

Thermodynamics and Spontaneity: Enthalpy, Entropy, and Free Energy

Goal and Overview

The spontaneous dissolution (dissociation) of two salts in water will be investigated. Each will be viewed as the system in a thermodynamic “universe”. The temperature change in the surroundings, which reflect the exothermicity or endothermicity nature of the salt’s dissociation, will be used to calculate an estimate of enthalpy change associated with the dissolution process. To explain and analyze the spontaneous nature of the dissociation process, which implies a negative overall (Gibbs) free energy change, the change entropy will be employed. The assumptions made regarding the nature of the system and surroundings will be assessed in terms of the error and uncertainty that they introduce to the observed results.

Objectives and Science Skills

Set up an experimental thermodynamic “universe”; identify and explain the system and surroundings.

Describe heat transfer processes quantitatively and qualitatively, including those related to heat capacity and enthalpy of reaction.

Use standard molar enthalpies, entropies, and free energies to calculate theoretical values for a dissociation reaction and use those values to assess experimental results.

Quantitatively and qualitatively compare experimental results with theoretical values.

Identify and discuss factors or effects that may contribute to deviations between theoretical and experimental results and formulate optimization strategies.

Suggested Review and External Reading

Reference material and textbook sections on thermochemistry, calorimetry, heat capacity, enthalpy, entropy, free energy, and spontaneity

Introduction

In thermodynamics, the spontaneity or favorability of a given chemical process or reaction occurring at constant pressure and temperature can be assessed based on its associated (Gibbs) free energy change, ΔG (under standard conditions, ΔG°). ΔG can be calculated using the Gibbs-Helmholtz equation: $\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy change and ΔS is the entropy change. ΔG for a process or reaction that proceeds spontaneously under a given set of conditions is negative (free energy decreases).

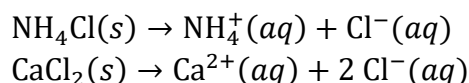
Enthalpy, Entropy, and Free Energy Changes

	ΔH	ΔS	ΔG
1.	negative	positive	always negative (always spontaneous)
2.	positive	positive	negative at higher T; positive at lower T*; <i>entropy-driven</i>
3.	negative	negative	positive at higher T; negative at higher T*; <i>enthalpy-driven</i>
4.	positive	negative	always positive (nonspontaneous)

*Crossover T positive to negative: $\Delta G = 0 = \Delta H - T\Delta S$ so $T_{\text{crossover}} = \frac{\Delta H}{\Delta S}$

$\Delta H^\circ > 0$	System releases heat energy (T_{surr} increases; $\Delta T_{\text{observed}} > 0$)
$\Delta H^\circ < 0$	System absorbs heat energy (T_{surr} decreases; $\Delta T_{\text{observed}} < 0$)
$\Delta S^\circ > 0$	System "disorder"/"randomness"/"arrangements" increase
$\Delta S^\circ < 0$	System "disorder"/"randomness"/"arrangements" decrease

In this experiment, the dissolution (or dissociation) of two salts in water will be studied and analyzed in terms of thermodynamics parameters. The dissociation processes will be investigated at a temperature and pressure relatively close to standard conditions, such that $\Delta H \approx \Delta H^\circ$ and $\Delta S \approx \Delta S^\circ$.



Each dissociation process will be considered the system in a thermodynamic "universe"; the surroundings will be the solution in which the dissociation occurs. The "universe" will be considered closed and isolated, meaning all heat transfers are assumed to take place between the dissociating salt and the solution in which the dissociation occurs.

$\Delta H^\circ_{\text{diss}}$, $\Delta S^\circ_{\text{diss}}$, and $\Delta G^\circ_{\text{diss}}$ will be used refer to the thermodynamic changes associated with the system.

An experimental value for $\Delta H^\circ_{\text{diss}}$ will be calculated from data: $\Delta H_{\text{sys}} = \Delta H^\circ_{\text{diss}} \approx -\Delta H_{\text{surr}}$.

$$\Delta h^\circ_{\text{diss}} \text{ in } \frac{\text{J}}{\text{g salt}} = -\Delta h_{\text{surr}} = -\frac{m_{\text{solution}} c_{\text{solution}} \Delta T_{\text{solution}}}{\text{mass of salt used}}$$

m_{solution} = mass of the solution (mass of salt + mass of water) in g

c_{solution} = specific heat capacity of the solution in J/g · °C

$$\Delta H^\circ_{\text{diss}} \text{ in } \frac{\text{kJ}}{\text{mol salt}} = m \Delta h^\circ_{\text{diss}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \text{molar mass of salt} = n \Delta H^\circ_{\text{diss}}$$

m = mass of salt in g; $\Delta h^\circ_{\text{diss}}$ = enthalpy change in J/g

n = moles of salt in mol; $\Delta H^\circ_{\text{diss}}$ = enthalpy change in kJ/mol

A theoretical $\Delta H^\circ_{\text{diss}}$ value will be calculated from enthalpies of formation data.

You will make qualitative predictions and assessments regarding ΔS°_{diss} and calculate a theoretical value from entropies of formation data.

You will compare experimental and theoretical values and suggest possible reasons for differences in their values. You will also analyze and explain the thermodynamics and spontaneity of the dissociation of each salt in water in terms of ΔH°_{diss} , ΔS°_{diss} , and ΔG°_{diss} .

Equipment List

Labeled 150-mL beaker, thermometer

Weigh boats, scoopulas

Pan and analytical balances

Procedure

For NH_4Cl and CaCl_2 , please use the analytical balance (four decimal places). All other masses should be measured on the pan balance (two decimal places). The balances must be kept clean.

Temperatures should be recorded to one decimal place.

Assume the specific heat capacities of the solutions are equal to that of pure liquid water ($c_w = 4.184 \text{ J/g} \cdot ^\circ\text{C}$).

Please wait to do any calculations until after you have finished the experimental procedure and have cleaned up your lab bench.

Thermodynamic formation information (literature values under standard conditions):

Species	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S_f° (J/K · mol)
$\text{NH}_4\text{Cl}(s)$	-314	-203	96
$\text{NH}_4^+(aq)$	-132	-79	113
$\text{Cl}^-(aq)$	-167	-131	57
$\text{CaCl}_2(s)$	-796	-748	105
$\text{Ca}^{2+}(aq)$	-543	-553	-55

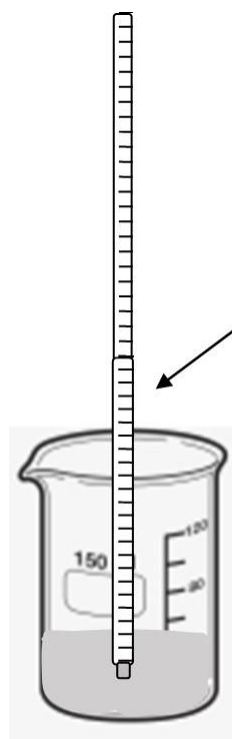
Caution

Please follow lab safety rules and instructions, including wearing your goggles and appropriate attire, washing your hands frequently, and practicing good housekeeping.

NH_4Cl and CaCl_2 are possible eye irritants, and ingestion or inhalation can cause internal irritation. Please do not heat the solid salts or their solutions.

Skin irritation is possible in cases of prolonged exposure to solutions, particularly those that are very concentrated.

In the case of direct skin contact, wash the affected area, flush with water, and tell your TA. Fill out any required paperwork.



Caution

Hold the thermometer when it is in the beaker. Do not let it rest against the side of the beaker or the beaker may tip over.

You can very gently agitate or swirl the beaker to aid the dissolving of the salt. Take care not to bump or break the thermometer, and be careful not to spill any solution.

Part 1. ΔH for NH_4Cl dissolution

1. On the analytical balance, carefully mass out ~ 5.3490 g NH_4Cl in a weigh boat. Make sure that you have tared the balance to zero after placing the weigh boat on the pan prior to massing any NH_4Cl solid. Check that the balance is clean.
2. Record the mass of a labeled 150-mL beaker on the pan balance to two decimal places.
3. Add ~ 50 mL of room temperature deionized water to the beaker and record the new mass (beaker + water) on the pan balance to two decimal places. Calculate the mass of water in the beaker.

$$\# \text{ g H}_2\text{O}_{\text{part 1}}^* = (\text{mass of beaker} + \text{H}_2\text{O})_{\text{part 1}} - (\text{mass of beaker})_{\text{part 1}}$$

4. Record the temperature of the water in °C to one decimal place (room temperature). Be careful with the thermometer. Make sure to hold it while it is in the beaker.
5. Add the massed NH_4Cl and monitor the temperature of the solution as the salt dissolves. Record the lowest temperature that the solution reaches to one decimal place. The solid NH_4Cl should have completely dissolved.
6. Carefully pour the solution into the liquid waste container and wash all equipment well.

Part 2. ΔH for CaCl_2 dissolution

7. On the analytical balance, carefully mass out ~ 11.0765 g CaCl_2 in a weigh boat. Make sure that you have tared the balance to zero after placing the weigh boat on the pan prior to massing any CaCl_2 solid. Check that the balance is clean.
8. Record the mass of a labeled 150-mL beaker on the pan balance to two decimal places.
9. Add ~ 50 mL of room temperature deionized water to the beaker and record the new mass (beaker + water) on the pan balance to two decimal places. Calculate the mass of water in the beaker.

$$\# \text{ g H}_2\text{O}_{\text{part 2}}^* = (\text{mass of beaker} + \text{H}_2\text{O})_{\text{part 2}} - (\text{mass of beaker})_{\text{part 2}}$$

10. Record the temperature of the water in °C to one decimal place (room temperature). Be careful with the thermometer. Make sure to hold it while it is in the beaker.
11. Add the massed CaCl_2 and monitor the temperature of the solution as the salt dissolves. Record the lowest temperature that the solution reaches to one decimal place. The solid CaCl_2 should have completely dissolved.
12. Carefully pour the solution into the liquid waste container and wash all equipment well.

Follow your TA's instructions regarding waste disposal.

All equipment and glassware should be washed thoroughly using 1) soap and tap water, 2) tap water rinses, and 3) a final rinse with deionized water.

Calculations

For each salt:

13. Calculate the moles of salt used (NH_4Cl in part 1 and CaCl_2 in part 2).

$$n_{\text{NH}_4\text{Cl}} = m_{\text{NH}_4\text{Cl used (g)}} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.492 \text{ g NH}_4\text{Cl}}$$
$$n_{\text{CaCl}_2} = m_{\text{CaCl}_2 \text{ used (g)}} \times \frac{1 \text{ mol CaCl}_2}{110.984 \text{ g CaCl}_2}$$

13. Calculate the mass of the solution in grams.

$$m_{\text{NH}_4\text{Cl solution (g)}} = m_{\text{NH}_4\text{Cl used (g)}} + \# \text{ g H}_2\text{O}_{\text{part 1}}^*$$

$$m_{\text{CaCl}_2 \text{ solution (g)}} = m_{\text{CaCl}_2 \text{ used (g)}} + \# \text{ g H}_2\text{O}_{\text{part 2}}^*$$

$$*\# \text{ g H}_2\text{O}_{\text{part 1 or 2}} = (\text{mass of beaker} + \text{water}) - (\text{mass of beaker})$$

14. Calculate $\Delta h^\circ_{\text{diss}}$ in J/g salt.

$$\Delta h^\circ_{\text{diss}} = -\Delta h_{\text{surr}} = -(m_{\text{solution}} \times c_{\text{solution}} \times \Delta T)$$

Assume $c_{\text{solution}} \approx c_w = 4.184 \text{ J/g} \cdot ^\circ\text{C}$.

Temperatures should have one decimal place: $\Delta T(^{\circ}\text{C}) = T_{\text{final}} - T_{\text{initial}}$.

16. Calculate $\Delta H^\circ_{\text{diss}}$ in kJ/mol salt.

$$\Delta H^\circ_{\text{NH}_4\text{Cl diss}} = \Delta h^\circ_{\text{NH}_4\text{Cl diss}} \text{ in } \frac{\text{J}}{\text{g}} \times \frac{53.492 \text{ g NH}_4\text{Cl}}{1 \text{ mol NH}_4\text{Cl}} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta H^\circ_{\text{CaCl}_2 \text{ diss}} = \Delta h^\circ_{\text{CaCl}_2 \text{ diss}} \text{ in } \frac{\text{J}}{\text{g}} \times \frac{110.984 \text{ g CaCl}_2}{1 \text{ mol CaCl}_2} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

17. Do your observations suggest that the dissociation process is endo- or exothermic ($\Delta H^\circ_{\text{diss}} > 0$ or $\Delta H^\circ_{\text{diss}} < 0$)?

Use the given thermodynamic formation data to calculate $\Delta H^\circ_{\text{diss}}$.

$$\Delta H^\circ_{\text{diss}} = \Sigma \Delta H^\circ_{\text{f,products}} - \Sigma \Delta H^\circ_{\text{f,reactants}}$$

Is $\Delta H^\circ_{\text{diss}}$ positive or negative? How does the theoretical value compare to that obtained by experiment, particularly in terms of sign?

Calculate the percent difference in the experimental $\Delta H^\circ_{\text{diss}}$ relative to the theoretical value under standard conditions.

$$\% \text{ difference} = \left| \frac{\text{theoretical value} - \text{experimental value}}{\text{theoretical value}} \right| \times 100\%$$

Calculate the temperature change that you should have observed in the surroundings (use $\Delta H_{\text{diss}}^{\circ}$ to work backward to the theoretical ΔT).

$$\Delta T_{\text{theoretical, NH}_4\text{Cl}} (\text{°C}) = -1 \times \frac{(\text{mol}_{\text{NH}_4\text{Cl}} \times \Delta H_{\text{diss, theor}}^{\circ} \times 1000)}{(\text{mass}_{\text{solution}} \times c_{\text{water}})}$$

$$\Delta T_{\text{theoretical, CaCl}_2} (\text{°C}) = -1 \times \frac{(\text{mol}_{\text{CaCl}_2} \times \Delta H_{\text{diss, theor}}^{\circ} \times 1000)}{(\text{mass}_{\text{solution}} \times c_{\text{water}})}$$

18. Do you think entropy increases, decreases, or remains the same during the dissociation process ($\Delta S_{\text{diss}}^{\circ} > 0$ or $\Delta S_{\text{diss}}^{\circ} < 0$)?

Use the given thermodynamic formation data to calculate $\Delta S_{\text{diss}}^{\circ}$.

$$\Delta S_{\text{diss}}^{\circ} = \Sigma S_{\text{f, products}}^{\circ} - \Delta S_{\text{f, reactants}}^{\circ}$$

Is $\Delta S_{\text{diss}}^{\circ}$ positive or negative? Does the calculated theoretical value support your qualitative prediction?

19. Based on your experimental observations, do you think $\Delta G_{\text{diss}}^{\circ}$ is positive or negative?

Calculate $\Delta G_{\text{diss}}^{\circ}$ at 298 K using the Gibbs-Helmholtz equation:

$$\Delta G_{\text{diss}}^{\circ} = \Delta H_{\text{diss}}^{\circ} - T\Delta S_{\text{diss}}^{\circ}$$

Is $\Delta G_{\text{diss}}^{\circ}$ positive or negative? How does the theoretical value compare to what you observed experimentally, particularly in terms of sign?

20. Explain the spontaneity of the dissociation process in terms of $\Delta H_{\text{diss}}^{\circ}$; $\Delta S_{\text{diss}}^{\circ}$, and $\Delta G_{\text{diss}}^{\circ}$. How does $\Delta H_{\text{diss}}^{\circ}$ affect $\Delta G_{\text{diss}}^{\circ}$ (e.g., make it more positive or more negative)? How does $\Delta S_{\text{diss}}^{\circ}$ affect $\Delta G_{\text{diss}}^{\circ}$ (e.g., make it more positive or more negative)? Do both $\Delta H_{\text{diss}}^{\circ}$ and $\Delta S_{\text{diss}}^{\circ}$ support $\Delta G_{\text{diss}}^{\circ} < 0$? If not, which drives spontaneity under the experimental conditions?

Results / Sample Calculations

Experimental $\Delta h_{\text{diss}}^{\circ}$ and $\Delta H_{\text{diss}}^{\circ}$; theoretical $\Delta H_{\text{diss}}^{\circ}$; % difference; theoretical ΔT ; analysis
 Experimental $\Delta S_{\text{diss}}^{\circ}$ (qualitative predictions); theoretical $\Delta S_{\text{diss}}^{\circ}$; analysis

$\Delta G_{\text{diss}}^{\circ}$ and analysis

Complete the online inlab or write a lab report as directed by your TA.

Discussion Questions and Review Topics

What did you find and how did you do it?

What were the primary sources of error? How valid were any the assumptions made (*e.g.*, all of the heat transfers remained within the solution and its contents)?

How could the accuracy of the results be improved? What conclusions can you draw about the experimental method and your results?

How do theoretical values compare to experiment?

Why does a dissociation process happen spontaneously? Analyze the spontaneity of each dissociation in terms of $\Delta H_{\text{diss}}^{\circ}$; $\Delta S_{\text{diss}}^{\circ}$, and $\Delta G_{\text{diss}}^{\circ}$.