Investigation 4: Thermodynamics of Solution Reactions

Question: What factors influence the spontaneity of a complexation reaction?

Pre-lab required reading

Atkins & Jones (6th ed.): Sections 9.9 – 9.13

Primers:

- Spectrophotometry
- SpectraVis Plus spectrophotometer
- Volumetric glassware use – General
- Volumetric glassware use – volumetric flask
- Volumetric glassware use – volumetric pipet
- Coordination chemistry

Safety and Waste Disposal

- Eye protection should be worn at all times.
- Nickel salts and their solutions will irritate the eyes upon contact.
- Be careful handling ethylenediamine solutions. Ethylenediamine is caustic and its vapors are irritating to the skin, eyes, and respiratory system.
- Concentrated aqueous ammonia is very irritating to the skin, eyes and respiratory system. It should be handled in a hood.
- Dispose of all solutions in the appropriate waste container.

Background

A first approximation to the spontaneity of a reaction follows the Second Law of Thermodynamics – in an isolated system, spontaneous processes must increase in entropy. However, it has been shown that in non-isolated systems, the spontaneity depends on the change in Gibbs free energy (G_{rxn}^o). If the change in Gibbs free energy (ΔG_{rxn}^o) is negative, the process is spontaneous. The total free energy is a combination of the enthalpy and entropy changes in the system:

$$\Delta G_{rxn}^o = \Delta H_{rxn}^o - T\Delta S_{rxn}^o \qquad (1)$$

where T is the temperature of the system. Under standard conditions, it is possible to predict the spontaneity of a reaction using the standard enthalpies of formation (ΔH_f^o) and the standard molar entropies (S_m^o) or the standard Gibbs free energy of formation (ΔG_f^o) values for the reactants and products of the reaction. However, when standard conditions are not met, the reaction may not proceed as predicted by standard state values. Note that standard conditions are T = 298 K, P = 1 atm, and for aqueous reactions, c = 1 M.

In this lab, observation will be made on the reaction of aqueous nickel (II) coordination complexes. The color of the solution is caused by the complexation of the Ni^{2+} ion in solution. The nickel (II) ion is surrounded by water in the aqueous $NiSO_4$ solution, $Ni(H_2O)_6^{2+}$. When the second solution is added, the water molecules are replaced. For example,

$$[Ni(H_2O)_6]^{2+}\ (aq) + 6\ NH_3\ (aq) \rightarrow [Ni(NH_3)_6]^{2+}\ (aq) + 6\ H_2O\ (l)$$

The color of the solution indicates whether the reaction is spontaneous or not because it reflects what is happening to the nickel ion center of the complex. Ammonia and water are monodentate ligands and ethylenediamine is a bidentate ligand.

Procedure
Spontaneity at Different Concentrations

Part 1:

Collect 40 mL of 1 *M* $NiSO_4$ and 5 mL of the following two aqueous solutions: 5 *M* NH_3, and 1 *M* ethylenediamine ($NH_2CH_2CH_2NH_2$). For each solution, make a serial dilution using 2 50-mL volumetric flasks. Add 1 mL of the original solution to the first 50-mL flask. Fill the flask to the mark with DI water. Take 1 mL of the diluted solution and add it to the second 50-mL flask. Fill to the mark with DI water. Calculate the concentrations of the new solutions. In the end, there should be 9 different solutions. Fill a cuvette with the 1 *M* $NiSO_4$ (*aq*) solution and find λ_{max}. In a beaker, mix 5 mL of the 1 *M* $NiSO_4$ solution with 5 mL of the 5 *M* NH_3 (*aq*) solution. Record any observations. Add 1 mL of this mixture to a cuvette and determine λ_{max}. Repeat this procedure by mixing the 1 *M* $NiSO_4$ solution with the original ethylenediamine solution. Repeat this procedure using the diluted solutions. Make sure that you mix the first dilution of $NiSO_4$ (*aq*) with the first dilution of the other solutions and the second dilution of $NiSO_4$ (*aq*) with other second dilutions.

Part 2:

In three separate clean beakers, add 5 mL of the 1 *M* $NiSO_4$ solution, label beakers 1, 2, and 3. To the first beaker add 4 mL of the 1 *M* ethylenediamine solution. Record any observations and find λ_{max}. To the second beaker add 8 mL of the ethylenediamine solution. Record observations and find λ_{max}. To the third beaker add 12 mL of the ethylenediamine solution. Record observations and find λ_{max}.

Part 3:

In a new clean beaker, add 5 mL of the nickel sulfate solution. In a random order add one 5mL aliquot of the original ammonia and three 5mL aliquots of the original ethylenediamine solutions. Repeat the experiment using a different random order of additions. Note the final color of the solution in each case. Record any observations and find λ_{max}.

References

Atkins, P.; Jones, L. “Chemical Principles: The Quest for Insight”, 6th ed.; Freeman: New York. 2013.
Shakhashiri, B. Z.; Dirreen, G. E.; Juergens, F. *J. Chem. Ed*., 57, 12, 1980, pp. 900 – 901.