500.
5. Adjust the sensitivity on the flame photometer so that the $3.75 \times 10^{-4} \text{ K}^+$ standard reads 375 emission units.
6. Measure and record the K emission intensity of the standard solutions, the diluted saturated KHP solutions, and the diluted Gatorade.
7. Titrate 4 mL of the saturated KHP solution with 0.50 M KCl with 0.10 M NaOH (standardized) to a phenolphthalein indicator endpoint to determine the HP^- concentration. Perform this titration a minimum of three times.

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Table 1. Flame Emission Data

Standards	[K ⁺]/(10 ⁻⁵ M)	Intensity
1	7.50	81
2	15.0	158
3	22.5	228
4	30.0	303
5	37.5	375
Blank	0	0
KHP Samples	T/°C	Intensity
Ice Bath	3.0	122
Room Temp	22.4	192
Temperature Bath 1	33.8	238
Temperature Bath 2	44.9	288
Temperature Bath 3	54.8	353
Temperature Bath 4	64.2	422
Room Temp, 0.50 M KCl	22.4	271
Gatorade	Dilution Factor	Intensity
Gatorade	25	129

Hazards

Students are advised to avoid any physical contact with KHP and NaOH. NaOH is caustic.

Results and Discussions

The emission data indicated in Table 1 were obtained by a randomly selected student (RSS). From their emission data, students plot graphs and perform calculations using the Excel spreadsheet template provided. At the 95% confidence level and based on RSS data, the calibration equation from the graph of intensity versus the K⁺ concentration (mol/L) is

$$I = (99.4 \pm 3.1)10^4 \frac{\text{L}}{\text{mol}} [\text{K}^+] + 4.3 \pm 7.0$$

$$R^2 = 0.9995 \quad (5)$$

Having determined the calibration equation (eq 5), students determine the concentrations of the K⁺ in the saturated solutions. For saturated solutions without KCl, the K⁺ concentration and the HP⁻ concentration are equal. The solubility product, $\Delta_{\text{soln}} G^\circ$, $1/T$, and $\ln(K_{\text{sp}})$ are calculated. The values are shown in Table 2 based on flame emission data in Table 1. A plot of $\ln(K_{\text{sp}})$ versus $1/T$, in Kelvin, at the 95% confidence level using the data in Table 2 can be described by the equation

$$\ln(K_{\text{sp}}) = -\frac{(3.82 \pm 0.16) \text{ K}}{T} + 11.38 \pm 0.53$$

$$R^2 = 0.999 \quad (6)$$

Table 2. Calculated Thermodynamic Parameters from the Experimental Data

T/°C	[K ⁺]/(mol/L)	K _{sp}	$\Delta_{\text{soln}} G^\circ$ (J/mol)	(1/T)/(K ⁻¹)	ln(K _{sp})
3.0	0.296	0.087	5594	0.00362	-2.437
22.4	0.472	0.222	3703	0.00337	-1.503
33.8	0.587	0.345	2716	0.00326	-1.064
44.9	0.713	0.508	1789	0.00314	-0.677
54.8	0.876	0.768	720	0.00305	-0.264
64.2	1.050	1.102	-272	0.00296	0.097

Based on the data presented herein (RSS), the calculated values of the enthalpy of solution and the entropy of solution are 31.76 ± 0.50 kJ/mol and 94.7 ± 1.7 J/(K mol), respectively. Based on class data (48 students), the enthalpy is 32.1 ± 5.9 kJ/mol and the entropy of solution is 89 ± 14 J/(K mol).

From titration with NaOH, the HP⁻ concentration in the saturated KHP solution with 0.50 M KCl at room temperature was found to be 0.308 M and the K⁺ concentration was found to be 0.670 M yielding a K_{sp} value of 0.21. This value is comparable to the value of 0.22 determined with KHP alone at room temperature (see Table 2). About 90% of the students obtain K_{sp} values within 10% of each other. By determining K⁺ and HP⁻ concentration in a saturated solution of KHP with 0.50 M KCl and showing that the K_{sp} is equal to that obtained without KCl in the solution, the constancy of K_{sp} is comprehensively demonstrated. The K_{sp} values with and without KCl are the same in this case because the K_{sp} of KHP is insensitive to ionic strength. For example, the potassium emission intensities obtained for saturated solutions with and without 0.5 M NaCl (aq) are the same.

Finally the students determined the K⁺ concentration in Gatorade. The students' value of 32 ± 3 mg K⁺/8 fl. oz. compared favorably with the 30 mg/8 fl. oz. labeling by the Coca-Cola Company.

Conclusions

The intention is that students learn the following about making solutions: (i) clean glassware is essential, (ii) volumetric glassware should be used, (iii) to make a dilute solution, it is best to first make a more concentrated solution (mass should exceed 100 mg) and dilute a portion to the target concentration, (iv) it is essential that all the weighed substance end up in the solution, (v) solute must fully dissolve, (vi) all solutions should be thoroughly mixed.

Students have little difficulty performing the experiment. Most students complete the experiment in less than two hours of a three-hour period. Most of the lab time is used to make the solutions, as it takes less than 4 minutes

to measure the intensities. The postlab report (see Supplemental Material^W) is challenging. More students seek help with this experiment than any other experiment in the course. The students are required to program their calculations in the Excel spreadsheet and we randomly require electronic files for verification.

Given the limited lab exposure we are able to provide in general chemistry, it is essential that, where possible and appropriate, students perform experiments that combine multiple concepts. This experiment is a combination of three experiments all of which we have performed as individual experiments in the past: (i) flame emission analysis, (ii) K_{sp} and thermodynamics, and (iii) solution preparation.

^WSupplemental Material

Student handouts, notes for the instructor, and an example of a postlab report are available in this issue of *JCE Online*.

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