

American Chemical Society



USNCO Coaching Session National Exam Preparation Tutorial Notes: Thermodynamics

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28 Jan 2022

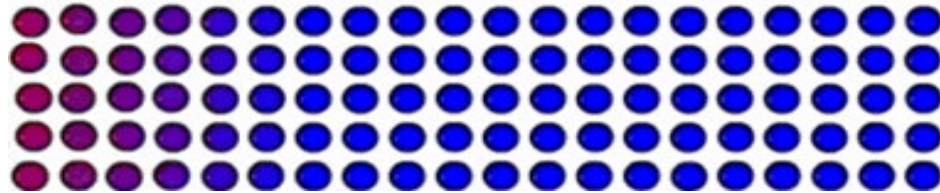
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Thermodynamics

Tracks heat flow between a system
and its surroundings



Important Terms & Equations



The terms energy, enthalpy, and heat are often used interchangeably, but they mean different things.

- **Energy (E)** - the ability to do work or produce heat, potential or kinetic
- **Heat (q)** - the amount of energy that is transferred from one system to its surroundings because of a temperature difference.
- **Enthalpy (H)** - internal energy of a system and usually measured as a change.

$$\Delta E = q + W$$

$$q = \Delta H, \text{ at constant pressure (no volume change)}$$

$$W = -P\Delta V$$

Heat and Enthalpy



Usually we will equate heat with enthalpy.

- Heat (q) is measured by how much energy is lost/gained by the system (when it flows to or away from the system), q is extensive (Joules)

$$q = \Delta H \times \text{amount}$$

- Enthalpy (H) describes the change in the internal energy of the system based on a certain amount, H is intensive (Joules/mole)

Enthalpy - 4 ways to find it

1. **Calorimetry**
2. Enthalpy of formation
3. Hess's Law
4. Bond enthalpies

Specific Heat

Energy required to raise the temperature of 1 g of a substance by 1 °C (or 1 K).

Example: you can handle aluminum foil seconds after removing it from a hot oven. In contrast, a cast iron skillet will stay hot for many minutes.



Specific Heat Capacity, C_p



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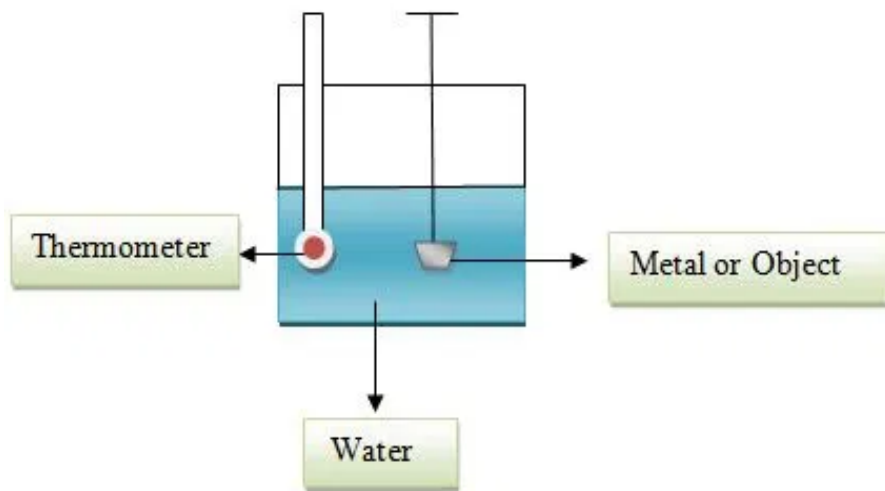


Table of specific heat capacities at 25 °C

Substance	Phase	Specific heat -cp- J/gK
Air	gas	1.0035
Aluminium	solid	0.897
Beryllium	solid	1.82
Cadmium	solid	0.231
Carbon Dioxide	gas	0.839
Helium	gas	5.1932
Hydrogen	gas	14.3
Iron	solid	0.412
Lead	solid	0.129
Nitrogen	gas	1.04
Oxygen	gas	0.918
Polyethylen	solid	2.3027
Sodium	solid	1.23
Steel	solid	0.466
Uranium	solid	0.116
Water (25°C)	liquid	4.1813
Water (100°C - steam)	gas	2.08

Energy Unit - Joule

A physicist would define a Joule as the kinetic energy possessed by a 2 kg mass moving at a speed of 1 meter per second.

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}(2kg)\left(\frac{1m}{1s}\right)^2 = \frac{1 \text{ kg } m^2}{s^2} = 1 \text{ Joule}$$

In chemistry, we will mostly consider thermal energy (q) and electrical energy. So a Joule is the amount of heat required to change the temperature of ~0.25 g of water by 1°C. ($q = mC\Delta T$)

#1 Calorimetry

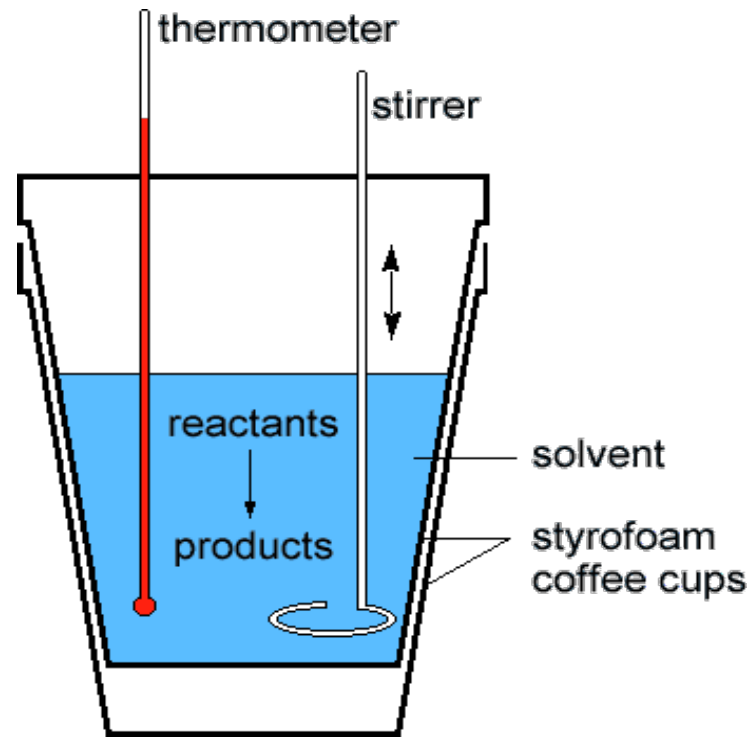
Since we cannot measure the exact enthalpy of the reactants or products, we measure q through calorimetry, the measurement of heat flow.

Heat lost = Heat gained

$$-q_{lost} = q_{gained}$$

$$-mc\Delta T = mc\Delta T$$

$$\Delta T = T_{final} - T_{initial}$$



#1 Calorimetry

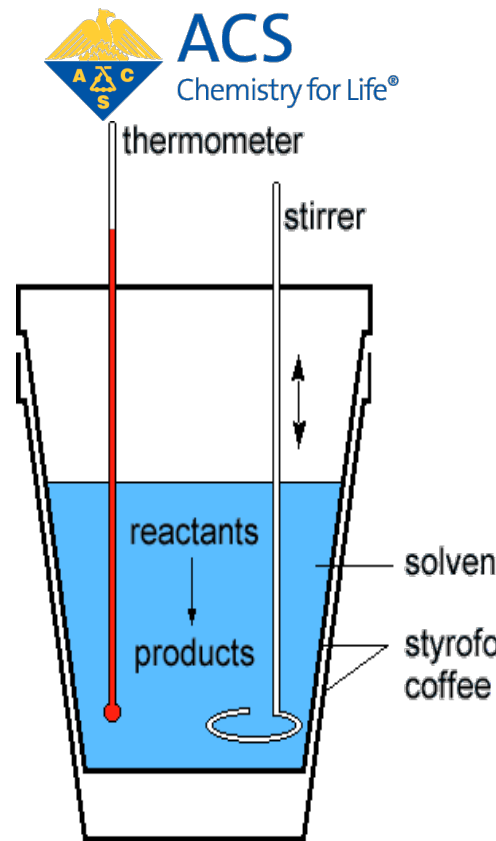
EX: 2.0 g of NaCl is dissolved in 100.0 g of water and the temperature goes from 22.4 °C to 21.8 °C, determine the ΔH_{soln} for NaCl.



#1 Calorimetry

EX: 2.0 g of NaCl is dissolved in 100.0 g of water and the temperature goes from 22.4 °C to 21.8 °C, determine the ΔH_{soln} for NaCl.

$$\begin{aligned}\Delta H_{\text{soln}} &= Q_{\text{soln}}/\text{mol}_{\text{solute}} = mC\Delta T/\text{mol} \\ &= 102*4.18*(-0.6)/0.0342 \\ &= -255.8/0.0342 \\ &= -7480 \text{ J/mol}\end{aligned}$$



Enthalpy - 4 ways to find it

1. Calorimetry
- 2. Enthalpy of formation**
3. Hess's Law
4. Bond enthalpies

Enthalpy of Formation



$$\Delta H_f^\circ$$

Enthalpy change when **one mole** of a compound is made from its elements **@ 1 atm , 25 °C**.



#2 ΔH_f° Enthalpy of formation

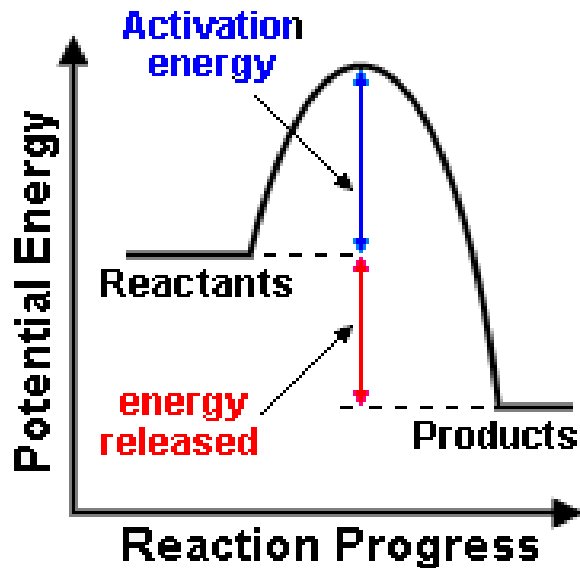


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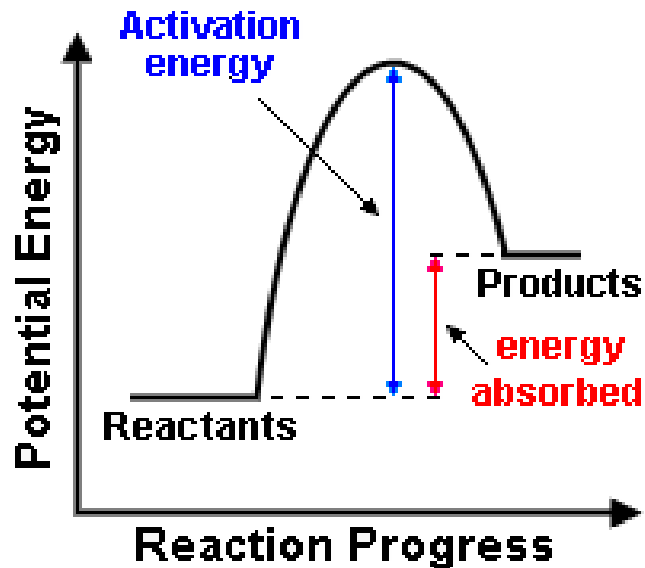
A-8 Appendixes

Appendix G Thermodynamic Quantities for Substances and Ions at 25°C

Substance or Ion	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol·K)	Substance or Ion	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol·K)								
e^- (g)	0	0	20.87	CaO(s)	-635.1	-603.5	38.21	Boron	H_2CO_3 (aq)	-692.0	-680.8	91.2			
Aluminum				Ca(OH) ₂ (s)	-986.1	-898.4	83.39	B(s)	0	0	5.834	<i>Hydrocarbons</i>			
Al(s)	0	0	28.28	Ca ₃ (PO ₄) ₂ (s)	-4120.8	-3884.8	236.0	BCl ₃ (l)	-427.2	-387.4	206	CH ₄ (g)	-74.87	-50.80	186.1
Al ³⁺ (aq)	-531	-485	-321.7	CaSO ₄ (s)	-1434.1	-1321.9	106.7	BF ₃ (g)	-1135.6	-1119.0	254.2	C ₂ H ₂ (g)	226.7	209.2	200.9
AlCl ₃ (s)	-705.6	-630.0	109.3	Carbon				B ₂ O ₃ (s)	-1271.9	-1192.8	53.95	C ₂ H ₄ (g)	52.47	68.39	219.2
Al ₂ O ₃ (s)	-1675.7	-1582.3	50.95	C(g)	716.7	671.3	158.0	Bromine				C ₂ H ₆ (g)	-84.68	-32.89	229.5
Barium				C(s, diamond)	1.897	2.900	2.377	Br(g)	111.9	82.40	174.9	C ₃ H ₈ (g)	-104.7	-23.6	270.2
Ba(g)	179.1	147.0	170.1	C(s, graphite)	0	0	5.740	Br ⁻ (aq)	-121.5	-104.0	82.4	C ₄ H ₁₀ (g)	-125.6	-17.2	310.1
Ba(s)	0	0	62.48	CCl ₄ (g)	-95.98	-53.65	309.7	Br ⁻ (g)	-219.0	-238.8	163.4	C ₆ H ₆ (g)	82.6	129.7	269.2
Ba ²⁺ (aq)	-537.6	-560.7	9.6	CCl ₄ (l)	-135.4	-65.27	216.4	Br ₂ (g)	30.91	3.159	245.3	C ₆ H ₆ (l)	49.0	124.4	173.4
BaCO ₃ (s)	-1216.3	-1137.6	112.1	CF ₄ (g)	-933.2	-888.5	261.3	Br ₂ (l)	0	0	152.2	<i>Alcohols</i>			
BaCl ₂ (s)	-858.6	-810.3	123.7	CN ⁻ (aq)	151	166	118	HBr(g)	-36.44	-53.50	198.6	CH ₃ OH(g)	-200.7	-162.0	239.7
Ba(NO ₃) ₂ (aq)	-952.4	-783.4	302.5	CO(g)	-110.5	-137.2	197.5	Calcium				CH ₃ OH(l)	-238.7	-166.4	126.8
Ba(OH) ₂ (s)	-946.3	-859.3	107.1	CO ₂ (g)	-393.5	-394.4	213.7	Ca(g)	177.8	144.1	154.8	C ₂ H ₅ OH(g)	-235.1	-168.6	282.6
Ba(OH) ₂ ·8H ₂ O(s)	-334.2	-279.3	427	CO ₂ (aq)	-677.1	-521.9	-56.9	Ca(s)	0	0	41.59	C ₂ H ₅ OH(l)	-277.7	-174.9	160.7
BaSO ₄ (s)	-1473.2	-1362.3	132.2	CS ₂ (g)	116.9	66.85	237.9	Ca ⁺ (g)	773.8	732.1	160.5	<i>Aldehydes</i>			
Beryllium				CS ₂ (l)	89.70	65.27	151.3	Ca ²⁺ (aq)	-542.8	-553.5	-53.1	HCHO(g)	-117	-11.3	219.0
Be(s)	0	0	9.440	COCl ₂ (g)	-220.1	-205.9	283.9	Ca ²⁺ (g)	1925.9	—	—	CH ₃ CHO(g)	-166.1	-133.4	246.4
BeO(s)	-608.4	-579.1	13.77	HCN(aq)	150.6	172.4	94.1	CaCO ₃ (s, calcite)	-1206.9	-1128.8	92.9	CH ₃ CHO(l)	-191.8	-128.3	160.4
Be(OH) ₂ (s)	-905.8	-817.9	50.21	HCN(g)	135.1	124.7	201.7	CaCl ₂ (s)	-795.8	-748.1	104.6	<i>Carboxylic acids and ions</i>			
				HCN(l)	108.9	124.9	112.8	CaF ₂ (s)	-1225.9	-1173.5	68.57	HCOOH(aq)	-425.6	-351.0	92
				HC O ₃ ⁻ (aq)	-692.0	-586.8	91.2					HCOOH(l)	-424.7	-361.4	129



Exothermic
reaction



Endothermic
reaction



Endothermic or exothermic?



Enthalpy - 4 ways to find it

1. Calorimetry
2. Enthalpy of formation
3. **Hess's Law**
4. Bond enthalpies

Hess's Law



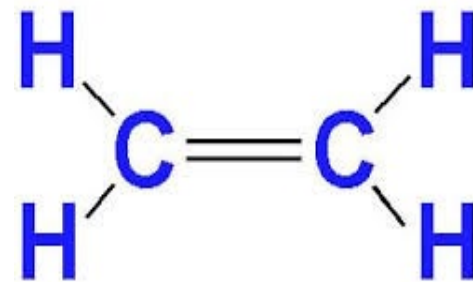
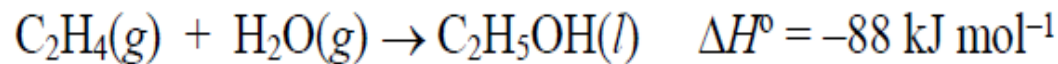
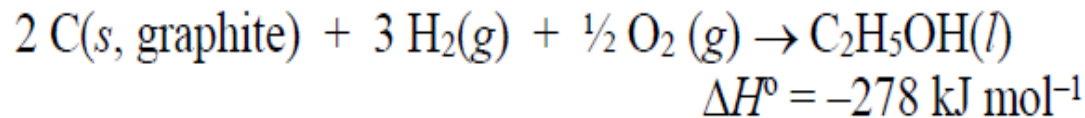
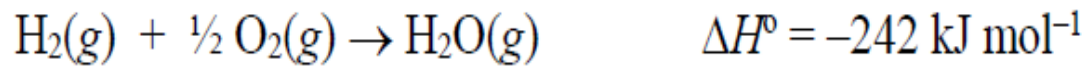
If two or more chemical equations are added, the DH of the individual equations may also be ADDED to find DH the of the final equation.

$$\Delta H_{\text{reaction}} = \sum(\Delta H_f \text{ products}) - \sum(\Delta H_f \text{ reactants})$$

Question #20 of the 2018 National Exam



20. What is the standard heat of formation (ΔH°_f) of gaseous ethylene, $C_2H_4(g)$?



Ethylene

- (A) 16 kJ mol^{-1} (B) 52 kJ mol^{-1}
(C) 83 kJ mol^{-1} (D) 285 kJ mol^{-1}

#4 Bond enthalpies

Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146	Cl—F	253
C—N	293	N—O	201	O—F	190	Cl—Cl	242
C—O	358	N—F	272	O—Cl	203	Br—F	237
C—F	485	N—Cl	200	O—I	234	Br—Cl	218
C—Cl	328	N—Br	243	S—H	339	Br—Br	193
C—Br	276	H—H	436	S—F	327	I—Cl	208
C—I	240	H—F	567	S—Cl	253	I—Br	175
C—S	259	H—Cl	431	S—Br	218	I—I	151
Si—H	323	H—Br	366	S—S	266		
Si—Si	226	H—I	299				
Si—C	301						
Si—O	368						

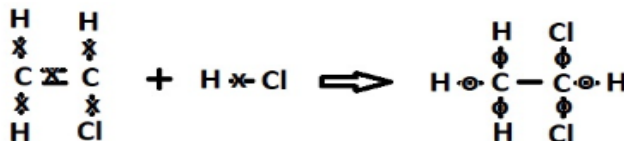
Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941	S=O	523
C=N	615			S=S	418
C≡N	891				
C=O	799				
C=O	1072				



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#4 Bond enthalpies



x = bond broken

o = bond formed

Bonds Broken (requires energy):

C=C +614

H-Cl +431

3x C-H +413x3

C-Cl +328

Bonds Formed (releases energy):

C-C -348

4x C-H -413x4

2 x C-Cl -328x2

- Total** = +2612 (broken) – 2,656 (formed) = -44 kJ/mol

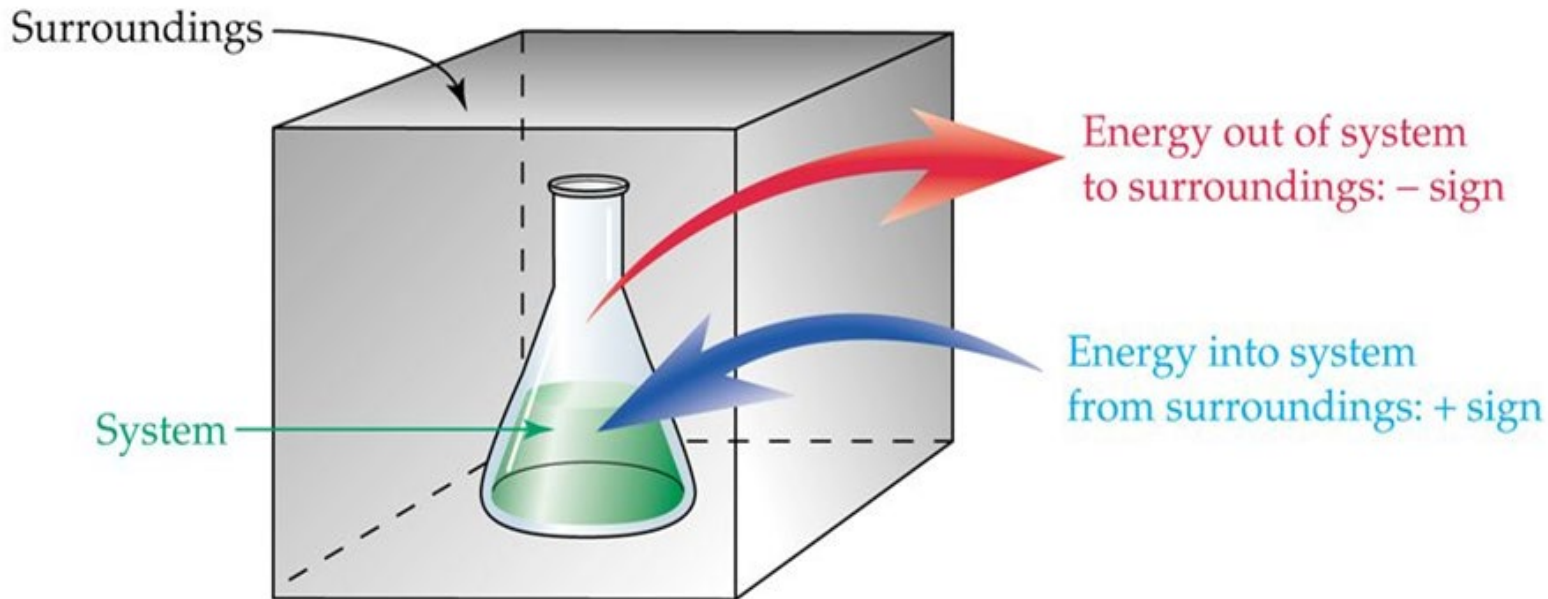
How does the universe like to operate?

- In terms of heat, processes/reactions tend to go in the direction of greater energy to less energy.
 - Example: when you leave your coffee or tea sitting out on the table, it spontaneously becomes _____?
- So, we can say that the universe favors what type of reaction – exothermic or endothermic?



Defining Systems

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



Systems

Gas molecules, ice



Surroundings
Cylinder, piston, your hands

Gibbs Free Energy Equation

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

• Where...

▪ $\Delta G =$

▪ $\Delta H =$

▪ $T =$

▪ $\Delta S =$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$\Delta S_{\text{universe}}$ tends towards a maximum

S is larger when

- There are more gas particles
- Temperature is higher
- Volume is larger
- Lattice structures break down
- Molecules are larger



Remember that if ΔG is -, the rxn is spontaneous,
 so since $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	T	ΔG
negative	negative	low	negative
negative	positive	n/a	always negative
positive	negative	n/a	never negative
positive	positive	high	negative

Free Energy & Spontaneity

Concept	Description	Unit	Favorable for Spontaneous Process
Enthalpy (H)	internal energy of a system and usually measured as a change	kJ/mol	$\Delta H < 0$
Entropy (S)	measure of dispersal/disorder of energy in a system	J/mol*K	$\Delta S > 0$
Gibbs Free Energy (G)	Free energy to do work	kJ/mol	$\Delta G < 0$

$$\Delta G^\circ = - RT \ln K$$

$$\Delta G = \Delta G^\circ - RT \ln Q$$

$$\Delta G^\circ = +$$

$$K < 1$$

$$\Delta G = +$$

$$Q > K$$

$$\Delta G^\circ = 0$$

$$K = 1 \text{ ish}$$

$$\Delta G = 0$$

$$Q = K$$

$$\Delta G^\circ = -$$

$$K > 1$$

$$\Delta G = -$$

$$Q < K$$

- ΔG° is where the equilibrium lies for a reaction,
- ΔG is where you are relative to equilibrium for a specific set of chemicals
- Q is the reaction quotient
- K is the equilibrium constant

EQUATIONS

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$\ln K = \left(\frac{-\Delta H^{\circ}}{R} \right) \left(\frac{1}{T} \right) + \text{constant}$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

ln K vs. 1/T

slope = $-\Delta H^{\circ}/R$

ln k vs. 1/T

slope = $-E_a/R$

$E = E^{\circ} - 0.0592/n * \log Q$ (@298 K)