Thermodynamics for Dissolving an Ionic Salt (NaNO_{3(s)})

This worksheet is worth 20 pts. There is no pre-lab.

Submit the worksheet, calculations, and answers to lab questions with your lab group. For Part B, use <u>Appendix G</u>, along with the table on page 2 for $NaNO_{3(s)}$.

Purpose

- \circ In this experiment, you will measure the temperature change (ΔT) that occurs when NaNO_{3(S)} is dissolved in H₂O_(L).
- \circ You will use the resulting ΔT to determine the molar enthalpy of solution ($\Delta H_{sol'n}$, in kJ/mol).
- You will also calculate the enthalpy of solution using the standard molar enthalpies of formation (ΔH^{o}_{f}) in your text, and you will compare this value with your experimental result.
- You will also calculate the entropy (ΔS°) and Gibb's free energy of solution (ΔG°).
- The ΔG° value will be calculated two different ways: first using ΔH° and ΔS° , and then by using free energies of formation (ΔG°_{f}). The two calculations will then be compared with each other.
- Finally, you will draw overall conclusions about the thermodynamic spontaneity of chemical reactions.

Introduction

When an ionic solid is dissolved in water, the ionic bonds in the crystal will break, causing the compound to dissociate. The individual ions will form ion-dipole intermolecular bonds with the positive and negative dipoles of the water molecules. When chemical bonds are broken and formed, a chemical change occurs, and heat will be absorbed or released.

When this heat is measured at standard conditions (298 K and 1 atm), it is the standard molar enthalpy of solution ($\Delta H^{o}_{sol'n}$). A reaction that releases heat ($\Delta T > 0$ and $\Delta H < 0$) is exothermic, and a reaction that absorbs heat is endothermic ($\Delta T < 0$ and $\Delta H > 0$).

However, enthalpy alone does not determine whether a reaction is spontaneous, that is whether it is thermodynamically favored. The randomization of molecular energy (primarily kinetic energy) which creates disorder must also be taken into account. The change in the randomization of energy due to a reaction is measured as its entropy change (Δ S).

Both enthalpy and entropy are used together to create a measure of spontaneity, that is the change in Gibb's free energy ($\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$). Where $\Delta G < 0$, the reaction is spontaneous, or exergonic. Where $\Delta G > 0$, the reaction is non-spontaneous, or endergonic.

Substances

8.5 g NaNO₃ per group (~125 g per lab section) 100 ml DI H₂O per group (1.5 L per lab section)

Apparatus

Coffee Cups (2 per group) Coffee Cup Lids (1 per group) 100-ml graduated cylinder (1 per group) Digital Thermometer (1 per group) Stirrer (1 per group) Ring Stand with Clamp (1 per group) Split Stopper (1 per group)

Procedure

- 1. Construct a coffee cup calorimeter. Refer to Figure 5.12 in the Open Stax text. Instead of using a standard thermometer and clamp, place the digital thermometer's lead into the calorimeter through a small hole in the lid.
- 2. Add 100.0 ml of water to the calorimeter, and record the initial temperature to the nearest 0.1 $^{\circ}$ C.
- 3. Obtain 8.50 (+/- 0.05) g of NaNO_{3(S)} and record the mass obtained.
- 4. Pour the $NaNO_{3(S)}$ sample into the calorimeter, replace the lid, and stir gently. Continue to stir, while reading the temperature at 10 second intervals, until a minimum temperature is obtained.
- 5. Dispose of solution in sink and rinse the wetted coffee cup.
- 6. Complete the following calculations and questions, using your experimental values, <u>Appendix G</u>, and the table below.

ΔH^{o}_{f} (kJ/mol)	ΔG^{o}_{f} (kJ/mol)	S ^o (J/K·mol)
-467.9	-367.1	+116.5

Standard State Thermodynamic Data for NaNO_{3(s)}

Calculations and Questions

Part A:	Experimental Calorimetry of the Dissolution Reaction

- 1. Set up coffee cup calorimeter as in Figure <u>5.12</u>, and add 100.0 ml of DI water.
- 2. Record initial temperature $(T_i) =$ _____ (to nearest $0.1^{\circ} \text{ C})$
- 3. Add 8.50 (+/- 0.05) g NaNO₃ to calorimeter, cover and stir. The dissolution reaction occurs as follows: NaNO_{3(s)} \rightleftharpoons Na⁺¹_(aq) + NO₃⁻¹_(aq)
- 4. Show calculation of moles for NaNO₃ (F.W. = 85.0 g/mol)

Mol NaNO₃ =

5. Measure T at 10-second time intervals immediately after adding NaNO₃ and find $T_{minimum}$. (You can graph T versus time if extrapolation is necessary to find $T_{minimum}$.)

 $T_{\text{minimum}} =$ (to nearest 0.1°C)

- 6. Show the calculation for ΔT in ^oC as $T_{minimum} T_i$.
 - ΔT =
- 7. Show calculation for total $\Delta H = -(s)(m)(\Delta T)$ in Joules using the values for water as follows: specific heat: s = 4.184 J/gCmass: m = 100.0 g

ΔH = _____

8. Show conversion of ΔH value from #7 into kJ. Include the correct conversion factor.

 $\Delta H_{total} =$

9. Show calculation for molar ΔH° in kJ/mol for the dissolution reaction as $\frac{\Delta H_{total}}{\text{mol NaNO3}}$

experimental molar ΔH° in kJ/mol = _____

Part B: Standard Thermodynamic Quantities for the Dissolution Reaction

10. Show calculation for ΔH^{o} in kJ/mol for the reaction using the equation below, <u>Appendix G</u>, and the NaNO_{3(s)} table on page 2. $\Delta H^{o} = \Sigma n \Delta H^{o}_{f}(\text{prod}) - \Sigma m \Delta H^{o}_{f}(\text{react}) = [\Delta H^{o}_{f}(Na^{+1}_{(aq)}) + \Delta H^{o}_{f}(NO_{3}^{-1}_{(aq)})] - [\Delta H^{o}_{f}(NaNO_{3(s)})]$ Be sure to use values for the correct phases!

 ΔH° in kJ/mol = _____

What is the error % of the experimentally determined value for Δ H in #9?

Error % = $\frac{\Delta H_{actual}^{o} - \Delta H_{experimental}^{o}}{\Delta H_{actual}^{o}} \times 100\% =$

11. Show calculations for ΔS° and ΔG° as well, using Σ equations similar to that of ΔH° in #10. Include the conversion factor from J to kJ.

 ΔS° in J/(K·mol) = _____

 ΔS° in kJ/(K·mol) = _____

 ΔG° in kJ/mol = _____

12. Show calculation for $\Delta H^{\circ} - T\Delta S^{\circ}$ using #10 and #11 with T = 298 K.

 $\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} = _$

- Part C: Thermodynamic Lab Questions
- 13. Explain in terms of ΔH and ΔT whether this reaction was endothermic or exothermic.
- 14. Frequently, the experimental ΔH^{o} has a lower value than the calculated value. Explain why this difference happens when using a simple styrofoam calorimeter, and determine the direction of heat flow in this experiment.

15. Explain in terms of just the sign on ΔG° whether or not the reaction is spontaneous at standard state (298 K). Based on that, would you expect NaNO₃ to dissolve in water?

- 16. How do the values for ΔG° compare in #11 and #12? Are they nearly the same? Find the % difference using $(\#12 \#11)/(\#12) \times 100\%$.
- 17. Explain in terms of $\Delta G^{\circ} = \Delta H^{\circ} T\Delta S^{\circ}$ how the reaction this experiment can be <u>spontaneous</u> ($\Delta G^{\circ} < 0$) even though it is endothermic ($\Delta H^{\circ} > 0$). That is, what is needed for T and ΔS° in order for the reaction to be spontaneous?

18. At what temperatures is the reaction spontaneous? Use $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ to find the T range where $\Delta G^{\circ} < 0$ (or where $\Delta H^{\circ} - T\Delta S^{\circ} < 0$)