

5.5: Enthalpies of Solution

Learning Objectives

- To understand Enthalpies of Solution and be able to use them to calculate the Heat absorbed or emitted when making solutions.

Enthalpies of Solution and Dilution

Physical changes, such as melting or vaporization, and chemical reactions, in which one substance is converted to another, are accompanied by changes in enthalpy. Two other kinds of changes that are accompanied by changes in enthalpy are the dissolution of solids and the dilution of concentrated solutions.

The dissolution of a solid can be described as follows:



The values of ΔH_{soln} for some common substances are given in Table 5.5.1. The sign and the magnitude of ΔH_{soln} depend on specific attractive and repulsive interactions between the solute and the solvent; these factors will be discussed in Chapter 13. When substances dissolve, the process can be either exothermic ($\Delta H_{\text{soln}} < 0$) or endothermic ($\Delta H_{\text{soln}} > 0$), as you can see from the data in Table 5.5.1.

Table 5.5.1 Enthalpies of Solution at 25°C of Selected Ionic Compounds in Water (in kJ/mol)

	Anion				
Cation	Fluoride	Chloride	Bromide	Iodide	Hydroxide
lithium	4.7	-37.0	-48.8	-63.3	-23.6
sodium	0.9	3.9	-0.6	-7.5	-44.5
potassium	-17.7	17.2	19.9	20.3	-57.6
ammonium	-1.2	14.8	16.8	13.7	—
silver	-22.5	65.5	84.4	112.2	—
magnesium	-17.7	-160.0	-185.6	-213.2	2.3
calcium	11.5	-81.3	-103.1	-119.7	-16.7
	Nitrate	Acetate	Carbonate	Sulfate	
lithium	-2.5	—	-18.2	-29.8	
sodium	20.5	-17.3	-26.7	2.4	
potassium	34.9	-15.3	-30.9	23.8	
ammonium	25.7	-2.4	—	6.6	
silver	22.6	—	22.6	17.8	
magnesium	-90.9	—	-25.3	-91.2	
calcium	-19.2	—	-13.1	-18.0	

Substances with large positive or negative enthalpies of solution have commercial applications as instant cold or hot packs. Single-use versions of these products are based on the dissolution of either calcium chloride (CaCl_2 , $\Delta H_{\text{soln}} = -81.3$ kJ/mol) or ammonium nitrate (NH_4NO_3 , $\Delta H_{\text{soln}} = +25.7$ kJ/mol). Both types consist of a plastic bag that contains about 100 mL of water plus a dry chemical (40 g of CaCl_2 or 30 g of NH_4NO_3) in a separate plastic pouch. When the pack is twisted or struck sharply, the inner

plastic bag of water ruptures, and the salt dissolves in the water. If the salt is CaCl_2 , heat is released to produce a solution with a temperature of about 90°C ; hence the product is an “instant hot compress.” If the salt is NH_4NO_3 , heat is absorbed when it dissolves, and the temperature drops to about 0° for an “instant cold pack.”

A similar product based on the *precipitation* of sodium acetate, not its dissolution, is marketed as a reusable hand warmer (Figure 5.5.1). At high temperatures, sodium acetate forms a highly concentrated aqueous solution. With cooling, an unstable *supersaturated* solution containing excess solute is formed. When the pack is agitated, sodium acetate trihydrate [$\text{CH}_3\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$] crystallizes, and heat is evolved:



A bag of concentrated sodium acetate solution can be carried until heat is needed, at which time vigorous agitation induces crystallization and heat is released. The pack can be reused after it is immersed in hot water until the sodium acetate redissolves.

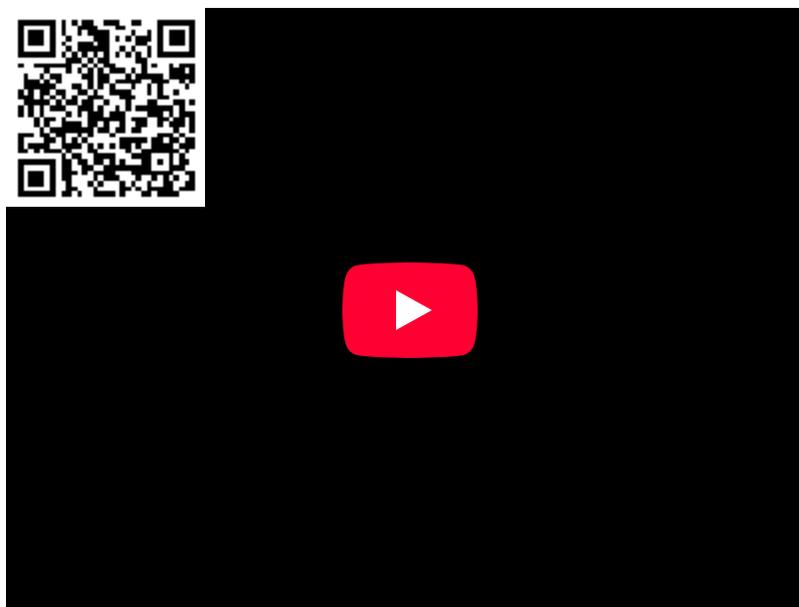


Figure 5.5.1 **An Instant Hot Pack Based on the Crystallization of Sodium Acetate** The hot pack is at room temperature prior to agitation (left). Because the sodium acetate is in solution, you can see the metal disc inside the pack. After the hot pack has been agitated, the sodium acetate crystallizes (right) to release heat. Because of the mass of white sodium acetate that has crystallized, the metal disc is no longer visible.

The amount of heat released or absorbed when a substance is dissolved is not a constant; it depends on the final concentration of the solute. The ΔH_{soln} values given previously and in Table 5.5.1 for example, were obtained by measuring the enthalpy changes at various concentrations and extrapolating the data to infinite dilution.

Because ΔH_{soln} depends on the concentration of the solute, diluting a solution can produce a change in enthalpy. If the initial dissolution process is exothermic ($\Delta H < 0$), then the dilution process is also exothermic. This phenomenon is particularly relevant for strong acids and bases, which are often sold or stored as concentrated aqueous solutions. If water is added to a concentrated solution of sulfuric acid (which is 98% H_2SO_4 and 2% H_2O) or sodium hydroxide, the heat released by the large negative ΔH can cause the solution to boil. Dangerous spattering of strong acid or base can be avoided if the concentrated acid or base is slowly added to water, so that the heat liberated is largely dissipated by the water. Thus you should **never add water to a strong acid or base**; a useful way to avoid the danger is to remember: *Add water to acid and get blasted!*

Summary

The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Conceptual Problems.

1. Describe the distinction between ΔH_{soln} and ΔH_{f} .
2. Does adding water to concentrated acid result in an endothermic or an exothermic process?
3. The following table lists $\Delta H^{\circ}_{\text{soln}}$ values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	$\Delta H^{\circ}_{\text{soln}}$ (kJ/mol)
KOH	-57.61
LiNO ₃	-2.51
KMnO ₄	43.56
NaC ₂ H ₃ O ₂	-17.32

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

Answers

Contributors

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