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The natural direction of change:

The second low

The natural direction of change





• Why things change?

 Cooling is spontaneous process





Energy initially localized

tends to disperse

C

0

The increase in entropy from solid to liquid to gas





Standard molar entropies

substance	S/JK ⁻¹ mol ⁻¹	
C diamond	2,4	
C graphite	5,7	
H ₂ O(I)	69.9	
etanol(I)	160.7	
H ₂ (g)	130,7	
NO ₂ (g)	239,9	

 Entropy is increased by dividing the substance into smaller parts





Valueless Gold The precious metals market provides an analogy for the value of the released energy in its "concentrated" usable/form and its "dispersed" unusable form. Suppose you have ~ 300 an ounce of gold dust in a small container. At current market prices, you could sell it for about \$300. Now you disperse the dust over an $\sim 4000 \text{ m}^2$ acre of land. Conservation of mass is satisfied because the ounce of gold is still present, but you'll receive a very negative response when you try to obtain \$300 in the market. In dispersed form, the gold's value is much reduced. To extract, concentrate, and purify it would require large expenditures of energy, materials, and knowhow-far more, in fact, than the gold is worth.

Chemical reactions as dispersers of energy



4 Fe(s) + $3O_2(g) \rightarrow 2Fe_2O_3(s)$

 $\Delta_r H^o = -1648, 4 \text{ kJmol}^{-1}$

The (exotermic) rusting of iron disperses

Entropy increases by forming more molecules of products from less number of reactant molecules





Chemical system (Reaction vessel)

4 Fe(s) + 3O₂(g) ® 2Fe₂O₃(s)

the reactants become more localized

 $\Delta S^{o} = 2 (87,4 \text{ JK}^{-1}\text{mol}^{-1}) - 4 (27,3 \text{ JK}^{-1}\text{mol}^{-1}) - 3(205,0 \text{ JK}^{-1}\text{mol}^{-1}) =$ = -549,4 K⁻¹mol⁻¹ oxidation of iron is exotermic, so energy is released from the reaction vessel (system), ΔH = - 1648,4 kJmol⁻¹ into the surroundings DS (surroundings) = - DH/T

- Δ S(surroundings) = -(-1648,4 · 10³Jmol⁻¹) / 298,15 K = + 5529 JK⁻¹mol⁻¹
- $\Delta S(total) = \Delta S(surroundings) + \Delta S(reaction vessel)$
- 4 Fe(s) + 3O₂(g) ® 2Fe₂O₃(s)
- Δ S=2 (87,4 JK-1mol-1)-4 (27,3 JK-1mol-1)-3(205,0 JK-1mol-1)= -549,4 JK⁻¹mol⁻¹
- $\Delta S(total) = \Delta S(surroundings) + \Delta S(reaction vessel)$

 $= + 5529 \text{ JK}^{-1}\text{mol}^{-1} + (-549,4 \text{ JK}^{-1}\text{mol}^{-1}) = + 4980 \text{ JK}^{-1}\text{mol}^{-1}$

The second low of thermodynamics

- Entropy of the universe increases in the course of every natural change
- The "universe" means the system and its surroundings

- $\Delta S(total) = \Delta S(surroundings) + \Delta S(reaction vessel)$
- $\Delta S(total) = -\Delta_r H/T + \Delta_r S / x(-T)$
- -T DS(total) = $\Delta_r H T \Delta_r S$
- + $\Delta S \Rightarrow -T \Delta S$ is negative
- $-\Delta S \Rightarrow -T(-\Delta S) = \text{ is positive}$
- DG = DH T DS
- **DG** = spontaneous processs (+ Δ S)

A process is spontaneous if it corresponds to a negative value of DG

DG = + non spontaneous process

- When DG_m° is large and negative the equilibrium lies strongly in favour of the products,
- when it is large and positive, the equilibrium lies strongly in favour of the reactants.

Greatness and Obscurity of J. Willard Gibbs

Even today, one of the most remarkable minds in science is barely known outside chemistry and physics. In 1878, Josiah Willard Gibbs (1839–1903), a professor of mathematical physics at Yale, completed a 323-page paper that virtually established the science of chemical thermodynamics and included major principles governing chemical equilibrium, phasechange equilibrium, and the energy changes in electrochemical cells. The European scientists James Clerk Maxwell, Wilhelm Ostwald, and Henri Le Châtelier appreciated Gibbs's significance long before those in his own country did. In fact, he was elected to the Hall of Fame of Distinguished Americans only in 1950, because he had not received enough votes until then!



- $\Delta \mathbf{G} = \Delta \mathbf{H} \mathbf{T} \Delta \mathbf{S}$
- $\Delta H T \Delta S = \Delta G$
- $\Delta H = DG + T \Delta S$ Q
- $\Delta U = W + Q$

Two different paths (W + Q) for the energy change of a system



• <u>\[\] H</u>	ΔS	$\Delta \mathbf{G}$
• 1	+	$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$
•		+
•		$\Delta G = -$ - process allways spontaneous
• 2	-	$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$
•		- + -
•		$\Delta G = -$ + spontaneous at low T
•		$\Delta G = - + non-spontaneus at high T$
• 3.+	+	$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$
•		+ - +
•		$\Delta G = +$ - spontaneous at high T
•		$\Delta G = +$. non-spontaneus at low T
• 4.+	-	$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$
•		+ + -
•		$\Delta G = +$ + process allways non-spontaneous

- glucose + P \Leftrightarrow glucose-6-P + H₂O $\Delta G^{o'} = 12,5 \text{ kJ/mol}$
- ATP + $H_2O \Leftrightarrow ADP + P$ $\Delta G^{o'} = -33,5 \text{ kJ/mol}$
- glucose + P + ATP + $H_2O \Leftrightarrow$ glucose-6-P + H_2O + ADP + P
- glucose + ATP \Leftrightarrow glucose-6-P + ADP $\Delta G^{o'} = -21 \text{ kJ/mol}$

- One reaction can drive another in its unnatural direction
- if the former is accompanied by a greater decrease in Gibbs function than the latter,
- so that the overall ΔG is negative.

glucose + ATP \Leftrightarrow

⇔ glucose-6-P + ADP

ADP + P \rightarrow ATP $\Delta_r G' = +30.5 \text{ kJmol}^{-1}$	-
Paakajia alikoliza	$\Delta_{ m r}G^{\Theta/}$
Reakcije glikolize	$kJ mol^{-1}$
1. glukoza \longrightarrow glukoza-6-fosfat	-16,7
 glukoza−6−fosfat fruktoza−6−fosfat 	+ 1,7
 fruktoza−6−fosfat → fruktoza−1,6−bisfosfat 	-14,2
 fruktoza-1,6-bisfosfat dihidroksiacetonfosfat + gliceraldehid-3-fosfat 	+23,8
 dihidroksiacetonfosfat gliceraldehid-3-fosfat 	+ 7,5
 6. gliceraldehid-3-fosfat 3-fosfogliceroil-1-fosfat 7. bisphosphoglycerate (BPG) 	+ 6,3
$\begin{array}{r} 3-\text{fosfoglicerat}(PG) + P\\ 8. \ 3\text{fosfoglicerat} \end{array}$ $\begin{array}{r} 2-\text{fosfoglicerat} \end{array}$	- 18,8
9. 2-fosfoglicerat	+ 1,7
10. fosfoenolpiruvat → piruvat + P	- 63,1



• ΔG_m^o is related to the equilibrium constant by:

$$\Delta G_m^o = -RT \ln K$$

- The standard molar Gibbs energy of reaction, ∆G_m°, is the change in energy accompanying complete reaction of 1 mol of substance, all species being in their standard state at 25° C
- For other conditions $\Delta G' = \Delta G^o + RT \ln K$

- BPG (bisphosphoglycerate) ⇔ PG (phosphoglycerate) + P
- $\Delta G' = \Delta G^{o} + RT \ln K$
- $\Delta G' = \Delta G^{\circ} + RT \ln [product 1][product 2]$ [reactant 1]
- $\Delta G' = \Delta G^{\circ} + RT \ln [PG][P] / [BPG]$
- △G′ = -18.8 + RT In [PG][P] RTIn [BPG]
- $\Delta G' = -30.5 \text{ kJmol}^{-1}$
- ADP + P \otimes ATP $DG' = +30.5 \text{ kJmol}^{-1}$
- Reaction will result in ATP synthesis when there is:
- a) [PG][P] > [BPG]
- b) [PG][P] < [BPG]
- b)



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due to the degradation of glucose.