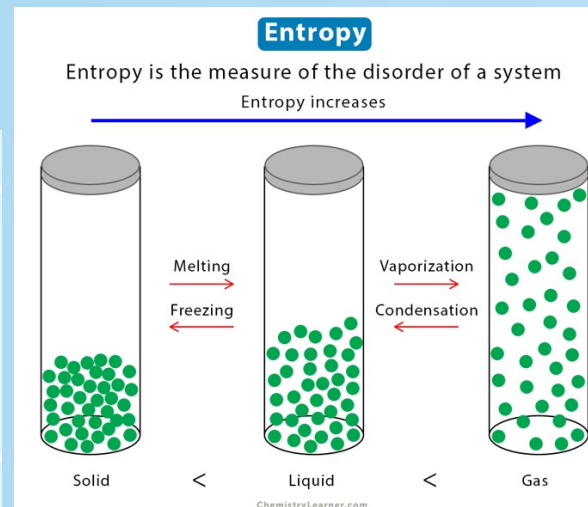
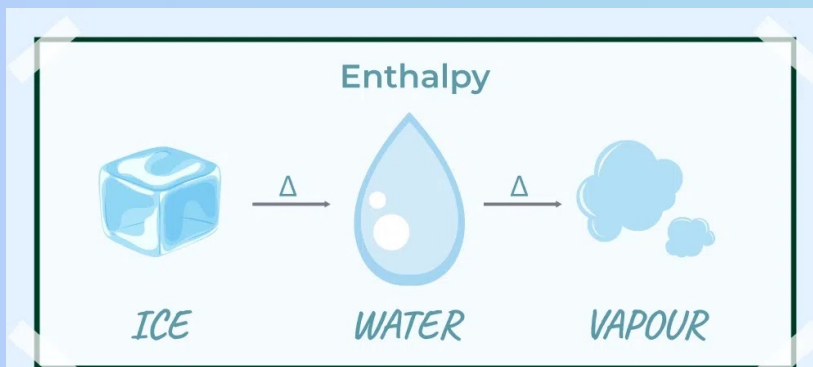


Thermodynamics

By Matthew Hryniewicki

Free Energy (G)

- Change (Δ) in free energy is the energy available to do work
- Predicts the direction in which a reaction will **spontaneously** occur
- Approaches 0 as reaction proceeds to equilibrium
- Defined by:
 - **Enthalpy ΔH** : change in **heat** content of reactants and products; **heat** released/absorber
 - + : Absorbs/requires heat = **ENDOTHERMIC**
 - - : Releases heat = **EXOTHERMIC**
 - **Entropy ΔS** : change in **randomness** or **disorder** of the reactants and products
 - + : more disordered
 - - : less disordered; more ordered



TEMPERATURE (K)

CHANGE IN GIBB'S FREE ENERGY

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

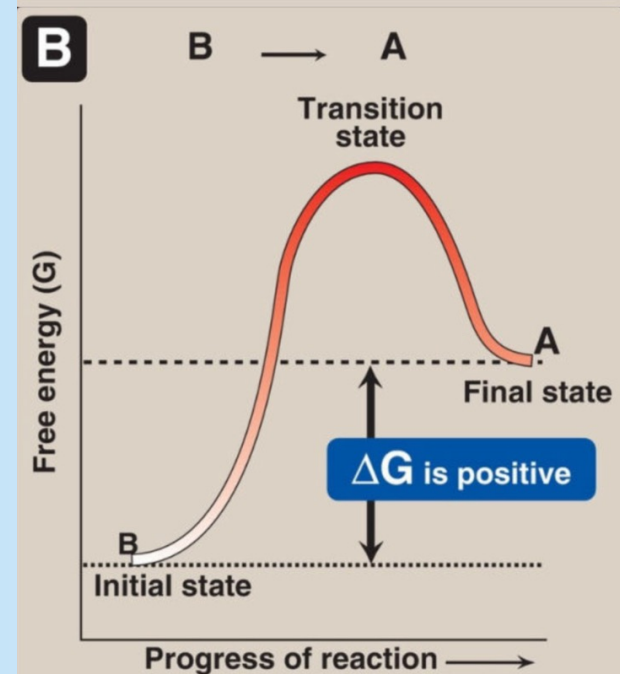
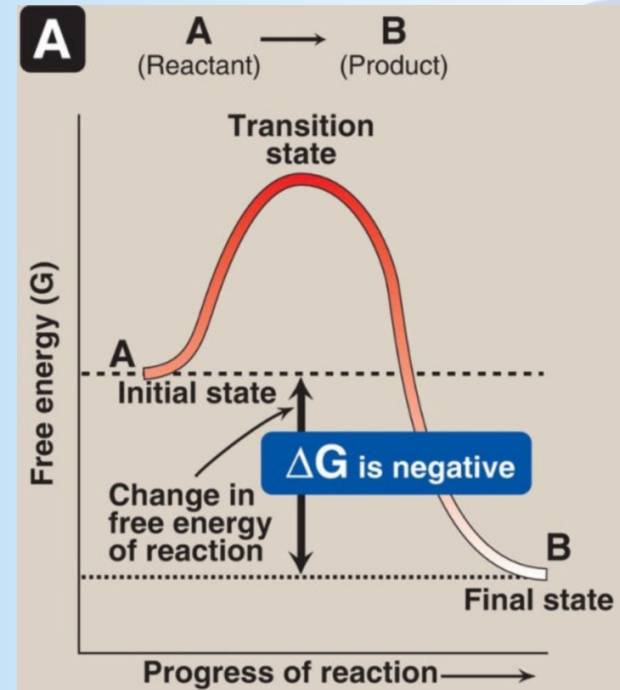
CHANGE IN ENTHALPY (kJ mol^{-1})

CHANGE IN ENTROPY ($\text{J K}^{-1} \text{mol}^{-1}$)

Free Energy Change (ΔG)

ΔG : change in free energy

- $-\Delta G$: net **LOSS** of energy; reaction goes spontaneously as written
 - **EXERGONIC**
 - Reaction continues until **equilibrium** ($\Delta G=0$)
- $+\Delta G$: net **GAIN** of energy; reaction does NOT go spontaneously from $B \rightarrow A$
 - **ENDERGONIC**
- $\Delta G=0$: **EQUILIBRIUM**



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

- Choose a-d to fill up the table below:
(explain your choice – is ΔG negative or positive?):
- spontaneous at all temperatures,
 - not spontaneous at all temperatures,
 - spontaneous at high temperatures,
 - spontaneous at low temperatures

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$		
$\Delta S < 0$		

$\Delta G = \ominus - T\oplus$ $-\Delta G$	$\Delta G = \oplus - T\oplus$ $-\Delta G$ @ high temps
$\Delta G = \ominus - T\ominus$ $\Delta G = \ominus + T\oplus$ $-\Delta G$ @ low temps	$\Delta G = \oplus - T\ominus$ $\Delta G = \oplus + T\oplus$ $+\Delta G$

ΔG^0 : standard free energy change

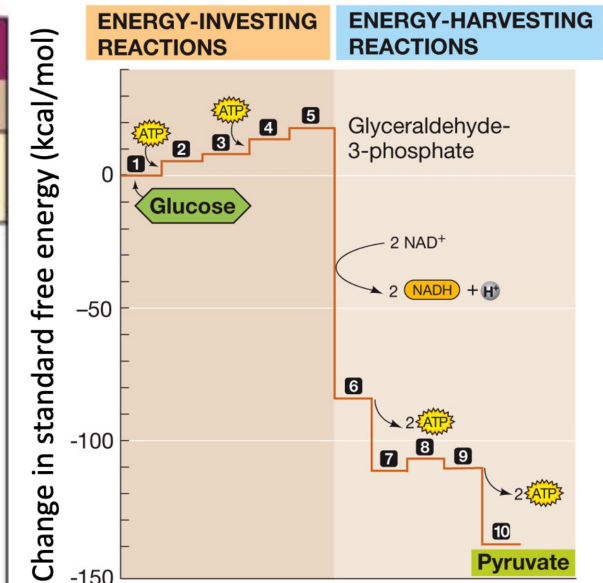
- ΔG^0 : Energy change under standard conditions, proceeding to equilibrium; products and reactants are at concentration of 1M, P=1atm, T= 25° C

$$\Delta G = \Delta G^0 + RT \ln \frac{[B]}{[A]}$$

- Can be used to predict the direction of a reaction under standard conditions because $\Delta G = \Delta G^0 + 0$
- Cannot predict the direction of a reaction under physiological conditions
 - $\Delta G'$: biological conditions (pH=7)
 - $\Delta G^{0'}$: the standard Gibbs free energy change under physiological conditions, (concentration=1M)(pH=7) (P=1 atm) (T=25° C) (Kelvin=273+° C)

Table 17.1
The Reactions of Glycolysis and Their Standard Free-Energy Changes

Step	Reaction	Enzyme	$\Delta G^{\circ'}$		ΔG^{**}
			kJ mol^{-1}	kcal mol^{-1}	kJ mol^{-1}
1	Glucose + ATP \rightarrow Glucose-6-phosphate + ADP	Hexokinase/ Glucokinase	-16.7	-4.0	-33.9
2	Glucose-6-phosphate \rightarrow Fructose-6-phosphate	Glucose phosphate isomerase	+1.67	+0.4	-2.92
3	Fructose-6-phosphate + ATP \rightarrow Fructose-1,6-bisphosphate + ADP	Phosphofruktokinase	-14.2	-3.4	-18.8
4	Fructose-1,6-bisphosphate \rightarrow Dihydroxyacetone phosphate + Glyceraldehyde-3-phosphate	Aldolase	+23.9	+5.7	-0.23
5	Dihydroxyacetone phosphate \rightarrow Glyceraldehyde-3-phosphate	Triose phosphate isomerase	+7.56	+1.8	+2.41
6	2(Glyceraldehyde-3-phosphate + NAD ⁺ + P _i \rightarrow 1,3-bisphosphoglycerate + NADH + H ⁺)	Glyceraldehyde-3-P dehydrogenase	2(+6.20)	2(+1.5)	2(-1.29)
7	2(1,3-bisphosphoglycerate + ADP \rightarrow 3-Phosphoglycerate + ATP)	Phosphoglycerate kinase	2(-18.8)	2(-4.5)	2(+0.1)
8	2(3-Phosphoglycerate \rightarrow 2-Phosphoglycerate)	Phosphoglyceromutase	2(+4.4)	2(+1.1)	2(+0.83)
9	2(2-Phosphoglycerate \rightarrow Phosphoenolpyruvate + H ₂ O)	Enolase	2(+1.8)	2(+0.4)	2(+1.1)
10	2(Phosphoenolpyruvate + ADP \rightarrow Pyruvate + ATP)	Pyruvate kinase	2(-31.4)	2(-7.5)	2(-23.0)
Overall	Glucose + 2ADP + 2P _i + NAD ⁺ \rightarrow 2 Pyruvate \rightarrow 2ATP + NADH + H ⁺	Lactate dehydrogenase	-73.3	-17.5	-98.0
	2(Pyruvate + NADH + H ⁺ \rightarrow Lactate + NAD ⁺)		2(-25.1)	2(-6.0)	2(-14.8)
	Glucose + 2ADP + 2P _i \rightarrow 2 Lactate + 2ATP		-123.5	-29.5	-127.6



Each glucose yields: 2 Pyruvate, 2 ATP, 2 NADH + 2 H⁺

Additive property

- Values are additive in any sequence of consecutive reactions
- As long as the sum is negative, the pathway can proceed *even if* individual reactions are positive

* $\Delta G^{\circ'}$ values are assumed to be the same at 25°C and 37°C and are calculated for standard-state conditions (1 M concentration of reactants and products pH 7.0).

** ΔG values are calculated at 310 K (37°C) using steady-state concentrations of these metabolites found in erythrocytes.

K_{eq} and ΔG^0

$$\Delta G = \Delta G^0 + RT \ln \frac{[B]}{[A]}$$

If we have $+\Delta G^0$, rxn can proceed forward if:
 $\frac{[B]}{[A]}$ is small (meaning: [reactants] > [products])

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

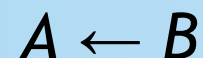
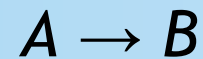
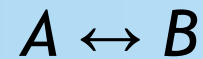
$$\Delta G = 0 = \Delta G^0 + RT \ln \frac{[B]_{eq}}{[A]_{eq}}$$

$$\Delta G^0 = -RT \ln (K_{eq})$$

If $K_{eq} = 1$, then $\Delta G^0 = 0$

If $K_{eq} > 1$, then $\Delta G^0 < 0$

If $K_{eq} < 1$, then $\Delta G^0 > 0$

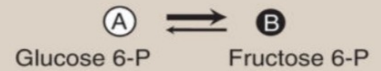
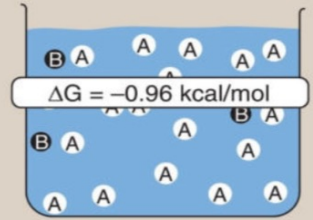


$$\ln (>1) = \oplus$$

$$\ln (<1) = \ominus$$

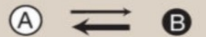
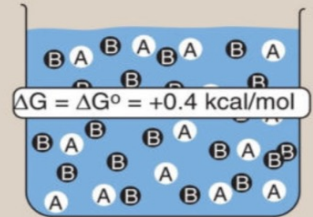
A Nonequilibrium conditions

(A) = 0.9 mol/l (B) = 0.09 mol/l



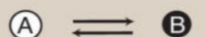
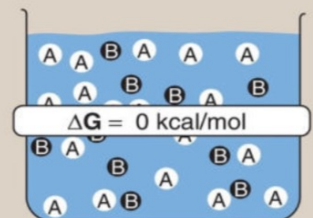
B Standard conditions

(A) = 1 mol/l (B) = 1 mol/l



C Equilibrium conditions

(A) = 0.66 mol/l (B) = 0.33 mol/l



$$K_{eq} = \frac{[\text{Fructose 6-phosphate}]}{[\text{Glucose 6-phosphate}]} = 0.50$$

For the chemical reaction of isomerization $A \rightarrow B$ $\Delta G^0 = -5.71 \text{ kJ/mol}$
($R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $T = 25^\circ \text{C} = 298\text{K}$).

- a. Calculate the equilibrium constant (K) for the reaction at 25°C .
What is the value of ΔG at equilibrium?

ΔG at equilibrium is 0!!!

$$\Delta G^0 = -RT \times \ln(K)$$

$$-5710 = -8.31 \times 298 \times \ln(K)$$

$$-5710 = -2476.38 \times \ln(K)$$

$$2.306 = \ln(K)$$

$$e^{2.306} = K$$

$$10 = K$$

- b. Check if the isomerization reaction $A \rightarrow B$ is spontaneous at 25°C
for the B and A concentrations that equal to 0.1M and 1mM
respectively.

$$\Delta G = \Delta G^0 + RT \times \ln \left(\frac{[B]}{[A]} \right)$$

$$\Delta G = -5710 + 8.31 \times 298 \times \ln \left(\frac{[0.1]}{[0.001]} \right)$$

$$\Delta G = -5710 + 2476.38 \times \ln(100)$$

$$\Delta G = -5710 + 11404.15$$

$$\Delta G = 5694.15$$

ΔG is positive, therefore NOT SPONTANEOUS

Laws of Thermodynamics

1st Law: **CONSERVATION OF ENERGY** - in any physical or chemical change, the total energy of a system, including the surroundings, remains constant

2nd Law: **UNIVERSE ♥ ENTROPY** - in all natural, spontaneous processes, the total entropy of a system always increases

First Law of Thermodynamics

The change in internal energy (ΔU) of a system equals to the heat added to the system minus the work done

Surrounding

Heat supplied (Q)

System (ideal gas)

Work done (W)

$\Delta U = Q - W$

ChemistryLearner.com

Second Law of Thermodynamics

The entropy (S) of any natural and spontaneous process either increases or remains constant

Example: Heat flow from a hot body to a cold body

Hot

Cold

$\Delta S = 0$ For reversible process

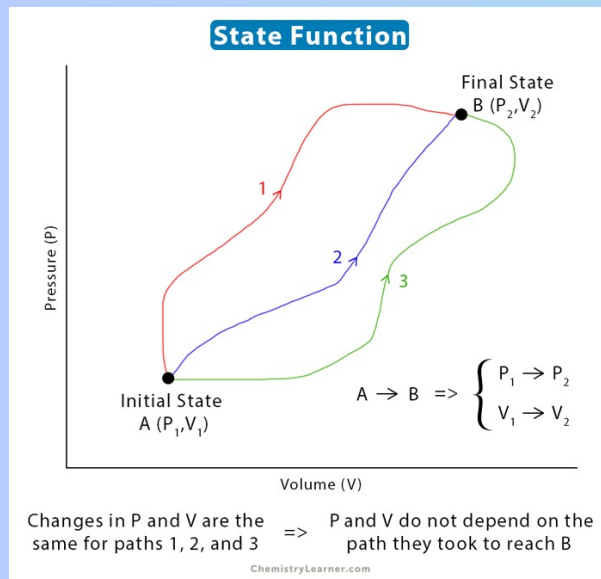
$\Delta S > 0$ For irreversible process

ChemistryLearner.com

State Functions

Properties of a system that depend only on its current state and are independent of the path by which the system reaches that state

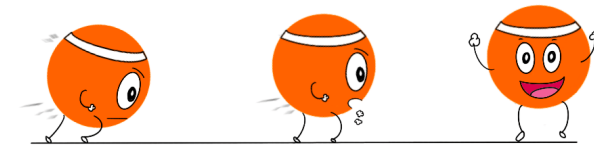
- ΔH
- ΔG
- ΔV
- ΔT



Path functions

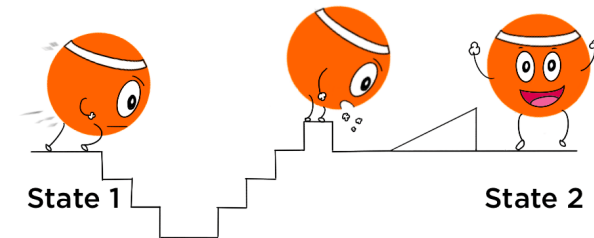
- Work (w)
- Heat (q)

State Functions in Thermochemistry



State 1

State 2



State 1

State 2

State functions are systems where only the start and end points matter rather than the path taken

THANK YOU!



- 1 Go to wooclap.com
- 2 Enter the event code in the top banner

Event code
INDDUB