

American Chemical Society



# USNCO Coaching Session Tutorial Notes: Thermodynamics

Scott Milam, Philip Pietrangelo, Johanna Foley, Jeannette Thompson  
8 January 2021

# Disclaimer



- ACS is providing a remake of these tutorials and images as a courtesy to and for the convenience of the reader. It makes no representations or warranties, express or implied, relative to the accuracy, veracity, ownership, or authority contained within the information provided therein. In accessing these slides, the reader knowingly, willingly, and voluntarily accepts the information's remake “as is”.

# 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.

$$\Delta E = q + W$$

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

$$W = -P\Delta V$$

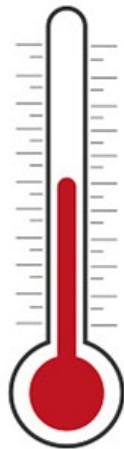
## Energy Unit - Joule

- 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. ( $q = mC\Delta T$ )

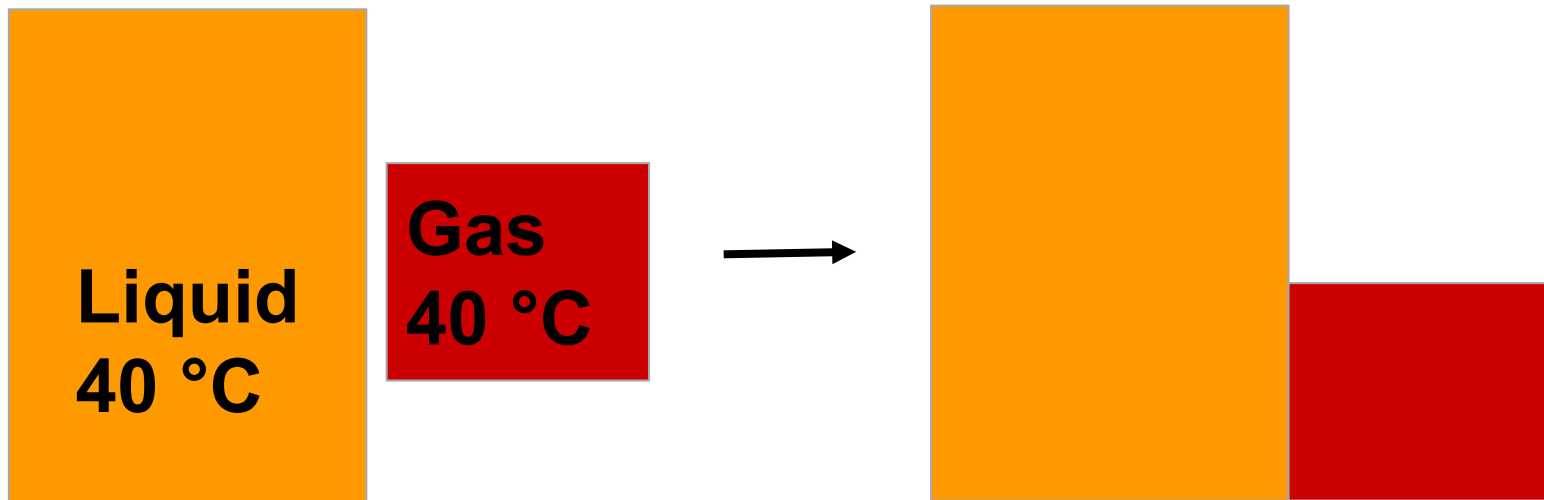
# Temperature



average  
kinetic  
energy

What  
will happen?

# What Will Happen?



# Specific Heat

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

- Highly unusual, but we're used to it

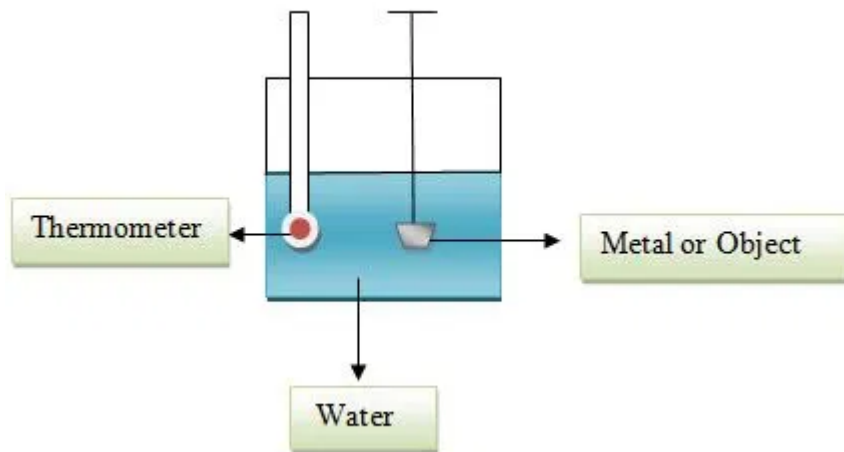
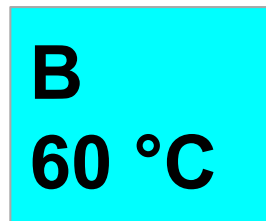
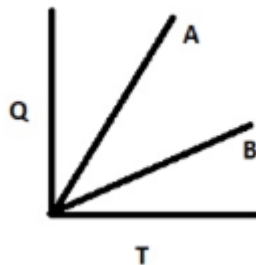


Table of specific heat capacities at 25 °C

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



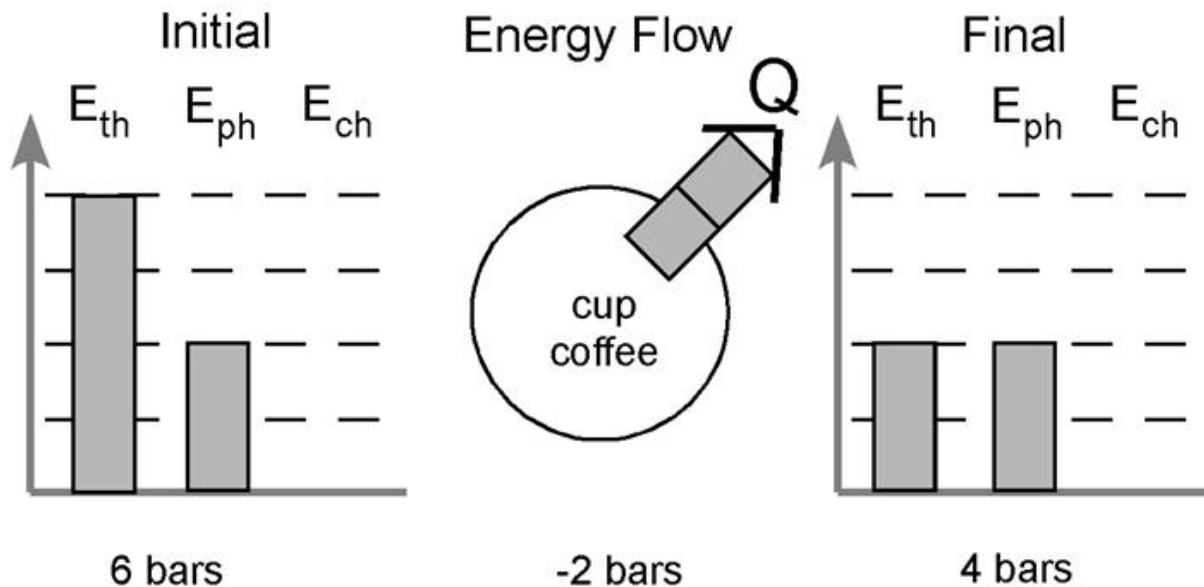
# What Will Happen?



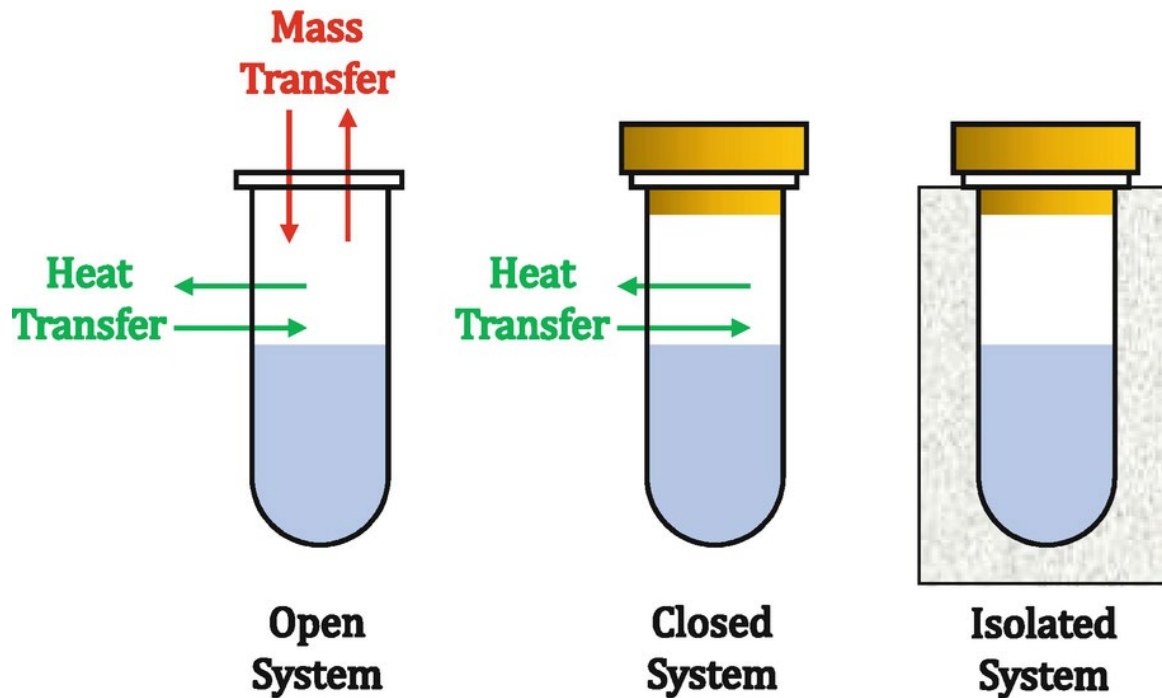
# Endothermic or exothermic?



# Endothermic or exothermic?

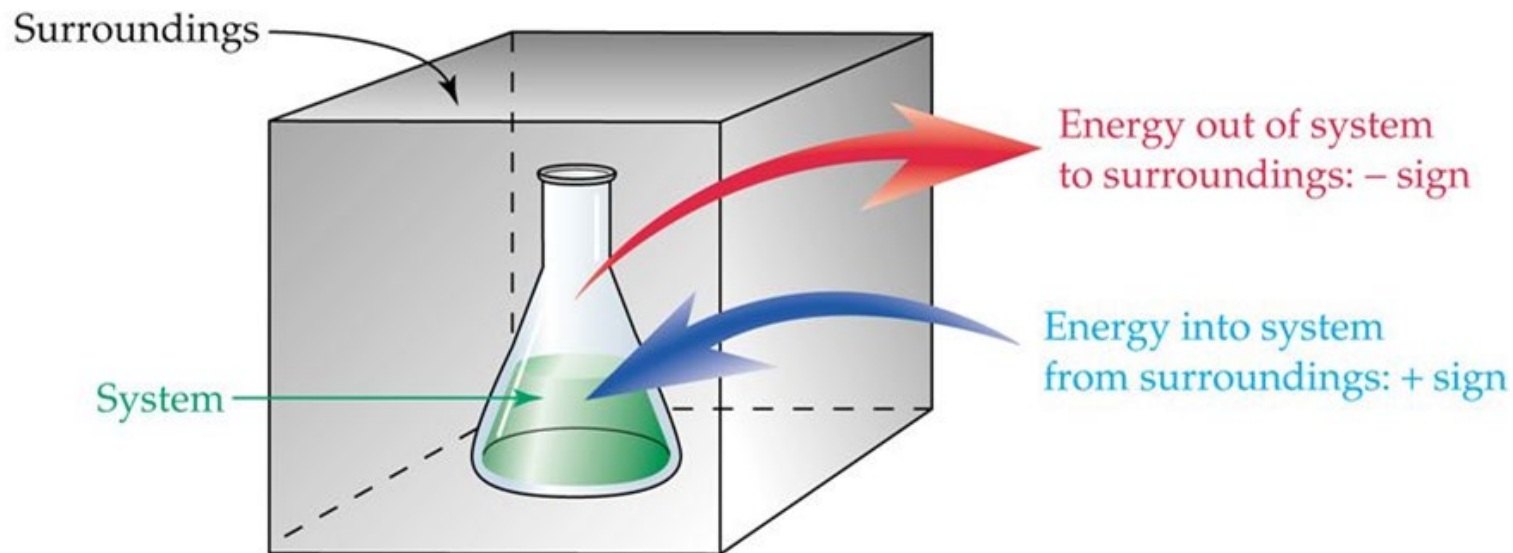


# Systems



# Defining Systems

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



# Systems and Surroundings

- Systems - gas molecules, ice
- Surroundings - cylinder, piston, your hands



# Enthalpy - Four Ways to Find It



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

# #1 Calorimetry

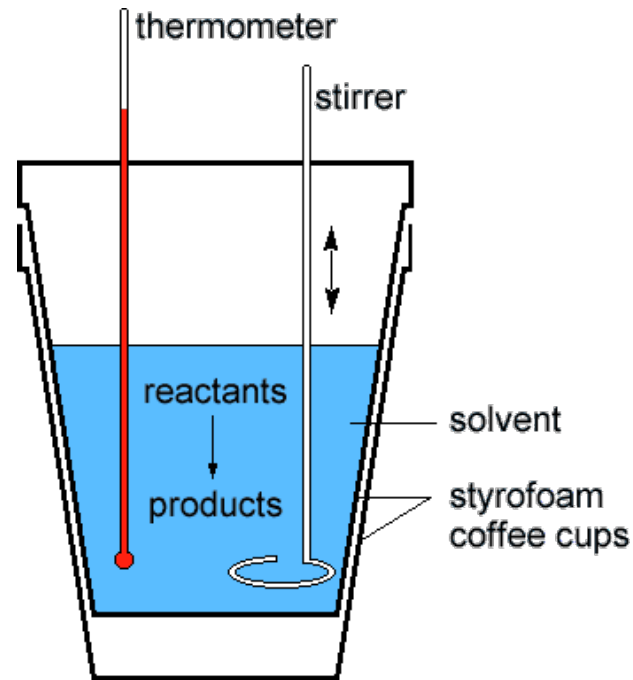
- Since we cannot measure the exact enthalpy of the reactants or products, we measure  $q$  through calorimetry, the measurement of heat flow.

Heat lost = Heat gained

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

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

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





# #1 Calorimetry

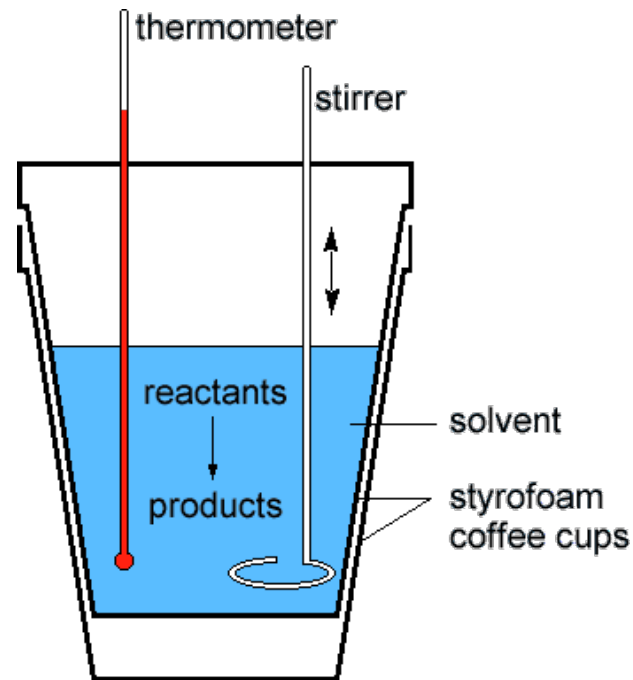
- EX: 2.0 g of NaCl is dissolved in 100.0 g of water and the temperature goes from 22.4 °C to 21.8 °C, determine the  $\Delta H_{\text{soln}}$  for NaCl.



# #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  $\Delta H_{\text{soln}}$  for NaCl.

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



# #2 $\Delta H_f^\circ$ Enthalpy of formation

A-8 Appendixes

## Appendix C | Thermodynamic Quantities for Substances and Ions at 25°C

Substance or Ion	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)	Substance or Ion	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)								
$e^-$ (g)	0	0	20.87	CaO(s)	-635.1	-603.5	38.21	<b>Boron</b>				HClO <sub>3</sub> (aq)	-69.40	-280.8	91.2
<b>Aluminum</b>				Ca(OH) <sub>2</sub> (s)	-986.1	-898.4	83.39	B(s)	0	0	5.834	<b>Hydrocarbons</b>			
Al(s)	0	0	28.28	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	-4120.8	-3884.8	236.0	BCl <sub>3</sub> (l)	-427.2	-387.4	206	CH <sub>4</sub> (g)	-74.87	-50.80	186.1
Al <sup>3+</sup> (aq)	-531	-485	-321.7	CaSO <sub>4</sub> (s)	-1434.1	-1321.9	106.7	BF <sub>3</sub> (g)	-1135.6	-1119.0	254.2	C <sub>2</sub> H <sub>2</sub> (g)	226.7	209.2	200.9
AlCl <sub>3</sub> (s)	-705.6	-630.0	109.3	<b>Carbon</b>				B <sub>2</sub> O <sub>3</sub> (s)	-1271.9	-1192.8	53.95	C <sub>2</sub> H <sub>4</sub> (g)	52.47	68.39	219.2
Al <sub>2</sub> O <sub>3</sub> (s)	-1675.7	-1582.3	50.95	C(g)	716.7	671.3	158.0	<b>Bromine</b>				C <sub>2</sub> H <sub>6</sub> (g)	-84.68	-32.89	229.5
<b>Barium</b>				C(s, diamond)	1.897	2.900	2.377	Br(g)	111.9	82.40	174.9	C <sub>3</sub> H <sub>8</sub> (g)	-104.7	-23.6	270.2
Ba(s)	179.1	147.0	170.1	C(s, graphite)	0	0	5.740	Br <sup>-</sup> (aq)	-121.5	-104.0	82.4	C <sub>4</sub> H <sub>10</sub> (g)	-125.6	-17.2	310.1
Ba <sub>2</sub> (s)	0	0	62.48	CCl <sub>4</sub> (g)	-95.98	-53.65	309.7	Br <sub>2</sub> (g)	-219.0	-238.8	163.4	C <sub>2</sub> H <sub>5</sub> (g)	82.6	129.7	269.2
Ba <sup>2+</sup> (aq)	-537.6	-560.7	9.6	CCl <sub>4</sub> (l)	-135.4	-65.27	216.4	Br <sub>2</sub> (l)	30.91	3.159	245.3	C <sub>2</sub> H <sub>6</sub> (l)	49.0	124.4	173.4
BaCO <sub>3</sub> (s)	-1216.3	-1137.6	112.1	CF <sub>4</sub> (g)	-933.2	-888.5	261.3	HBBr(g)	-36.44	-53.50	198.6	<b>Alcohols</b>			
BaCl <sub>2</sub> (s)	-858.6	-810.3	123.7	CN <sup>-</sup> (aq)	151	166	118	CH <sub>3</sub> OH(g)	-200.7	-162.0	239.7	CH <sub>3</sub> OH(l)	-238.7	-166.4	126.8
Ba(NO <sub>3</sub> ) <sub>2</sub> (aq)	-952.4	-783.4	302.5	CO(g)	-110.5	-137.2	197.5	CH <sub>2</sub> H <sub>3</sub> OH(g)	-235.1	-168.6	282.6	C <sub>2</sub> H <sub>5</sub> OH(l)	-277.7	-174.9	160.7
Ba(OH) <sub>2</sub> (s)	-946.3	-859.3	107.1	CO <sub>2</sub> (g)	-393.5	-394.4	213.7	<b>Calcium</b>				C <sub>2</sub> H <sub>5</sub> OH(l)	-277.7	-174.9	160.7
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O(s)	-3342.2	-2793	427	CO <sub>3</sub> <sup>2-</sup> (aq)	-677.1	-527.9	-56.9	Ca(g)	177.8	144.1	154.8	<b>Aldehydes</b>			
BaSO <sub>4</sub> (s)	-1473.2	-1362.3	132.2	CS <sub>2</sub> (g)	116.9	66.85	237.9	Ca <sup>+</sup> (g)	773.8	732.1	160.5	HCHO(g)	-117	-113	219.0
<b>Beryllium</b>				CS <sub>2</sub> (l)	89.70	65.27	151.3	Ca <sup>2+</sup> (aq)	-542.8	-553.5	-53.1	CH <sub>3</sub> CHO(g)	-166.1	-133.4	246.4
Be(s)	0	0	9.440	COCl <sub>2</sub> (g)	-220.1	-205.9	283.9	Ca <sup>2+</sup> (g)	1925.9	—	—	CH <sub>3</sub> CHO(l)	-191.8	-128.3	160.4
BeO(s)	-608.4	-579.1	13.77	HCN(aq)	150.6	172.4	94.1	CaCO <sub>3</sub> (s, calcite)	-1206.9	-1128.8	92.9	<b>Carboxylic acids and ions</b>			
Be(OH) <sub>2</sub> (s)	-905.8	-817.9	50.21	HCN(g)	135.1	124.7	201.7	CaCl <sub>2</sub> (s)	-795.8	-748.1	104.6	HCOOH(aq)	-425.6	-351.0	92
				HCN(l)	108.9	124.9	112.8	CaF <sub>2</sub> (s)	-1225.9	-1173.5	68.57	HCOOH(l)	-424.7	-361.4	129
				HCO <sub>3</sub> <sup>-</sup> (aq)	-692.0	-586.8	91.2								

## #2 $\Delta H_f^\circ$ Enthalpy of formation

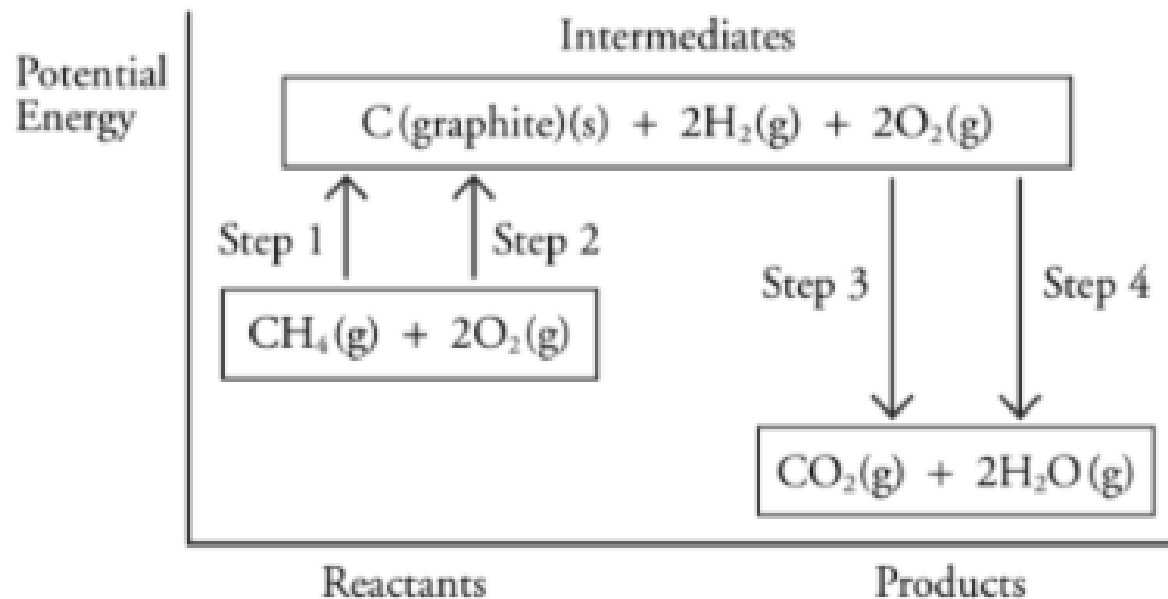


$$\Delta H_f^\circ$$

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



## #2 $\Delta H_f^\circ$ Enthalpy of formation



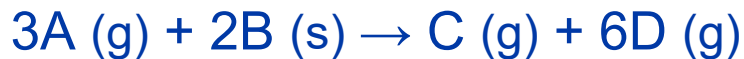
## #3 Hess's Law

- Prerequisite Info



## #3 Hess's Law

- Determine the enthalpy for the following reaction:



Given the following:



$$\Delta H = -34 \text{ kJ/mol}$$



$$\Delta H = +122 \text{ kJ/mol}$$

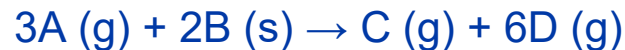


$$\Delta H = -12 \text{ kJ/mol}$$



$$\Delta H = -41 \text{ kJ/mol}$$

# #3 Hess's Law



1	$2A \rightarrow 2D + E$	$\Delta H = -34 \text{ kJ/mol}$	<b>Keep as is</b>	$2A \rightarrow 2D + E$	$\Delta H = -34 \text{ kJ/mol}$
2	$2F + C \rightarrow E$	$\Delta H = +122 \text{ kJ/mol}$	<b>Reverse</b>	$E \rightarrow 2F + C$	$\Delta H = -122 \text{ kJ/mol}$
3	$\frac{1}{2} A + B \rightarrow D$	$\Delta H = -12 \text{ kJ/mol}$	<b>Multiply by 2</b>	$A + 2B \rightarrow 2D$	$\Delta H = -24 \text{ kJ/mol}$
4	$2D \rightarrow 2F$	$\Delta H = -41 \text{ kJ/mol}$	<b>Reverse</b>	$2F \rightarrow 2D$	$\Delta H = +41 \text{ kJ/mol}$
Overall	$2A + E + A + 2B + 2F \rightarrow 2D + E + 2F + C + 2D + 2D$				<b><math>\Delta H = 139 \text{ kJ/mol}</math></b>



# #4 Bond Enthalpies



ACS  
Chemistry for Life®

## Average Bond Enthalpies (kJ/mol)

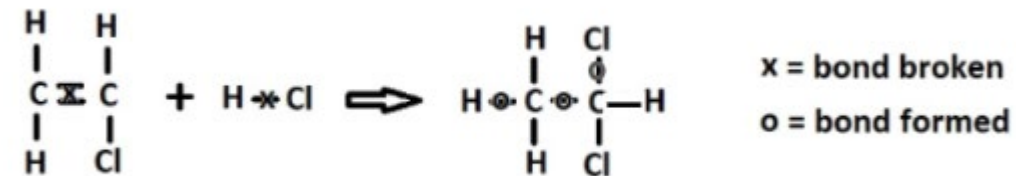
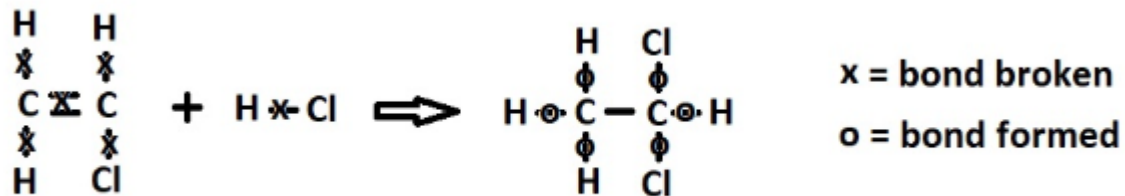
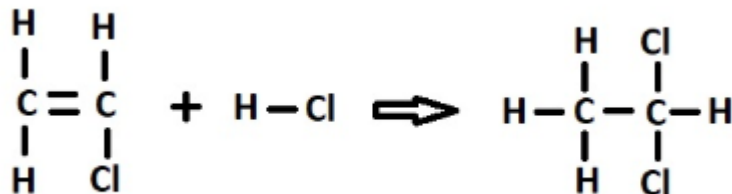
### Single Bonds

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

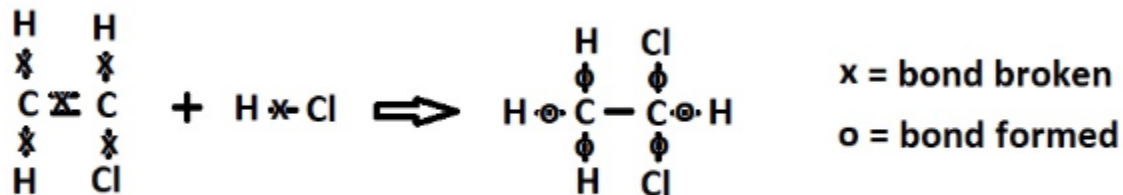
### Multiple Bonds

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

# #4 Bond Enthalpies



# #4 Bond Enthalpies



## Bonds Broken:

C=C	+614
H-Cl	+431
3x C-H	+413x3
C-Cl	+328

## Bonds Formed:

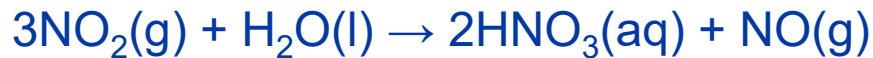
C-C	-348
4x C-H	-413 x 4
2 x C-Cl	-328 x 2

**Total = -44 kJ/mol**

# Enthalpy - Four Ways to Find It

- **Calorimetry** - temperature changes, amounts; be wary of signs
- **Enthalpy of formations** - just a reaction and nothing else (table exists somewhere)
- **Hess's Law** - multiple reactions, 1 with unknown enthalpy
- **Bond enthalpies** - Lewis structures for a reaction (table exists somewhere), don't use a formula for this one!

???



$$\Delta H = ???$$



$$\Delta H = -116 \text{ kJ}$$

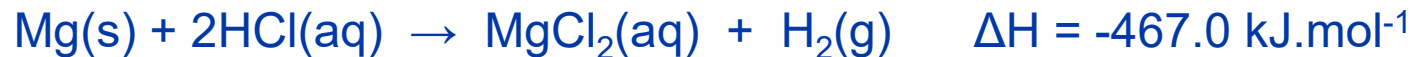


$$\Delta H = -256 \text{ kJ}$$



$$\Delta H = +183 \text{ kJ}$$

# What is Enthalpy Though?



Under standard pressure:

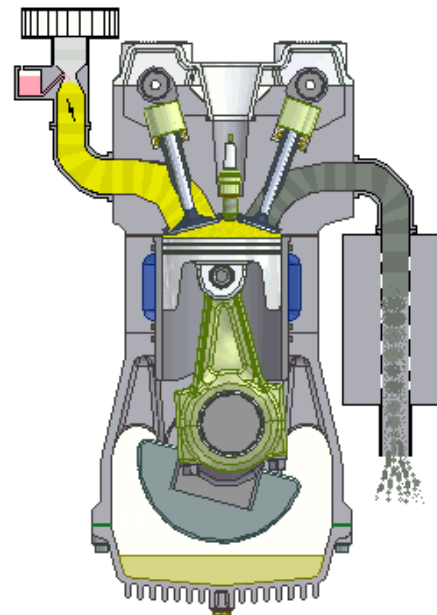
$$W = -2.2 \text{ kJ} \quad q = -467 \text{ kJ}$$

$$\Delta E = q + W$$

## Power Stroke

- $-\Delta E$  Energy Lost by the system
- $-q$  Heat is lost by the system  
*i.e. during combustion. Exothermic.*
- $-W = -P\Delta V$  As the gases expand, work is done by the system.  $\Delta V (+)$

Energy is transferred from the system (gases) to the piston (surroundings)



$$H = E + PV$$

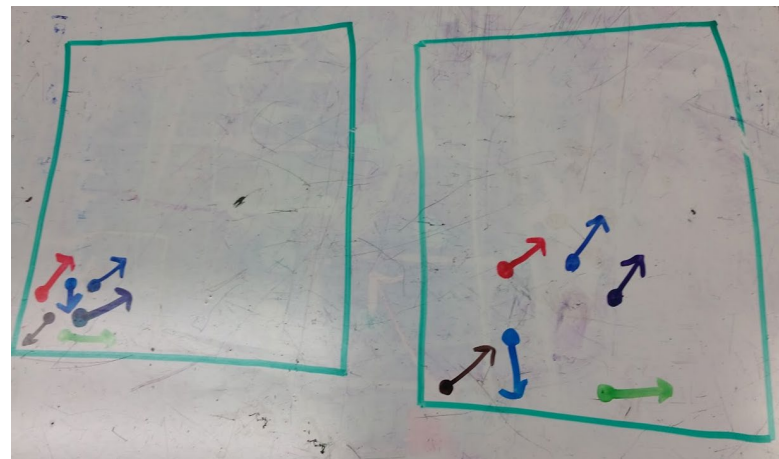
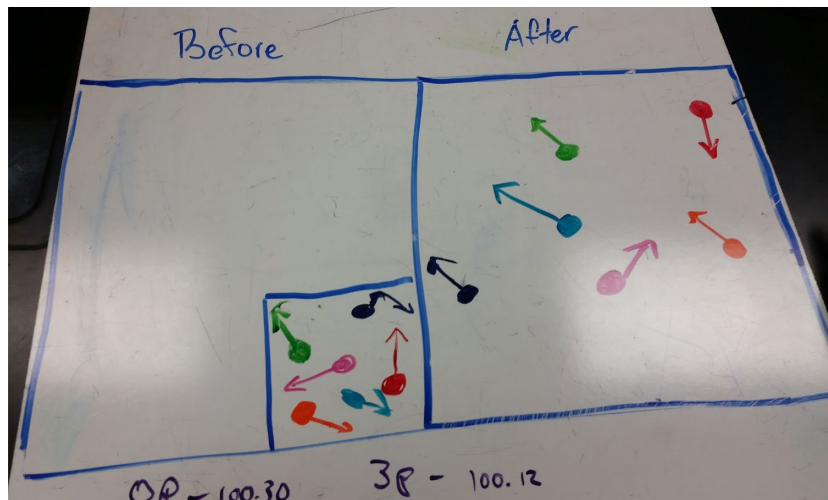
- $\Delta H = \Delta E + P\Delta V$
- $\Delta H = q$



# Why does the ball roll in a straight line?



# Why do gas particles fill their container?



# Why do gas particles fill their container?



# Entropy, Rudolph Clausius



- $dS = dq/T$
- $S = k \ln w$

# Entropy

- $dS_{\text{universe}} = dS_{\text{sys}} + dS_{\text{surr}}$
- $dS_{\text{universe}}$  tends towards a maximum

## S is larger when

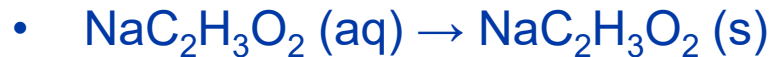
- There are more gas particles
- Temperature is higher
- Volume is larger
- Lattice structures break down
- Molecules are larger

# Willard Josiah Gibbs

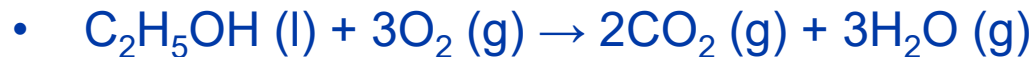


- $\Delta G = \Delta H - T\Delta S$
- $dG = -TdS_{\text{surr}} - TdS_{\text{sys}}$

## Willard Josiah Gibbs



$$\Delta H = - \qquad \Delta S = -$$



$$\Delta H = - \qquad \Delta S = +$$



# 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	$\Delta G < 0$

# Free Energy & Spontaneity



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

If  $\Delta H = -$  and  $\Delta S = -$

$\Delta G$  is - @ low T

If  $\Delta H = -$  and  $\Delta S = +$

$\Delta G$  is - always

If  $\Delta H = +$  and  $\Delta S = -$

$\Delta G$  is - never

If  $\Delta H = +$  and  $\Delta S = +$

$\Delta G$  is - @ high T

# Thermodynamically Favored - “Spontaneous”

- T and P can affect *favorability*
- Not favored in the opposite direction
- Favorable does not mean fast
- $\Delta H$ : (-) ( $\Delta S_{\text{surr}}$ ; (+))
- $\Delta S_{\text{sys}}$ ; (+)
- $\Delta G$ ; (-)



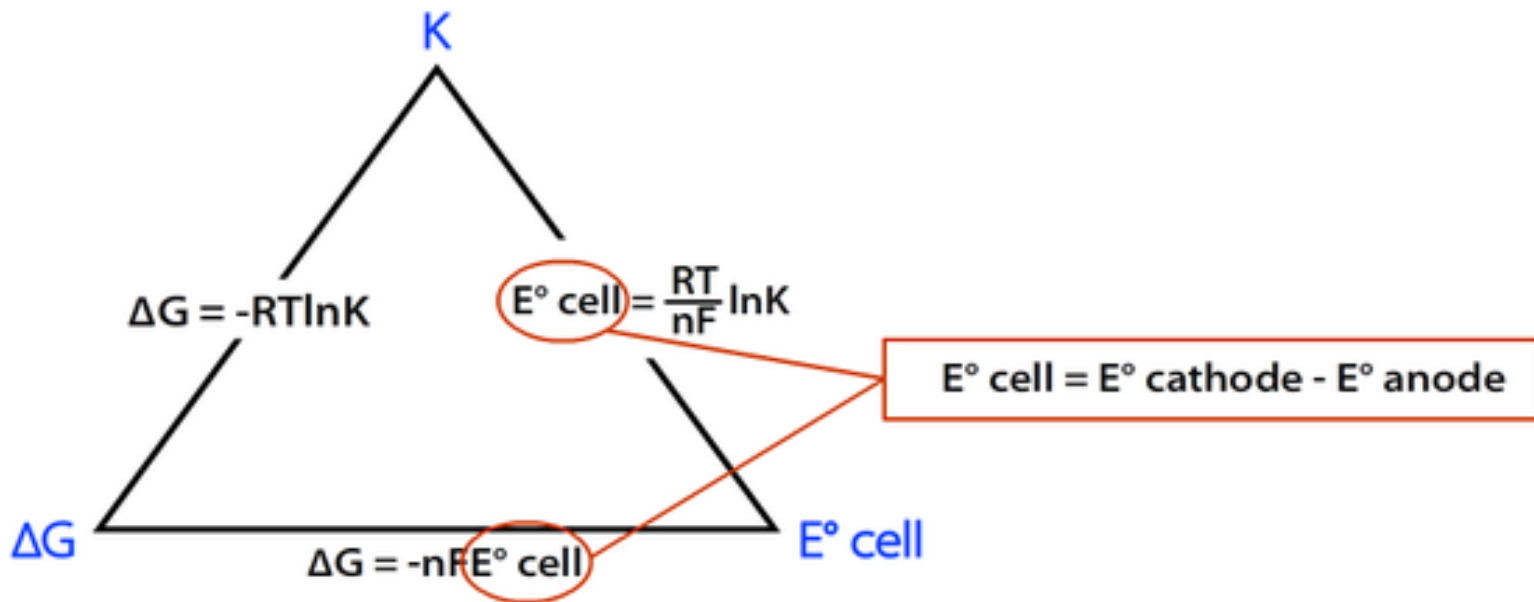
Not favored!

# Thermodynamically Favored - “Spontaneous”



$\Delta G^\circ$	$E^\circ$	K
-	+	large
0	0	~ 1
+	-	tiny

# Thermodynamically Favored - “Spontaneous”



# Thermodynamically Favored - “Spontaneous”



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

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

$\Delta G^{\circ} = +$	$K < 1$	$\Delta G = +$	$Q > K$
$\Delta G^{\circ} = 0$	$K = 1$ ish	$\Delta G = 0$	$Q = K$
$\Delta G^{\circ} = -$	$K > 1$	$\Delta G = -$	$Q < K$

- $\Delta G^{\circ}$  is where the equilibrium lies for a rxn
- $\Delta G$  is where you are relative to equilibrium for a specific set of chemicals

# Thermodynamically Favored - “Spontaneous”



- $E = E^\circ - 0.0592/n * \log Q$  (@298 K)
- $\ln K$  vs.  $1/T$             slope =  $-\Delta H^\circ/R$
- $\ln k$  vs.  $1/T$             slope =  $-E_a/R$

## EQUATIONS

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

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

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

# Heat and Enthalpy

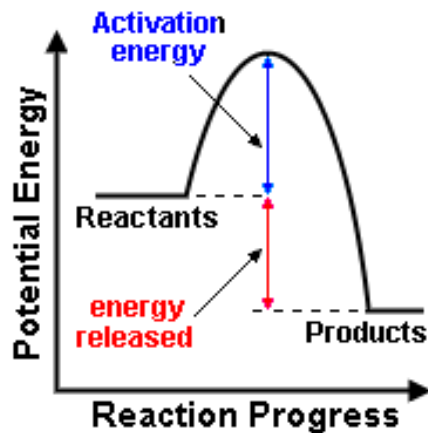


- Usually we will equate heat with enthalpy.
  - Heat ( $q$ ) is measured by how much energy is lost/gained by the system (when it flows to or away from the system),  $q$  is extensive (Joules)
  - Enthalpy ( $H$ ) describes the change in the internal energy of the system based on a certain amount,  $H$  is intensive (Joules/mole)

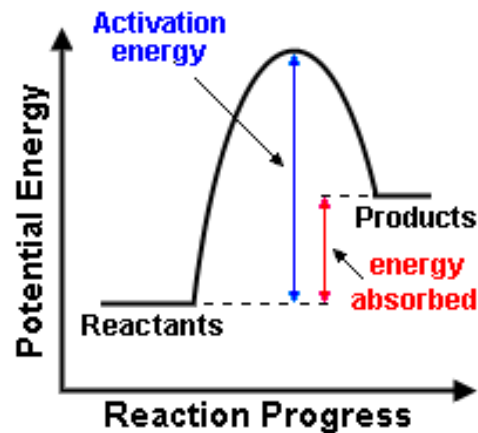
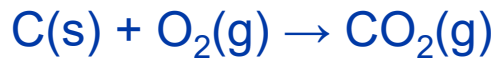
$$q = \Delta H \times \text{amount}$$



# Heat and Enthalpy



Exothermic  
reaction

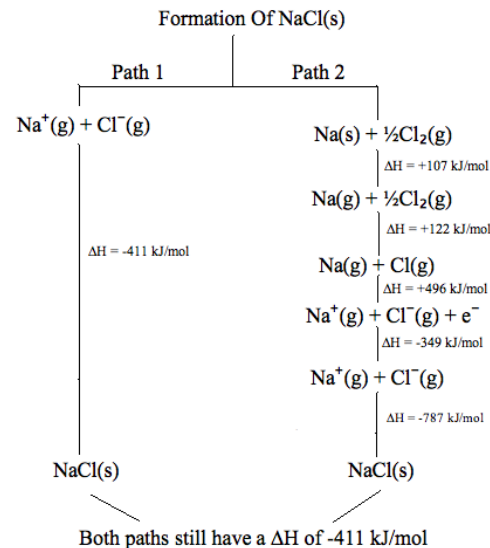
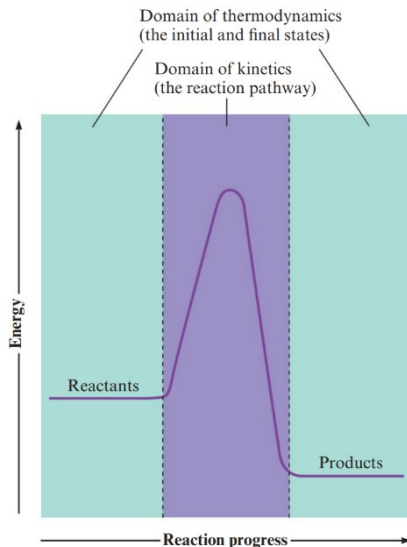


Endothermic  
reaction

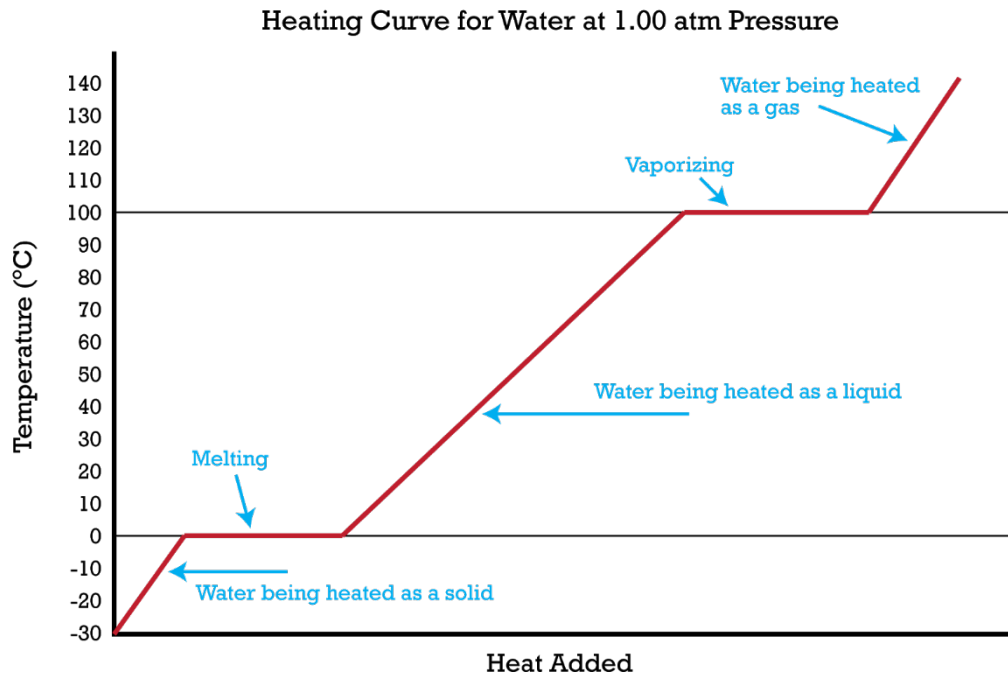


# Heat and Enthalpy

- All energy changes are **state functions** which means they are **pathway independent**.



# Heat and Enthalpy



# Free Energy & Equilibrium

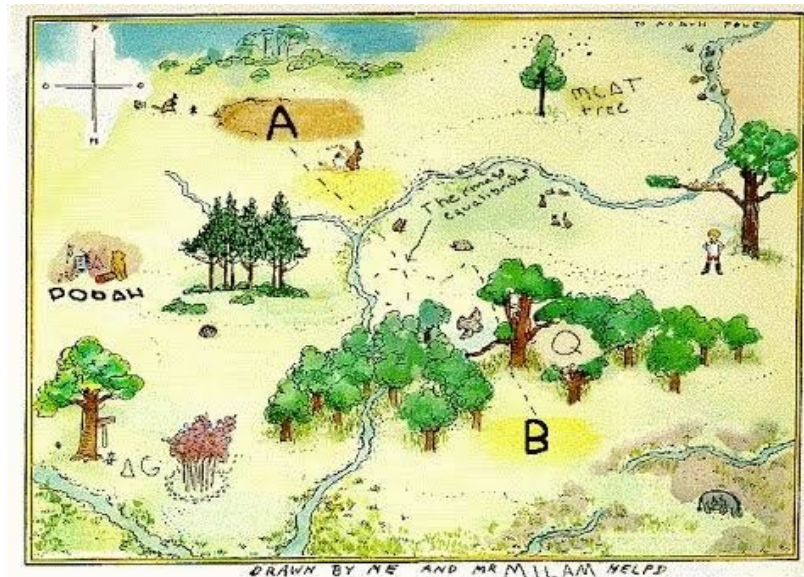
- $\Delta G^\circ = -RT \ln K$

Calculate  $\Delta G^\circ$  in kJ/mol for a reaction at 300K in which  $K_{eq} = 2.2 \times 10^{-4}$

Free Energy	Equilibrium Constant	Spontaneous Direction	Favored direction
$\Delta G^\circ < 0$	$K > 1$	Forward	Favors forward reaction (products)
$\Delta G^\circ > 0$	$K < 1$	Reverse	Favors reverse reaction (reactants)
$\Delta G^\circ = 0$	$K = 1$	Neither	The system is at equilibrium. No “net” movement of the reaction.

# Thermodynamics Song

- <https://www.youtube.com/watch?v=guxNFQBDFjk&list=PLtjPBoq7-geLJeEB2yGk3tZ2wRYtUkSLa&index=6&t=2s>



# Sample Questions



- Local Exam 2018, #21
- Local Exam 2018, #22
- National Exam 2018, #20
- National Exam 2018, #23