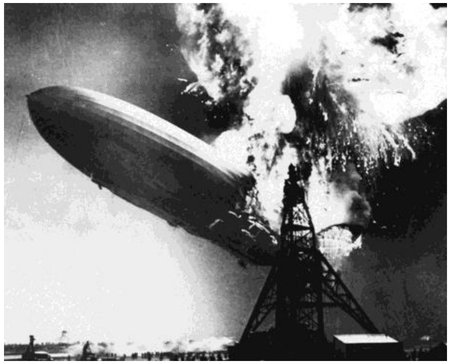
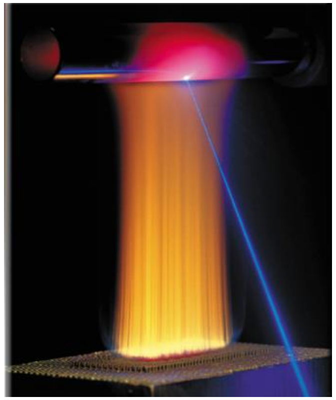


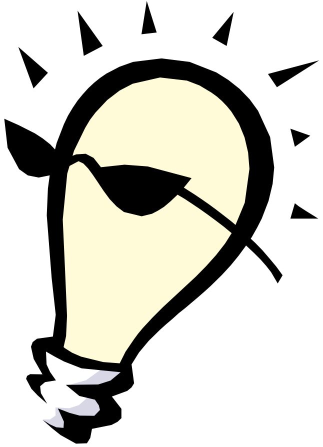


Thermochemistry: Problem Based Learning

Frank N. Crespilho

Review

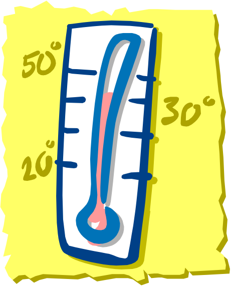
Energy is the capacity to do work



- ***Thermal energy*** is the energy associated with the random motion of atoms and molecules
- ***Chemical energy*** is the energy stored within the bonds of chemical substances
- ***Nuclear energy*** is the energy stored within the collection of neutrons and protons in the atom
- ***Electrical energy*** is the energy associated with the flow of electrons
- ***Potential energy*** is the energy available by virtue of an object's position

Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.



Temperature is a measure of the **thermal energy**.

Temperature ≠ Thermal Energy

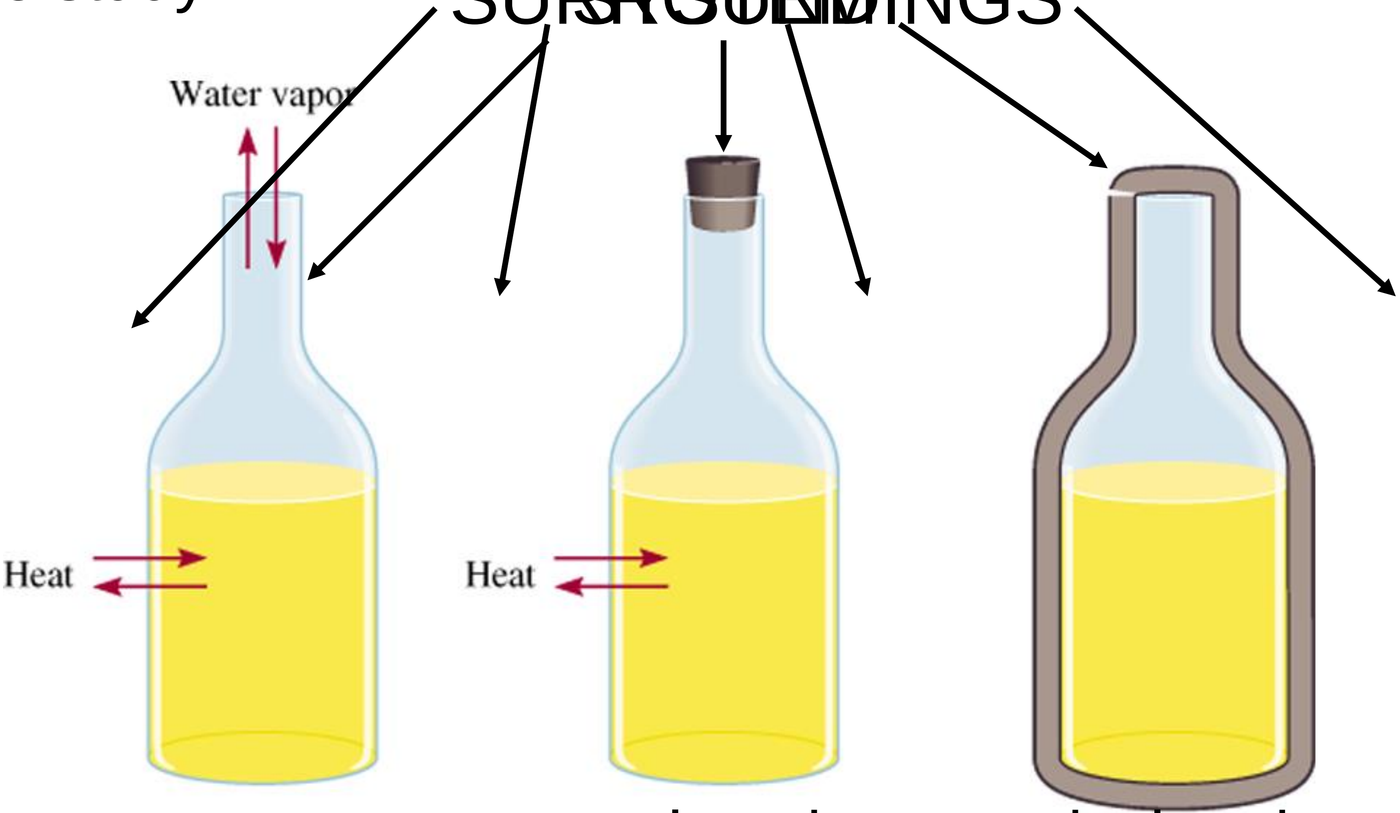
90^{0}C

40^{0}C

greater thermal energy

Thermochemistry is the study of heat change in chemical reactions.

The ***system*** is the specific part of the universe that is of interest in the study.



SURROUNDINGS

SYSTEM

open closed isolated

Exchange: mass & energy energy nothing

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l) + \text{energy}$$

$$H_2O\,(g) \longrightarrow H_2O\,(l) + \text{energy}$$

Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

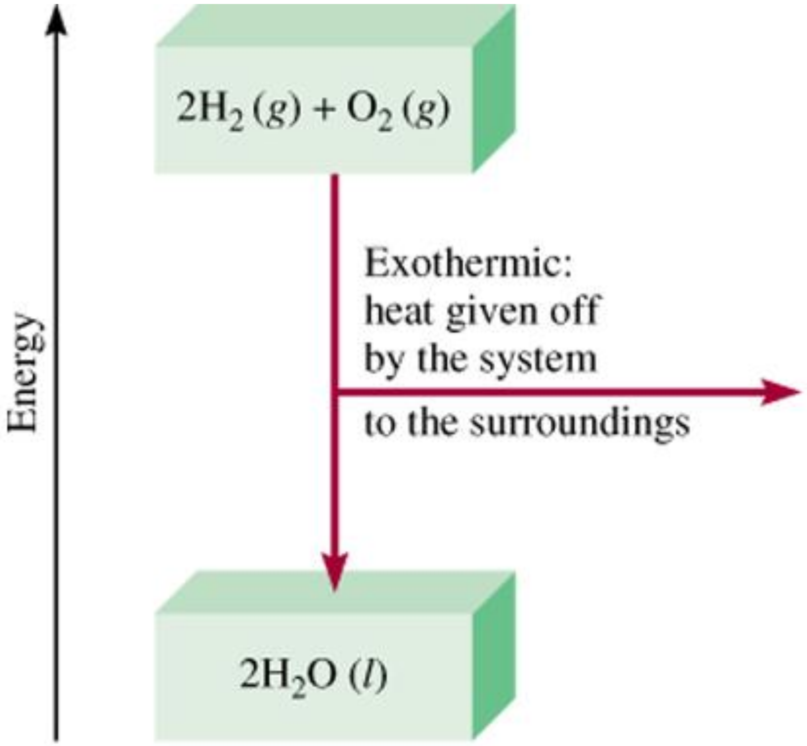
$$\text{energy} + 2HgO\,(s) \longrightarrow 2Hg\,(l) + O_2\,(g)$$

$$\text{energy} + H_2O\,(s) \longrightarrow H_2O\,(l)$$

Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

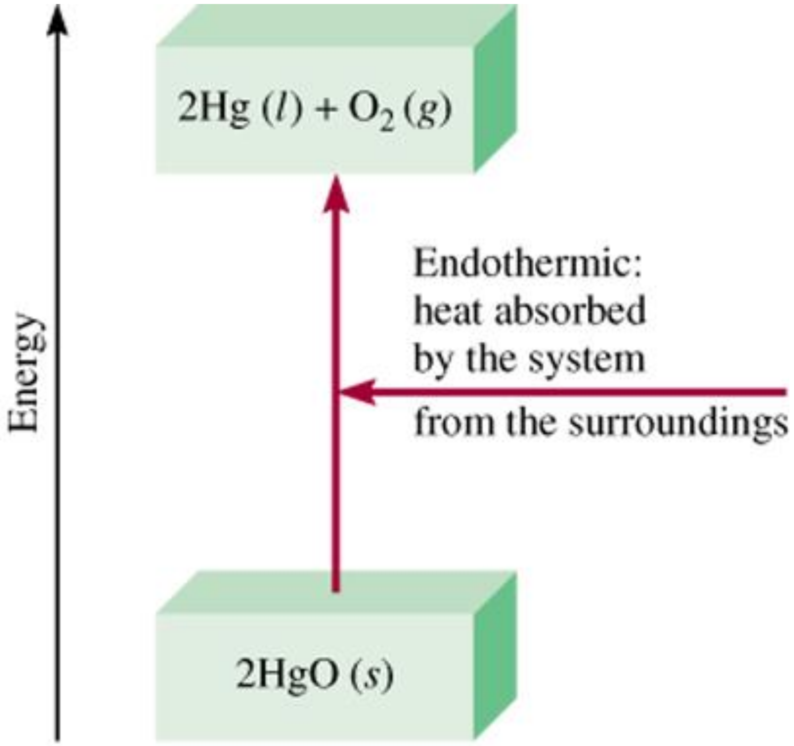
$$\Delta H = H\ (\text{products}) - H\ (\text{reactants})$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**



$H_{\text{products}} < H_{\text{reactants}}$

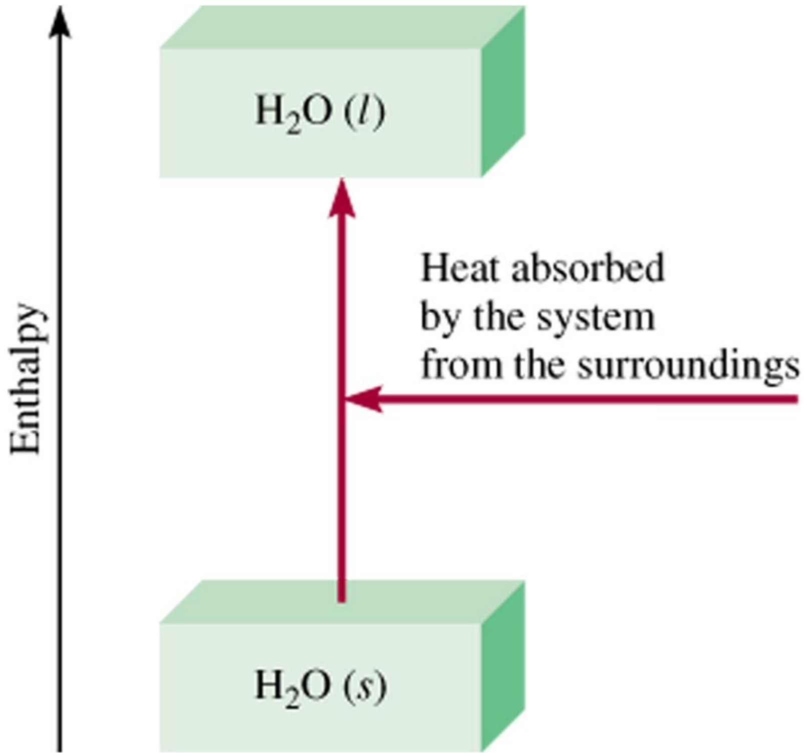
$\Delta H < 0$



$H_{\text{products}} > H_{\text{reactants}}$

$\Delta H > 0$

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

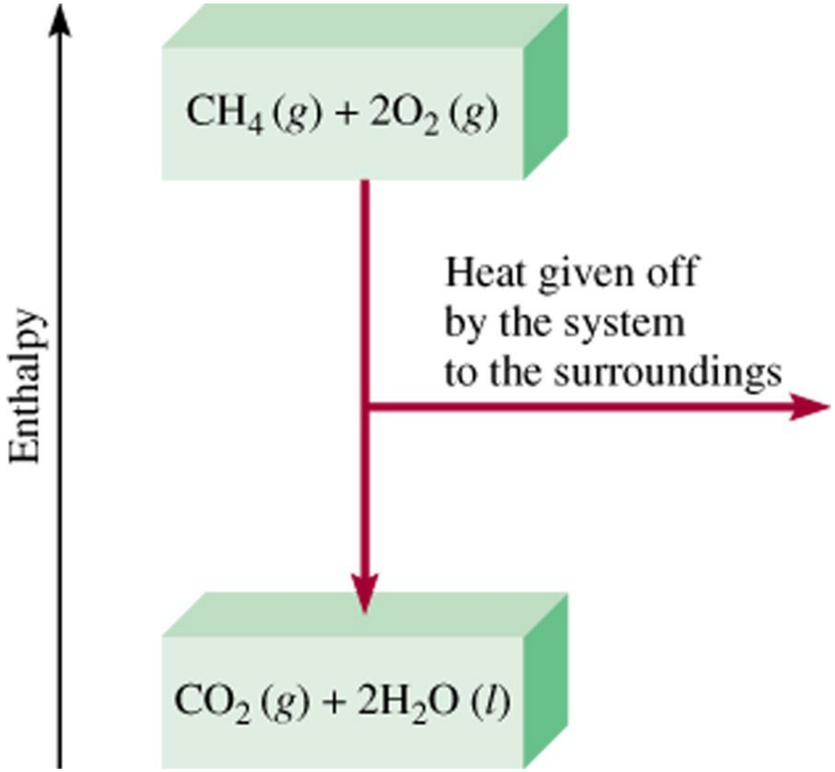
Endothermic

$\Delta H > 0$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \boxed{\Delta H = 6.01\ \text{kJ}}$$

Thermochemical Equations



Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25^0C and 1 atm.

$CH_4 (g) + 2O_2 (g) \longrightarrow CO_2 (g) + 2H_2O (l)$ $\Delta H = -890.4$ kJ

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01\ \text{kJ}$$

- If you reverse a reaction, the sign of ΔH changes

$$H_2O\ (l) \longrightarrow H_2O\ (s) \qquad \Delta H = -6.01\ \text{kJ}$$

- If you multiply both sides of the equation by a factor n, then ΔH must change by the same factor n.

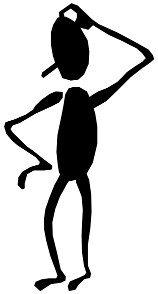
$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \qquad \Delta H = 2 \times 6.01 = 12.0\ \text{kJ}$$

Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O\,\boxed{(s)} \longrightarrow H_2O\,\boxed{(l)} \qquad \Delta H = 6.01\text{ kJ}$$

$$H_2O\,\boxed{(l)} \longrightarrow H_2O\,\boxed{(g)} \qquad \Delta H = 44.0\text{ kJ}$$



How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s) \qquad \Delta H = -3013\text{ kJ}$$

$$266\ \cancel{\text{g P}_4} \times \frac{1\ \cancel{\text{mol P}_4}}{123.9\ \cancel{\text{g P}_4}} \times \frac{3013\text{ kJ}}{1\ \cancel{\text{mol P}_4}} = 6470\text{ kJ}$$

The ***specific heat*** (***s***) of a substance is the amount of heat (*q*) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

The ***heat capacity*** (***C***) of a substance is the amount of heat (*q*) required to raise the temperature of **a given quantity** (*m*) of the substance by **one degree** Celsius.

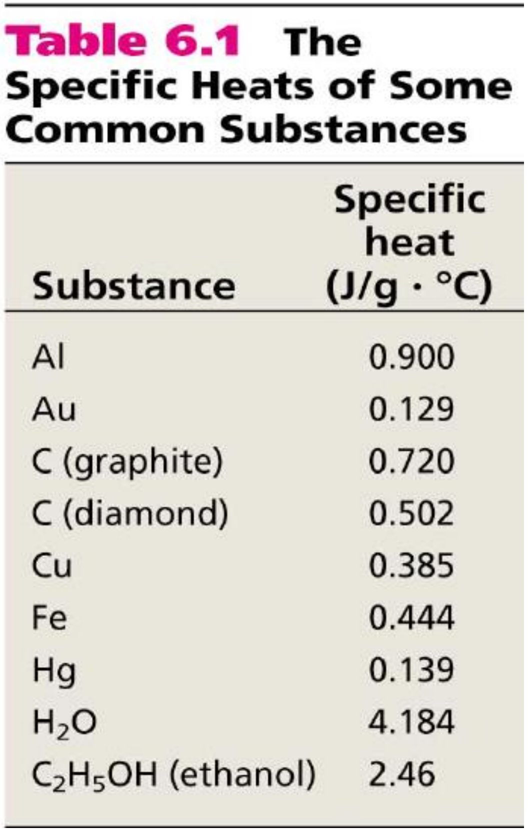


Table 6.1 **The Specific Heats of Some Common Substances**

Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

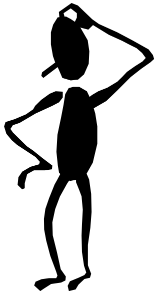
$$C = ms$$

<u>Heat (*q*) absorbed or released:</u>

$$q = ms\Delta t$$

$$q = C\Delta t$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$



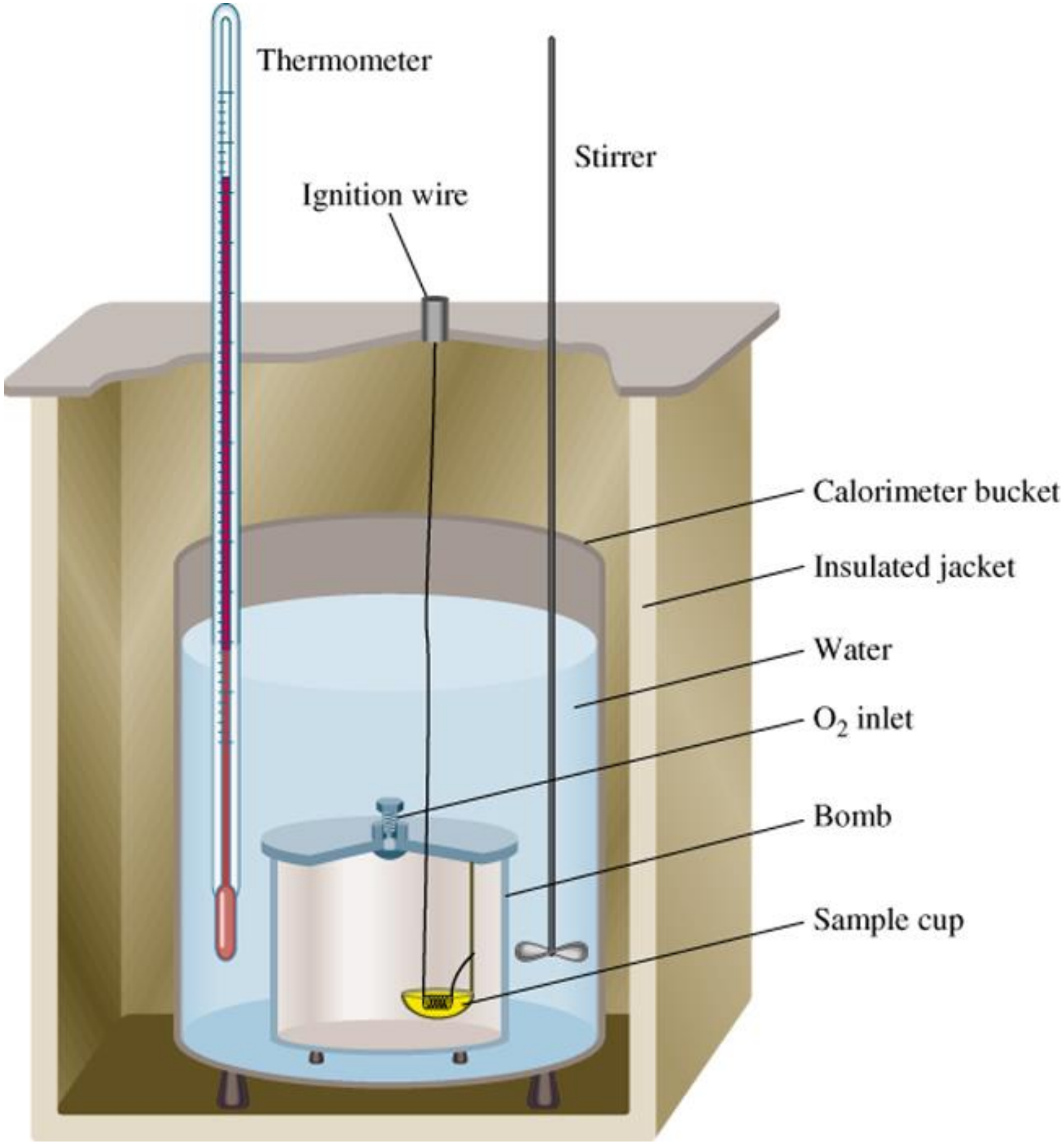
How much heat is given off when an 869 g iron bar cools from 94^0C to 5^0C?

s of Fe = 0.444 J/g • ^{0}C

$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^0\text{C} - 94^0\text{C} = -89^0\text{C}$

$q = ms\Delta t = 869\ \cancel{\text{g}} \times 0.444\ \text{J}/\cancel{\text{g}} \cdot {}^0\cancel{\text{C}} \times -89^0\cancel{\text{C}} = -34{,}000\ \text{J}$

Constant-Volume Calorimetry



$q_{\text{sys}} = q_{\text{water}} + q_{\text{bomb}} + q_{\text{rxn}}$

$q_{\text{sys}} = 0$

$q_{\text{rxn}} = -(q_{\text{water}} + q_{\text{bomb}})$

$q_{\text{water}} = ms\Delta t$

$q_{\text{bomb}} = C_{bomb}\Delta t$

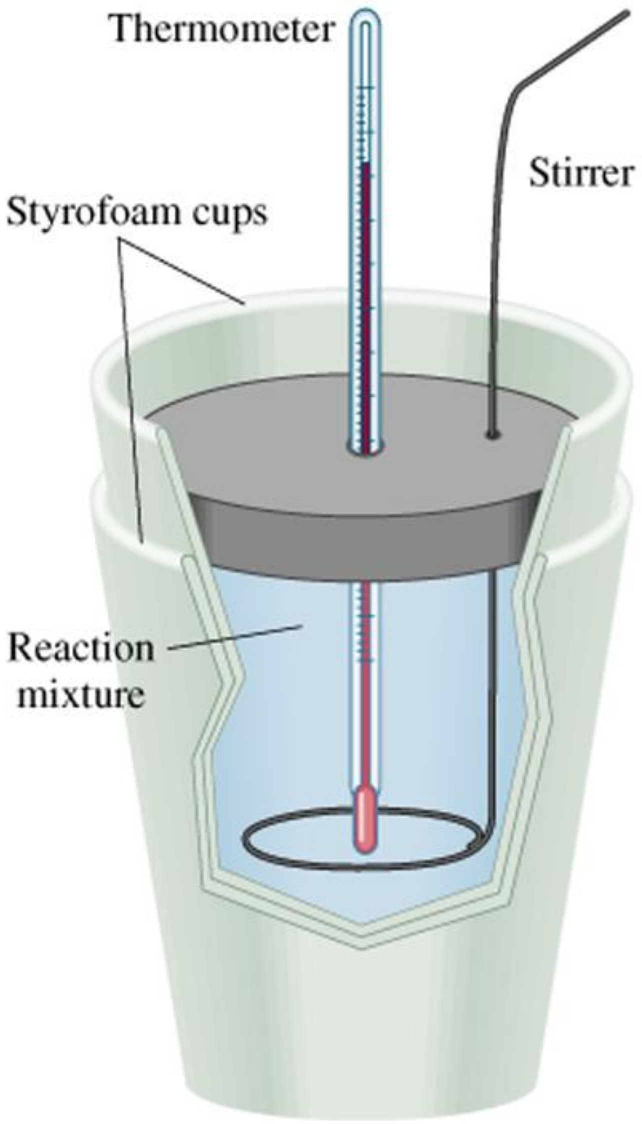
Reaction at Constant V

$\Delta H \neq q_{\text{rxn}}$

$\Delta H \sim q_{\text{rxn}}$

No heat enters or leaves!

Constant-Pressure Calorimetry



$q_{sys} = q_{water} + q_{cal} + q_{rxn}$

$q_{sys} = 0$

$q_{rxn} = -(q_{water} + q_{cal})$

$q_{water} = ms\Delta t$

$q_{cal} = C_{cal}\Delta t$

Reaction at Constant *P*

$\Delta H = q_{rxn}$

No heat enters or leaves!

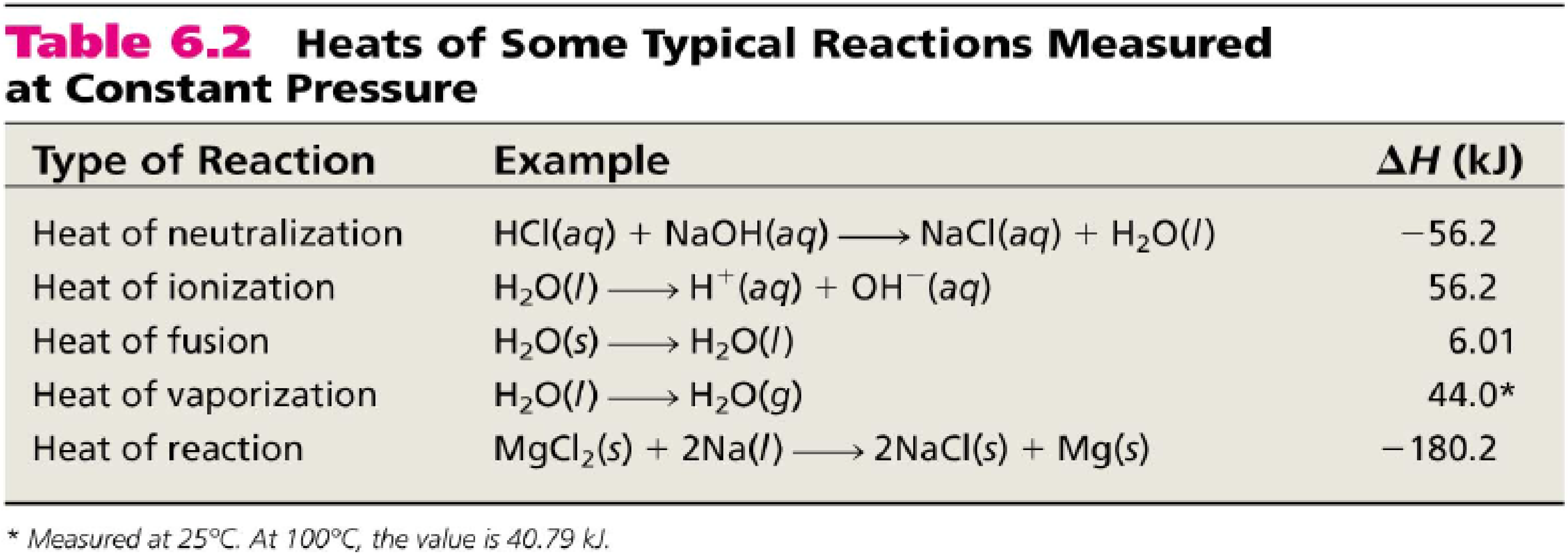
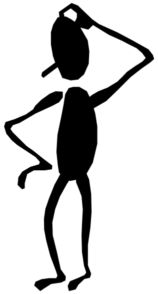


Table 6.2 **Heats of Some Typical Reactions Measured at Constant Pressure**

Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	−180.2

** Measured at 25°C. At 100°C, the value is 40.79 kJ.*



Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

The standard enthalpy of formation of any element in its most stable form is zero.

ΔH_f^0 (O_2) = 0

ΔH_f^0 (C, graphite) = 0

ΔH_f^0 (O_3) = 142 kJ/mol

ΔH_f^0 (C, diamond) = 1.90 kJ/mol

Table 6.3 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.04	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.94
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O_4(g)$	9.66
$CaCO_3(s)$	−1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−268.61	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$ZnO(s)$	−347.98
$H_2O(l)$	−285.8		

The **standard enthalpy of reaction** (ΔH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \longrightarrow cC + dD$$

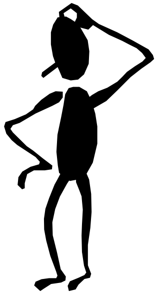
$$\Delta H^0_{rxn} = [c\Delta H^0_f(C) + d\Delta H^0_f(D)] - [a\Delta H^0_f(A) + b\Delta H^0_f(B)]$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

Review



Calculate the standard enthalpy of formation of $CS_2\,(l)$ given that:

$\text{C(graphite)} + O_2\,(g) \longrightarrow CO_2\,(g) \quad \Delta H^0_{rxn} = -393.5\ \text{kJ}$

$\text{S(rhombic)} + O_2\,(g) \longrightarrow SO_2\,(g) \quad \Delta H^0_{rxn} = -296.1\ \text{kJ}$

$CS_2(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g) \quad \Delta H^0_{rxn} = -1072\ \text{kJ}$

1. Write the enthalpy of formation reaction for CS_2

$$\text{C(graphite)} + 2\text{S(rhombic)} \longrightarrow CS_2\,(l)$$

2. Add the given rxns so that the result is the desired rxn.

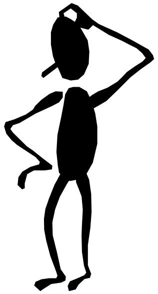
$$\text{C(graphite)} + \cancel{O_2}\,(g) \longrightarrow \cancel{CO_2}\,(g) \quad \Delta H^0_{rxn} = -393.5\ \text{kJ}$$

$$2\text{S(rhombic)} + \cancel{2O_2}\,(g) \longrightarrow \cancel{2SO_2}\,(g) \quad \Delta H^0_{rxn} = -296.1\text{x2 kJ}$$

$$+ \quad \cancel{CO_2}(g) + \cancel{2SO_2}\,(g) \longrightarrow CS_2\,(l) + \cancel{3O_2}\,(g) \quad \Delta H^0_{rxn} = +1072\ \text{kJ}$$

$$\text{C(graphite)} + 2\text{S(rhombic)} \longrightarrow CS_2\,(l)$$

$$\Delta H^0_{rxn} = -393.5 + (2\text{x}-296.1) + 1072 = 86.3\ \text{kJ}$$



Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.

$$\boxed{2C_6H_6}\ (l) + 15O_2\ (g) \longrightarrow 12CO_2\ (g) + 6H_2O\ (l)$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f\ \text{(products)} - \Sigma m\Delta H^0_f\ \text{(reactants)}$$

$$\Delta H^0_{rxn} = [12\Delta H^0_f\ (CO_2) + 6\Delta H^0_f\ (H_2O)] - [\,2\Delta H^0_f\ (C_6H_6)]$$

$$\Delta H^0_{rxn} = [\ 12\text{x}–393.5 + 6\text{x}–187.6\ ] – [\ 2\text{x}49.04\ ] = -5946\ \text{kJ}$$

$$\frac{-5946\ \text{kJ}}{2\ \text{mol}} = -\ 2973\ \text{kJ/mol}\ C_6H_6$$

The ***enthalpy of solution*** (ΔH_{soln}) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$\Delta H_{soln} = H_{soln} - H_{components}$$

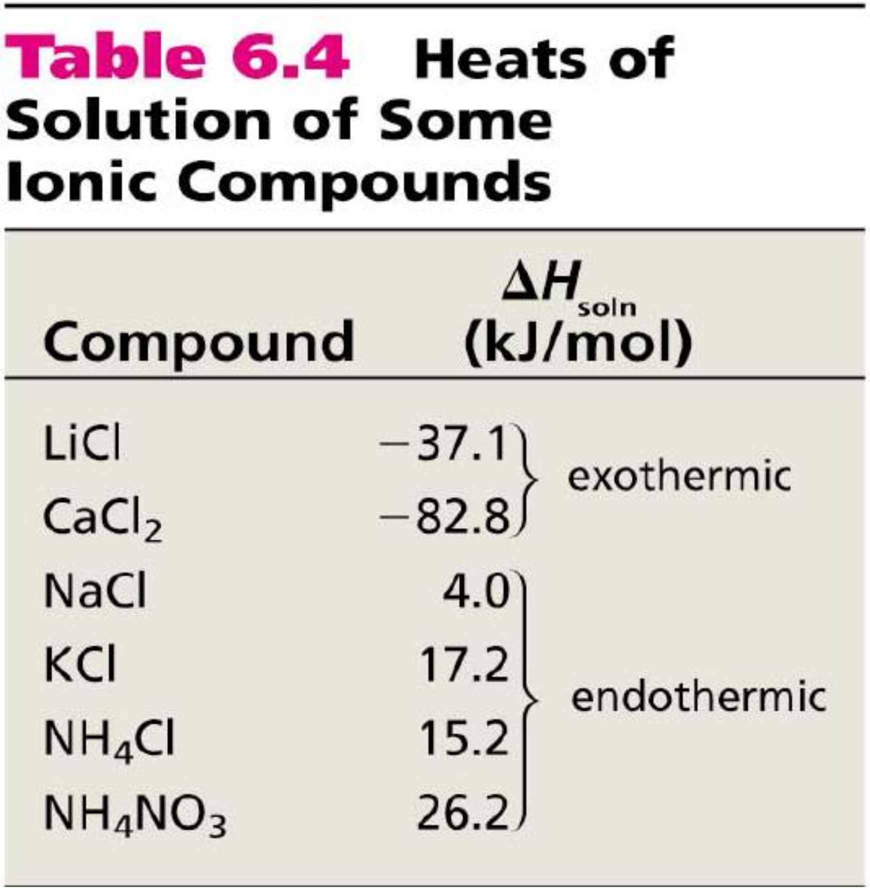


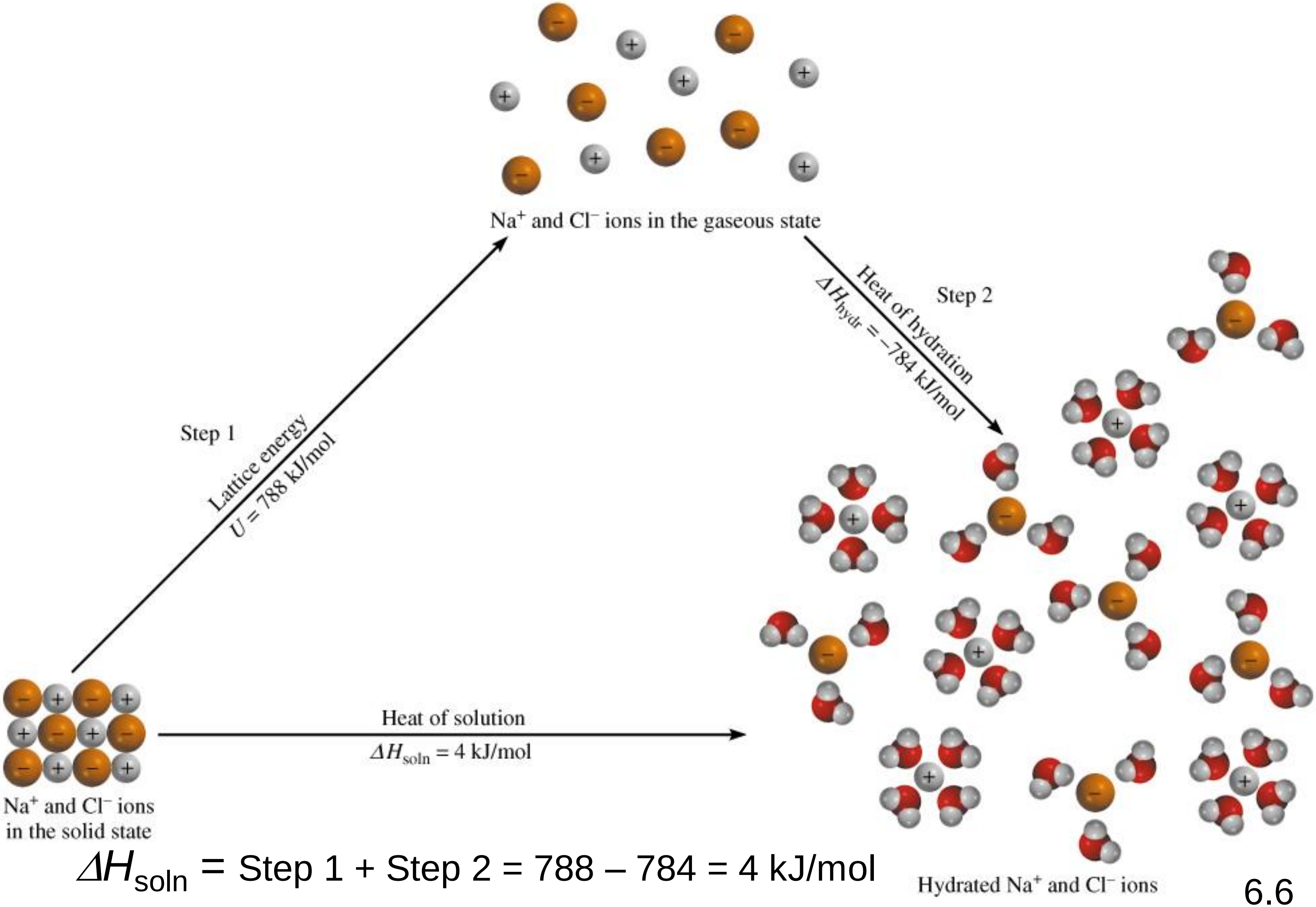
Table 6.4 **Heats of Solution of Some Ionic Compounds**

Compound	ΔH_{soln} (kJ/mol)	
LiCl	−37.1	exothermic
$CaCl_2$	−82.8	
NaCl	4.0	endothermic
KCl	17.2	
NH_4Cl	15.2	
NH_4NO_3	26.2	

Which substance(s) could be used for melting ice?

Which substance(s) could be used for a cold pack?

The Solution Process for NaCl



ΔH_{soln} = Step 1 + Step 2 = 788 – 784 = 4 kJ/mol