7.1 Endothermic reaction

Subjects: Thermodynamics – endothermic reactions, enthalpy, entropy, free energy

Description: An endothermic reaction involving the combination of two solids is demonstrated. The flask will rapidly become cold (45°C below room temperature) and frozen condensation will be visible on the surface of the flask. The flask can be placed on a block with a pool of water. The flask will freeze to the block.

Materials:
32 g Barium hydroxide ($Ba(OH)_2$)‡
11 g NH_4Cl (or 17 g NH_4NO_3 or 16 g NH_4SCN)‡
250 mL Erlenmeyer flask
Funnel
Small block of wood (optional)
Water in wash bottle (optional)
Thermometer (optional)

‡Barium hydroxide and ammonium chloride are located in the general chemical storage cabinets. Ammonium nitrate is located on the oxidizer shelf.

Procedure:
1. Using the funnel, place the solids in the flask and gently swirl the contents of the flask to mix.
2. A liquid slurry will form in the bottom of the flask.
3. Wet the small wood block with a few drops of water and set the reaction flask on it. The flask will freeze to the wood.

Alternatively, when the reaction is complete, pass the flask around the class.

Discussion:
The reaction for the above demonstration using ammonium chloride is given below:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2\ NH_4Cl(s) \rightarrow 2\ BaCl_2 \cdot 2H_2O(aq) + 2NH_3(aq) + 8\ H_2O(l)$$

For a reaction to be spontaneous at constant temperature and pressure, the change in free energy (ΔG) must be negative.

$$\Delta G = \Delta H - T\Delta S$$

In an endothermic reaction, the ΔH is positive corresponding to the absorbed heat. Thus this positive ΔH must be offset by a sufficient increase in entropy (ΔS). Two solids creating a new solid and an aqueous solution of ammonia represents a large increase in entropy.

The thermochemical date for Barium hydroxide, ammonium chloride, barium chloride, ammonia and water are given in the table below:

Substance	**ΔH°f (kJ/mol)**	**S°_{298}(J/mol·K)**	**ΔG°f (kJ/mol)**
$Ba(OH)_2 \cdot 8H_2O(s)$	-3342	427	-2793
$NH_4Cl(s)$	-341.4	94.6	-203
$BaCl_2 \cdot 2H_2O(s)$	-1460.1	203	-1296.5
$NH_3(aq)$	-80.29	111	-26.6
$H_2O(l)$	-285.83	75.291	-237.2

The enthalpy for the reaction is calculated using the following equation:
$\Delta_r H^\circ = \sum \Delta H^\circ_f$ (products) - $\sum \Delta H^\circ_f$(reactants)
$\Delta_r H^\circ$ = 63.5 kJ

The entropy for the reaction is calculated using the following equation:
$\Delta_r S^\circ = \sum \Delta S^\circ_f$ (products) - $\sum S^\circ_f$(reactants)
$\Delta_r S^\circ$ = 368 J/K = .368kJ/K

Calculating the free energy from the above values at 298K:
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ = 63.5-298(.368) = **-46.1 kJ**

Safety: Avoid inhalation of the ammonia produced by the reaction. Perform in a well-ventilated room. Avoid prolonged contact of the skin with the cold flask. Barium salts are poisonous. These as well as ammonium salts can cause skin irritations.

Disposal: The contents of the flask should be disposed of in an appropriate waste container.

References:
1. B.Z. Shakhashiri; *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; Wisconsin; 1983; Volume 1;p 10-12
2. L. Summerlin, J. Ealy; *Chemical Demonstrations: A Sourcebook for Teachers.* ACS publications. Washington D.C; 1983; p. 44