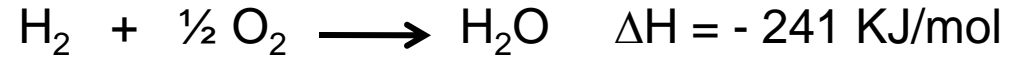
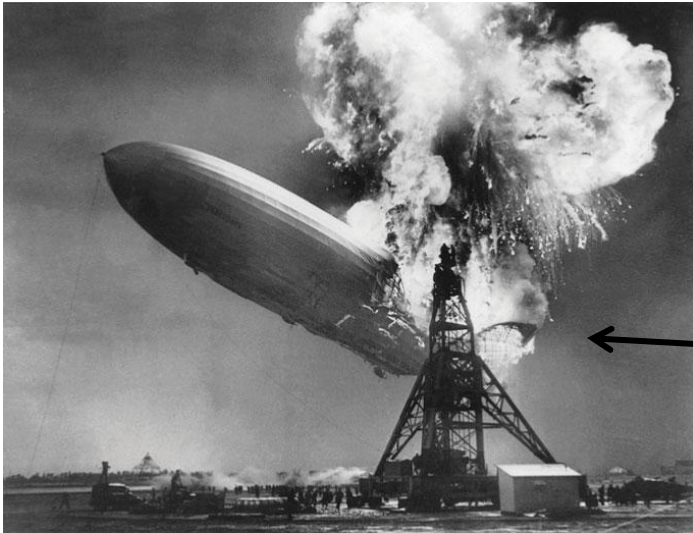
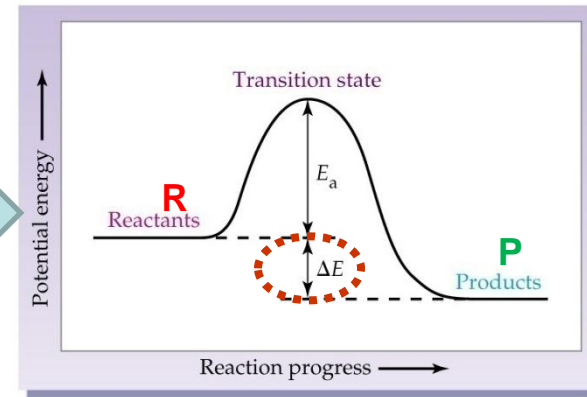


# Thermodynamics & kinetics

Zepelin "Hindenburg" 1937



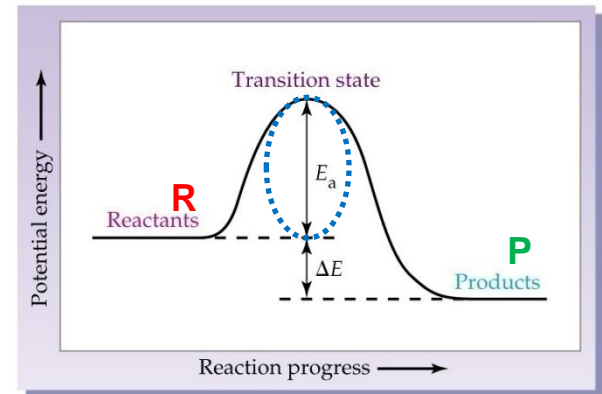
both  
spontaneous !



(b)



but rates?



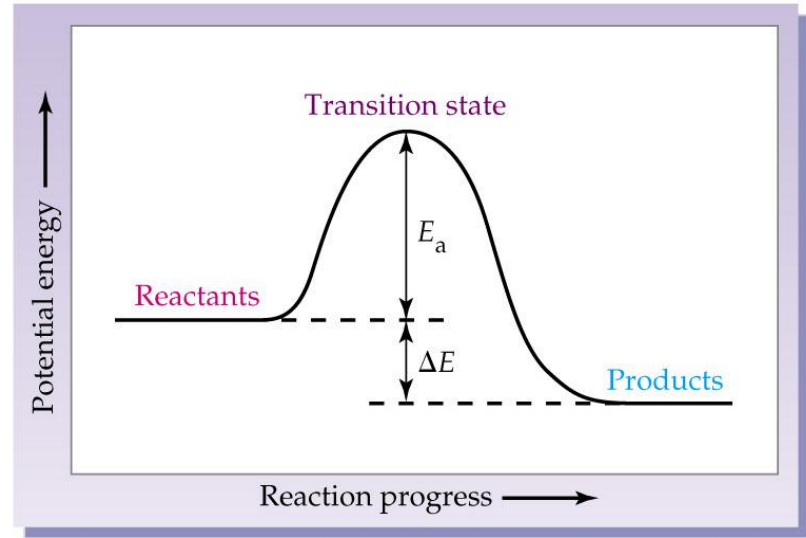
(b)





(a)

## Reaction coordinate



(b)

### Thermodynamics

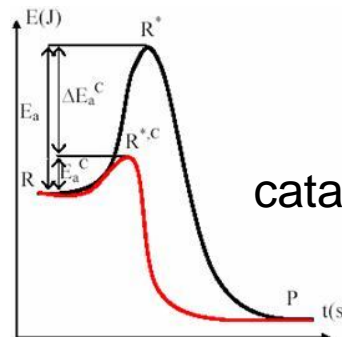
Deals with the relative stability of reactants and products

→  $\Delta E$

### Kinetics

How long does it take to reach the transition state ?

→  $E_a$



catalysis

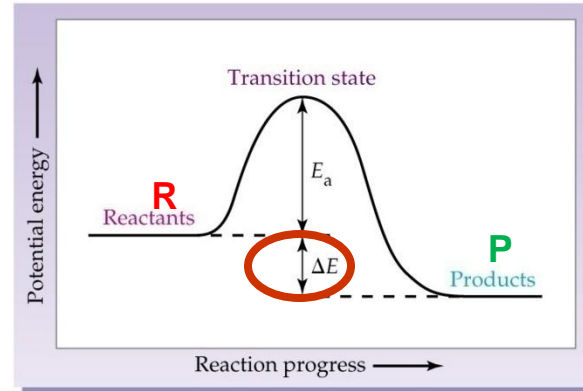
# THERMODYNAMICS

<http://www.slideshare.net/Emersius/energy-changes>

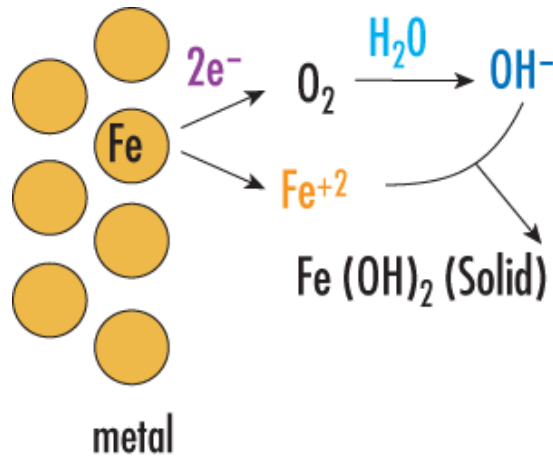
# A problem of relative energetic stability (P vs R)



(a)



(b)



## Definition of a chemical system

- a) **Isolated** : no exchange of mass ( $m$ ) and/or energy ( $E$ )      *dewar flask*
- b) **closed** : no exchange of  $m$  with exchange of  $E$       *reaction chamber*
- c) **open** : exchange of both  $m$  and  $E$       *lab beaker, human body...*

## Properties of matter (*homogeneous*)

- a) **Intensive** : independent on dimension      *density, T, P etc.*
- b) **extensive** : dependent on dimension      *molar mass, volume, weight, etc.*

## PRINCIPLES (*meaning*)

- I°: **Energy conservation** (Clausius 1865):      *energy is neither created or destroyed, it is converted.*
- II° **the Energy cannot be fully converted into useful work**  
the total entropy (Entropy of universe  $S_U$ ) always increases
- III° **the entropy value of a pure, perfect, crystal is**       **$S = 0$ , at  $T = 0$  K**  
(Nernst 1906)

## Parameters defining the energetic state of matter

### STATE FUNCTIONS:

- |                    |          |
|--------------------|----------|
| 1) INTERNAL ENERGY | <b>U</b> |
| 2) ENTHALPY        | <b>H</b> |
| 3) ENTROPY         | <b>S</b> |
| 4) FREE ENERGY     | <b>G</b> |
| 5) TEMPERATURE     | <b>T</b> |



**James Joule [1818-1889]**

## INTERNAL ENERGY $U$

$U$  = the sum of all energetic contribution in a system ( $E_{\text{bonds}}$ ;  $E_{\text{kinetic}}$ ;  $E_{\text{nuclear}}$ , etc.)

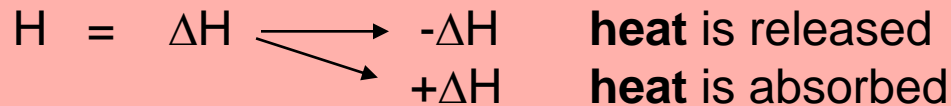
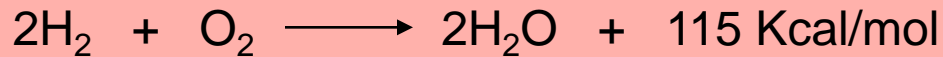
$U$  evaluation is difficult/impossible

***$U$  can be evaluated through variation ( $\Delta U$ ) of related parameters :***

- 1) *used/produced work* [ $L$ ;  $W$ ] (**changes in molecular structure**)
- 2) *heat exchange* [ $Q$ ]

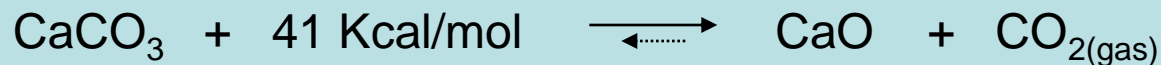
# ENTHALPY ( $\epsilon\nu\tau\alpha\lambda\pi\omicron$ = heat up) *easy... to measure*

Exothermic reaction (e.g. combustion...)



H = heat

Endothermic reaction



kilocalorie (Kcal) = large calorie = Cal = 1.000 calories  
1 Kcal = 4,1868 Kilojoules (KJ)



## The calorie unit

**1 (small) cal rises the temperature of 1 g H<sub>2</sub>O by 1 °C (from 14.5 to 15.5) (p = 1 atm)**

***In biology, medicine, dietetics***

**1 Kcal (large Calorie, C) raises temperature of 1 Kg H<sub>2</sub>O by 1 °C (from 14.5 to 15.5 °C)**

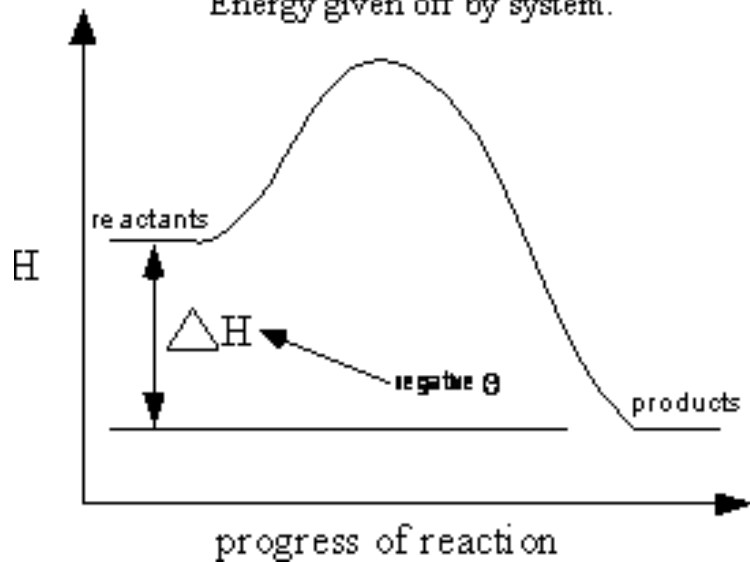
**100 Kcal bring 1Kg of H<sub>2</sub>O to the boiling point (p= 1 atm)**

**1 cal ~ 4.18 joules**

# exothermic - endothermic reactions

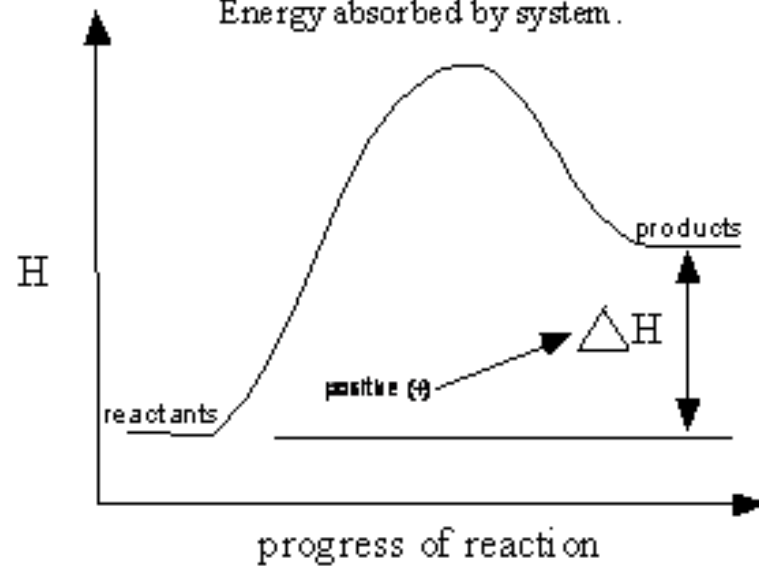
Heat is released

A. Exothermic reaction.  
Energy given off by system.

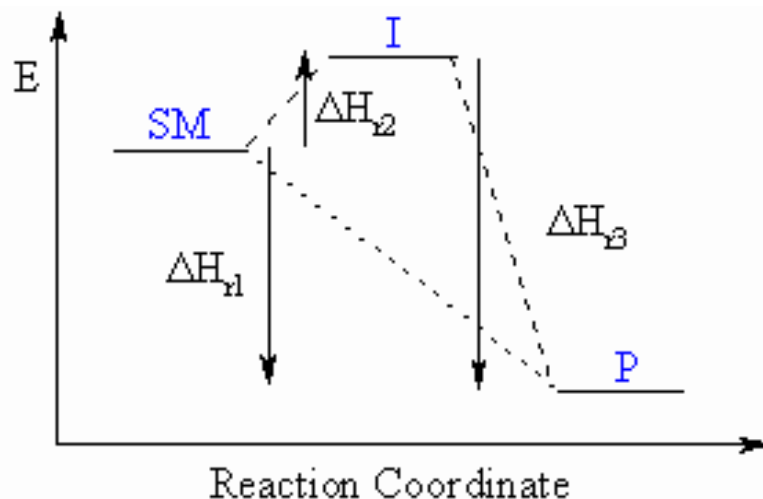


Heat is absorbed

B. Endothermic reaction.  
Energy absorbed by system.

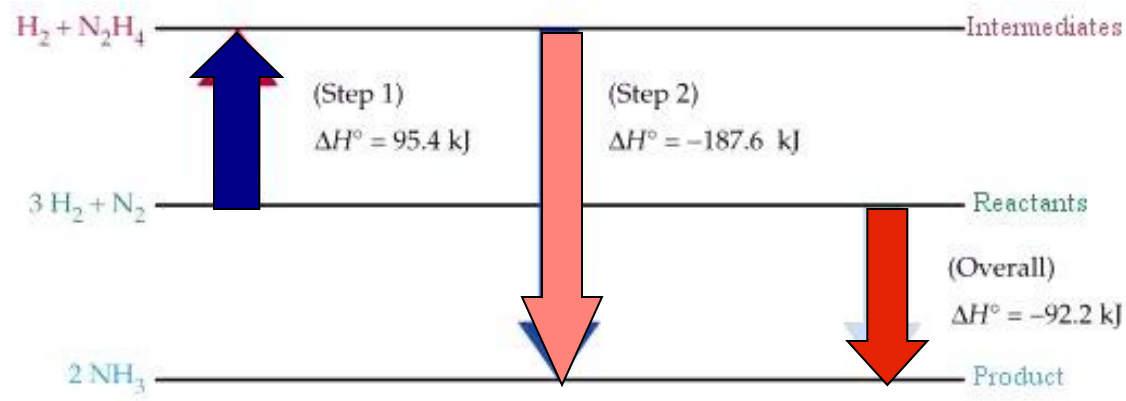


**Hess Law** : the enthalpy variation ( $\Delta H$ ) for the reaction converting reactants (SM) into products (P) is independent on the reaction pathway(s).



Prof. Hess  
S. Petersburg (1830)

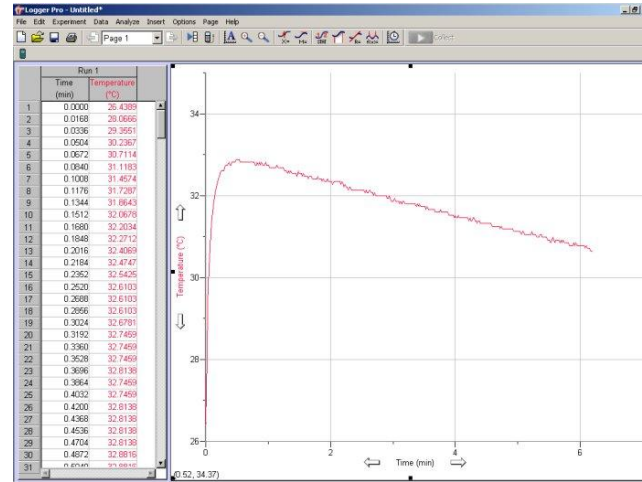
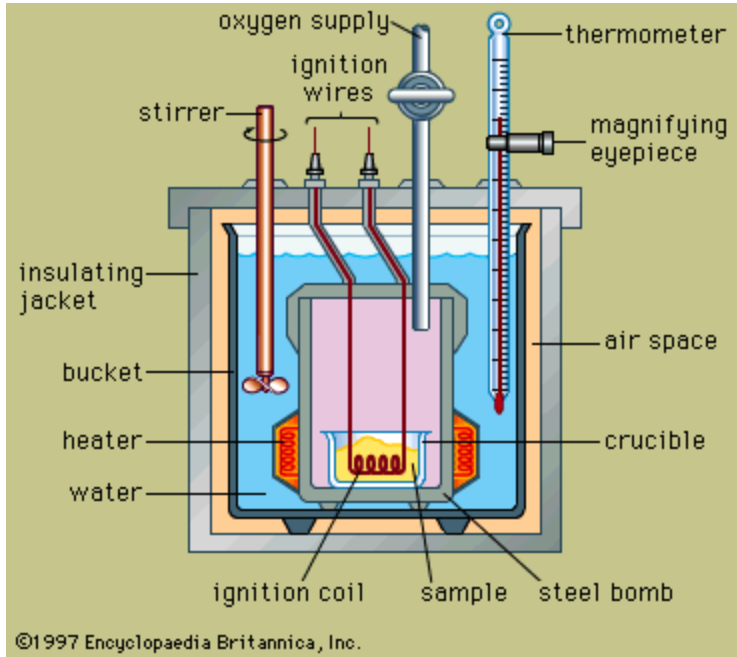
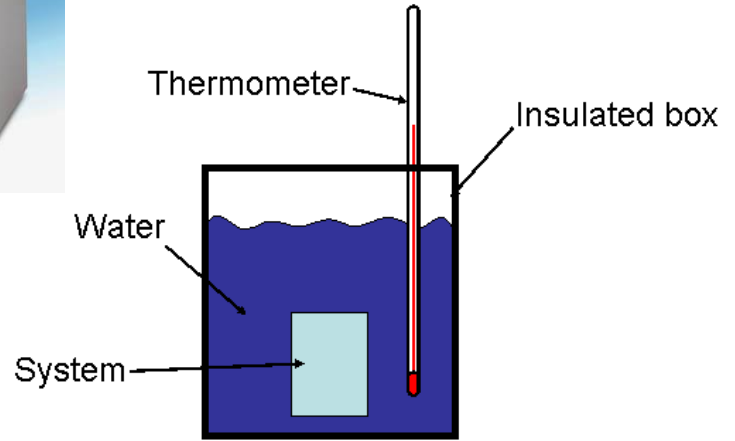
Hess's Law implies that :  $\Delta H_{r1} = \Delta H_{r2} + \Delta H_{r3}$



The reaction (overall) is **exothermic**

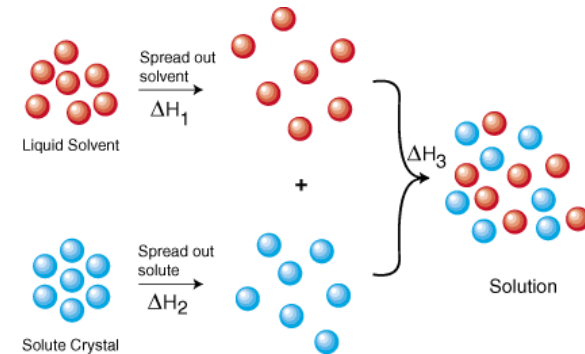
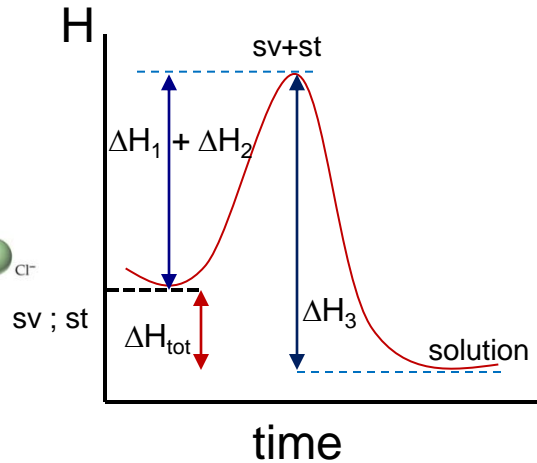
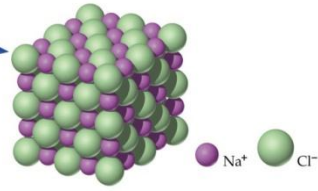
# The "Reaction Heat"

**calorimeter**



$+\Delta H$  = heat is absorbed to break the solute reticulum-bonds and to separate the solvent molecules  $\Delta H_1 + \Delta H_2$

$-\Delta H$  = heat is released in the solute hydration process  $\Delta H_3$



## Solubilization $\Delta H$ Kcal/mole

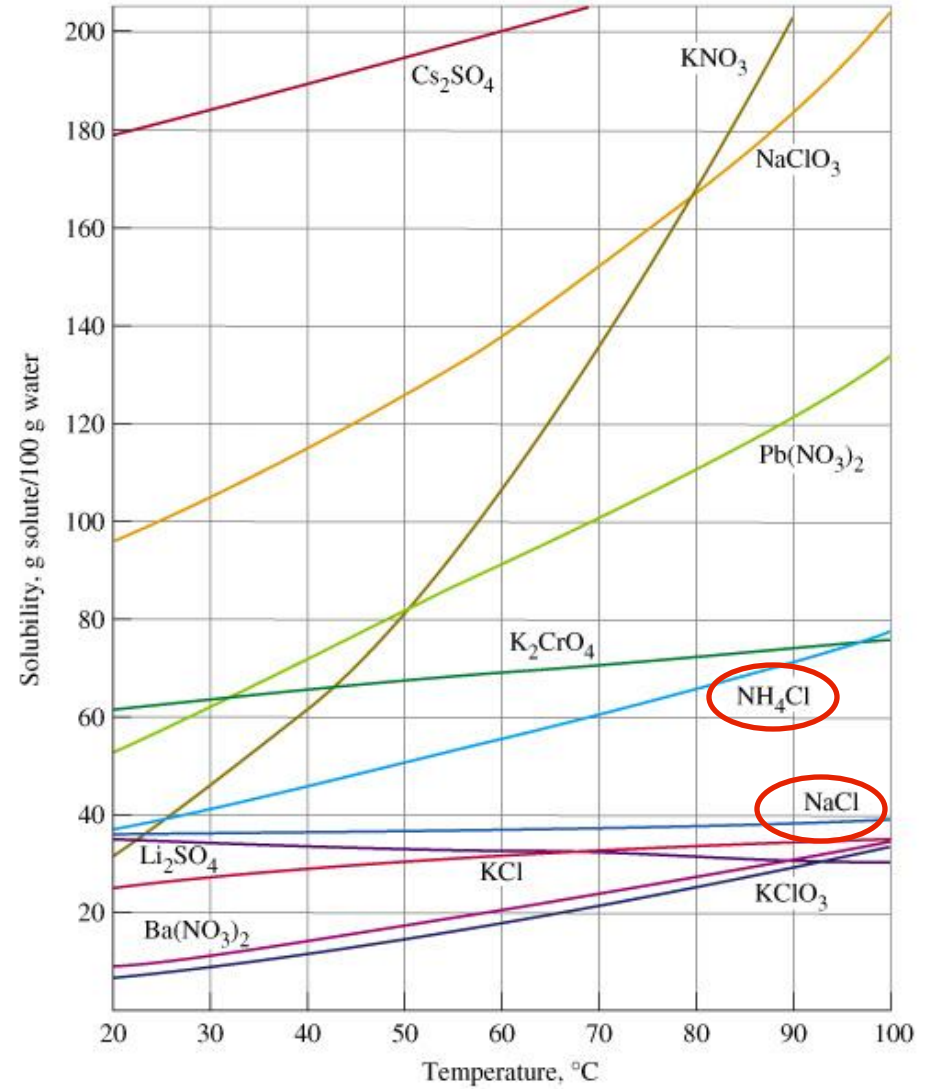
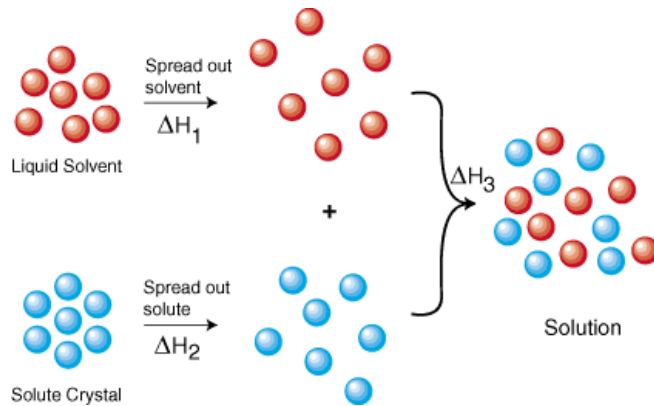
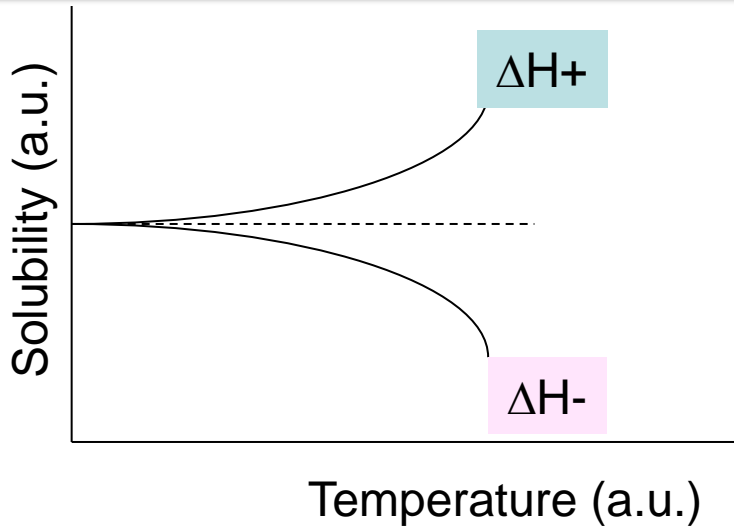
<i><b>solute</b></i>	$+\Delta H_{1,2}$	$-\Delta H_3$	$\Delta H_{tot}$
NaCl	186	185	+1
NaOH	176	186	-10
NH <sub>4</sub> Cl	152.6	149	+3.6

?

?

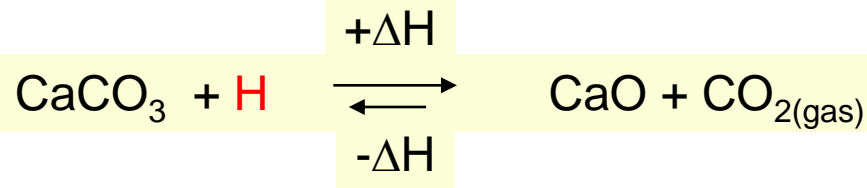
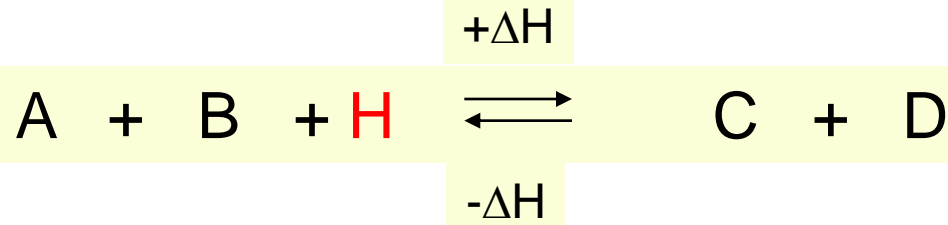
?

# Effect of temperature on solubility



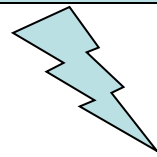
# Equilibrium and Enthalpy

H = heat



+  $\Delta\text{H}$  41 Kcal/mol  
-  $\Delta\text{H}$  41 Kcal/mol

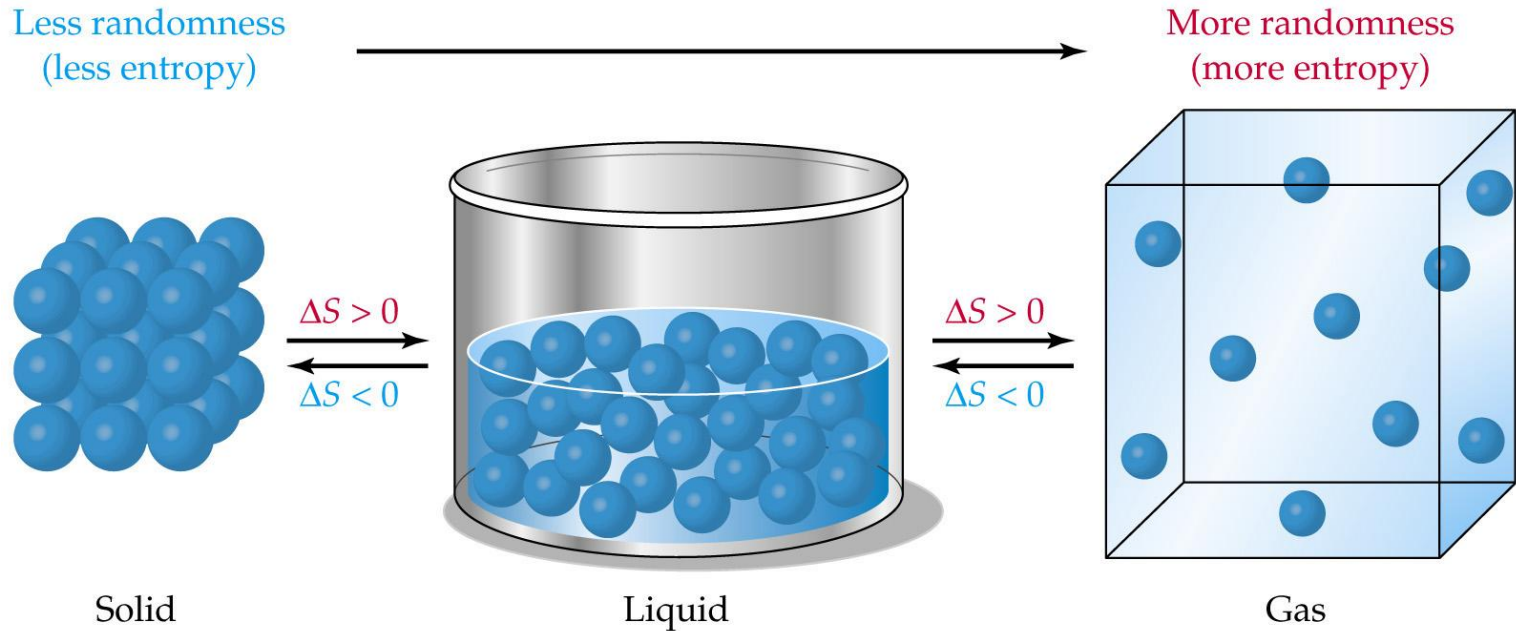
Can  
an endothermic reaction (+ $\Delta\text{H}$ )  
be spontaneous?!



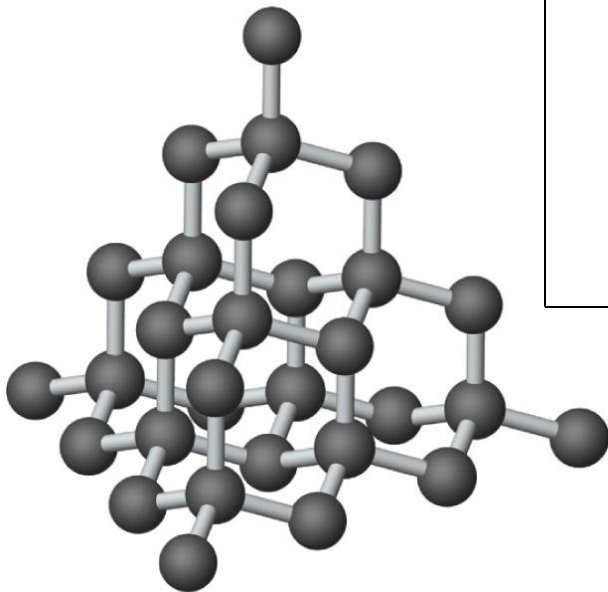
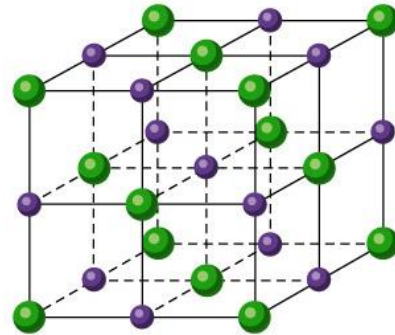
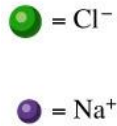
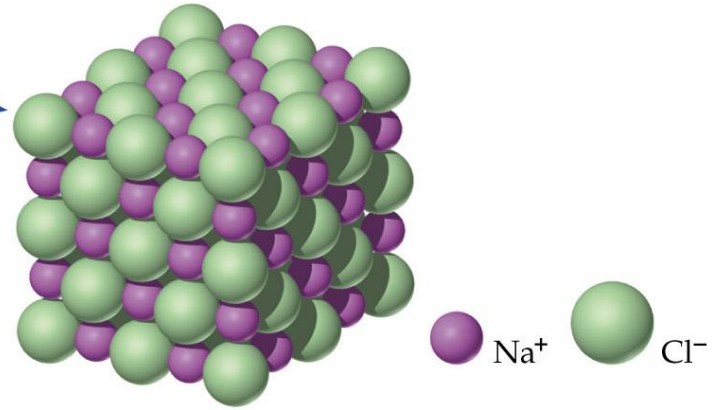
**Yes**  
**Owing to the (+) Entropy contribution!**

# ENTROPY

## Aggregation states and Entropy

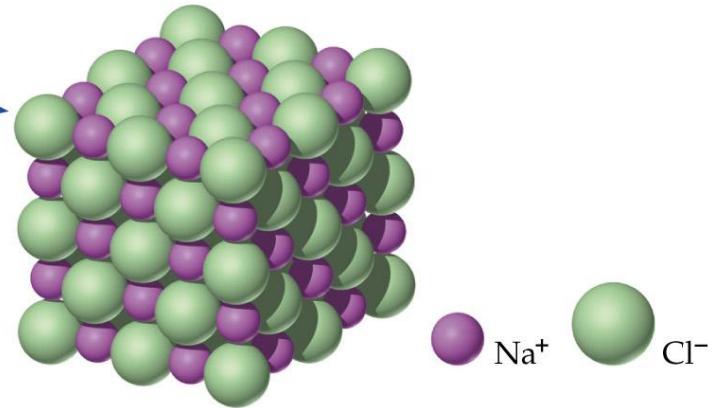




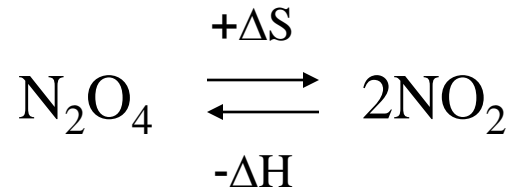


diamond

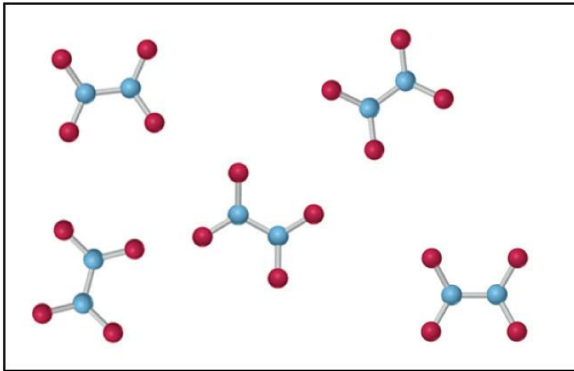
$\text{NaCl}_{\text{crist.}} \approx 2 \text{ u.e.}$



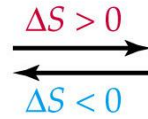
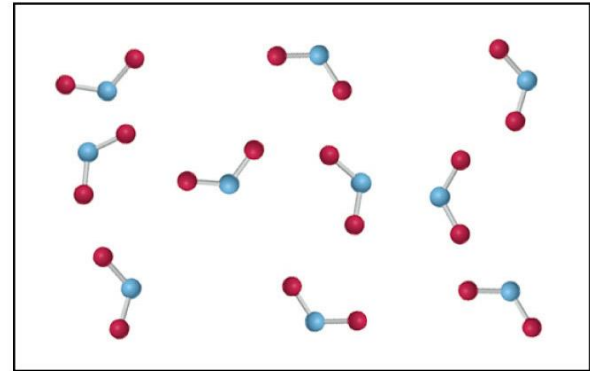
$\text{NaCl}_{\text{gas}} \approx 40 \text{ u.e.}$



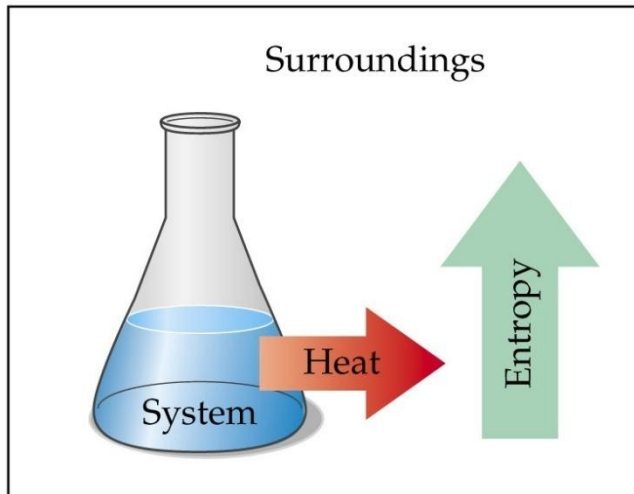
Less randomness  
(less entropy)



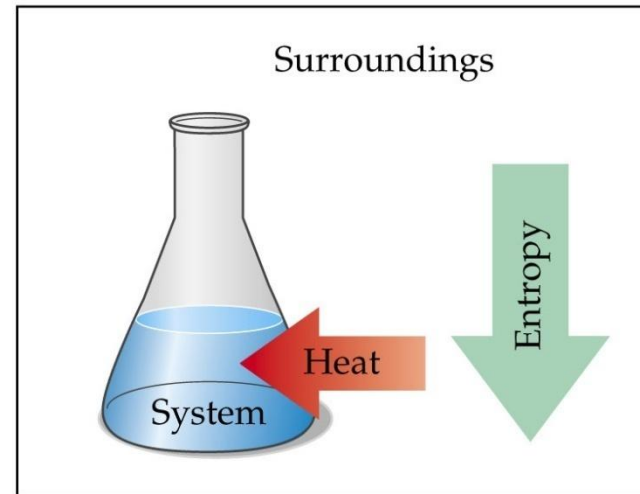
More randomness  
(more entropy)



# System Entropy ( $S_{sy}$ ) & Surroundings Entropy ( $S_{su}$ )



(a)

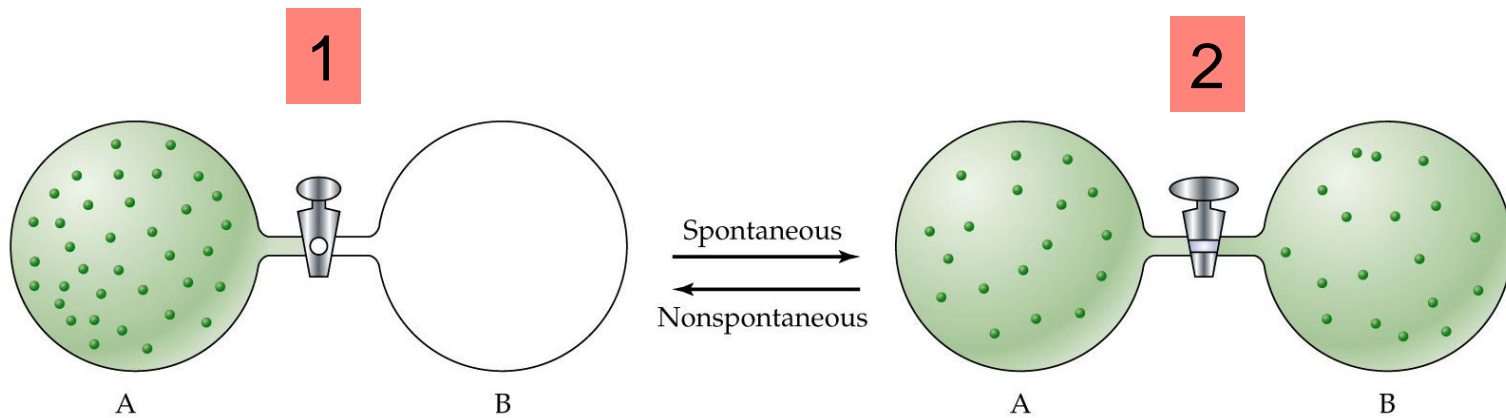


(b)

$$S_{su} \propto -\Delta H / T$$

$$\Delta H_{1,2} = 0$$

## Entropy & Spontaneity *of a reaction*



$$S_2 - S_1 \gg 0$$
$$\Delta S = +$$

# Entropy (S) [Sady Carnot]

S = is a measure of disorder (randomness)

2 components

Reagents and Products

surroundings

$S_s$

$S_{su}$

$$S_s = K_{Bz} \ln W$$

$$-\Delta H / T$$

$$S_{tot,univ} = S_s + S_{su}$$

$K_{Bz} 1.38062 \times 10^{-23}$  (joule/kelvin)

W = n° of molecular **microstates**

$K_{Bz}$  = Boltzman constant

# $\Delta H$ & $\Delta S$ & Spontaneous processes

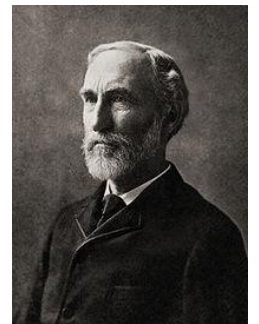
Do spontaneous endothermic reactions exist ( $+\Delta H$ )?  
Yes (e.g. salt solubilization)  $\rightarrow S_{sy}$  increases

Do spontaneous reactions with decreasing-entropy exist ( $-\Delta S$ )?  
Yes (e.g. crystallization)  $\rightarrow$  why?  $\rightarrow$  increases the surrounding entropy  $S_{su}$

A relationship between disorder of a system  
And the heat exchanged with surroundings  $\Delta H \equiv S_{su}$   
Must exist  
At a given temperature  
Accounting for spontaneity

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

Gibbs Equation



Gibbs 1863  
Yale University

**G = Gibbs, the free energy (to produce work)**

(by convention)  $\Delta G$  is negative ( $-\Delta G$ )

when the reaction occurs spontaneously and energy can be used up (*doing work*)

$$\Delta S_{\text{tot}} = \Delta S_{\text{su}} + \Delta S_{\text{sy}}$$

$$\Delta S_{\text{su}} = -\Delta H/T \quad (\text{given the same enthalpy change } (-\Delta H) \\ \text{the lower the } T, \text{ the bigger is } \Delta S_{\text{su}})$$

assuming  $\Delta S_{\text{sy}} \equiv \Delta S$

$$\Delta S_{\text{tot}} = -\Delta H/T + \Delta S \quad (\text{by multiplying for } T \text{ and changing the sign})$$

$$-T\Delta S_{\text{tot}} = \Delta H - T\Delta S$$

now we define as the Gibbs  
free energy  $-T\Delta S_{\text{tot}} = \Delta G$

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



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

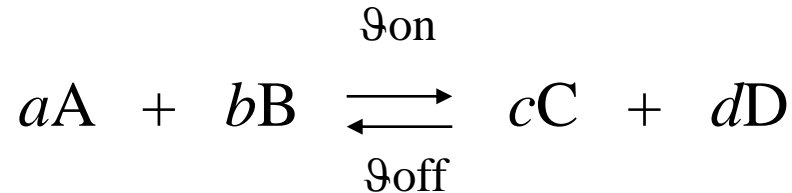
spontaneous process  $\Delta G < 0$

When does  $\Delta G < 0$  ?

- 1)  $\Delta H$  negative &  $\Delta S$  positive
- 2) Both  $\Delta S$  &  $\Delta H$  are negative, but  $\Delta H$  has an absolute value bigger than  $|T\Delta S|$
- 3)  $\Delta H$  positive,  $\Delta S$  positive &  $|T\Delta S| > |\Delta H|$

The reactions occurring in our body  
are very often  
Entropy driven !!!

# Free Energy & Equilibrium



$$K_{\text{eq}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

*High values of Keq = reaction shifted to the right*  
*Low values of Keq = reaction shifted to the left*

$\Delta G$  and  $K_{\text{eq}}$  (Van't Hoff equation)

$$\Delta G = (-RT \ln K_{\text{eq}} + RT \ln Q) = RT \ln Q/K_{\text{eq}}$$

For  $Q \cong K_{\text{eq}}$  ?



$$\Delta G = 0$$