

Big Idea 5: The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.

Enduring Understanding

- 5.A: Two systems with different temperatures that are in thermal contact will exchange energy. The quantity of thermal energy transferred from one system to another is called heat.
- 5.B: Energy is neither created nor destroyed, but only transformed from one form to another.
- 5.C: Breaking bonds requires energy, and making bonds releases energy.
5.D: Electrostatic forces exist between molecules as well as between atoms or ions, and breaking the resultant intermolecular interactions requires energy.
- 5.E: Chemical or physical processes are driven by a decrease in enthalpy or an increase in entropy, or both

Conservation of energy

- Energy entering or leaving a system can be classified in two ways
 - Heat: Usually thermal heat ($q = m * T * c$)
 - Work: Movement caused by expanding gases
- Total energy = $q + W$
 - In both cases they are conserved inside and outside of a system

System surroundings

$$+q \Rightarrow -q$$

$$+w \Rightarrow -w$$

$$-q \Rightarrow +q$$

$$-w \Rightarrow +w$$

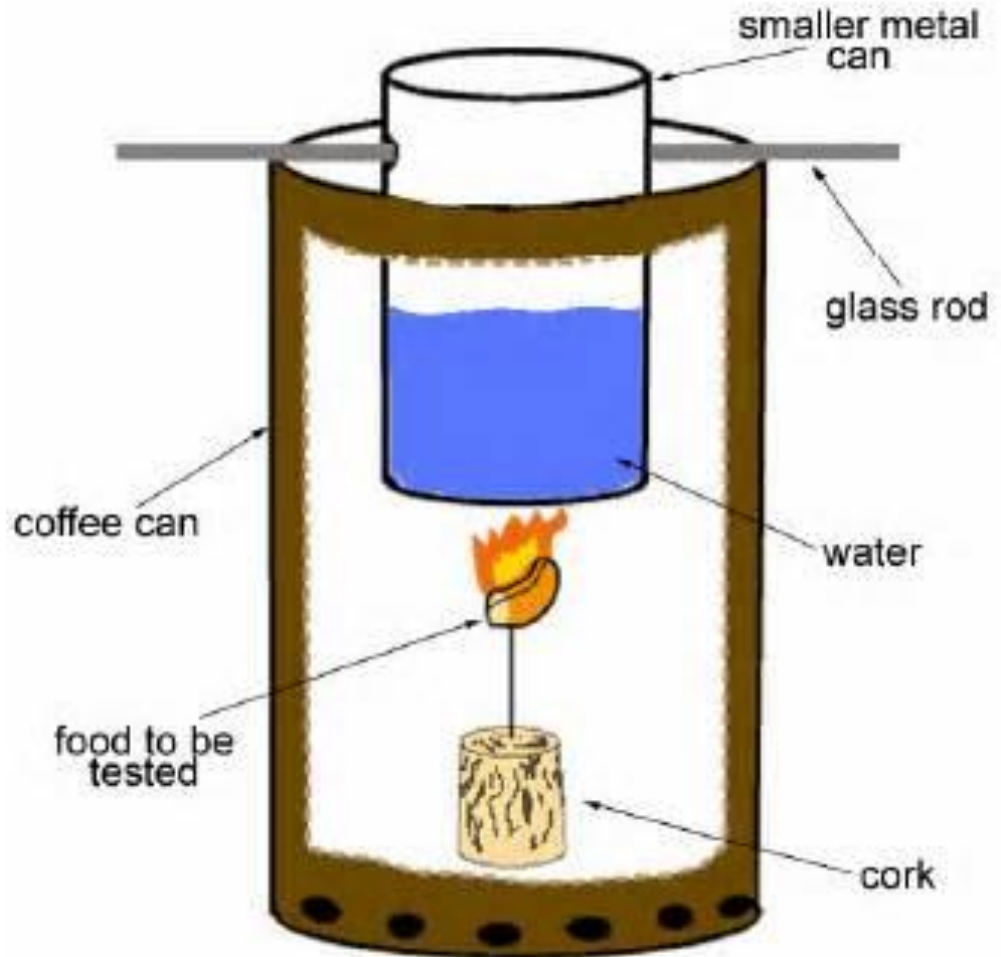
Second Law of thermodynamics

- For any spontaneous process Total entropy (system + surroundings) will increase!
- Entropy = disorder (movement)
- $+\Delta S$ = increasing in disorder increasing movement
 - $X(s) \Rightarrow X(l)$

Remember: A system is perfectly capable of losing disorder, just means surrounds must lose disorder. We are almost always only looking at the system itself.

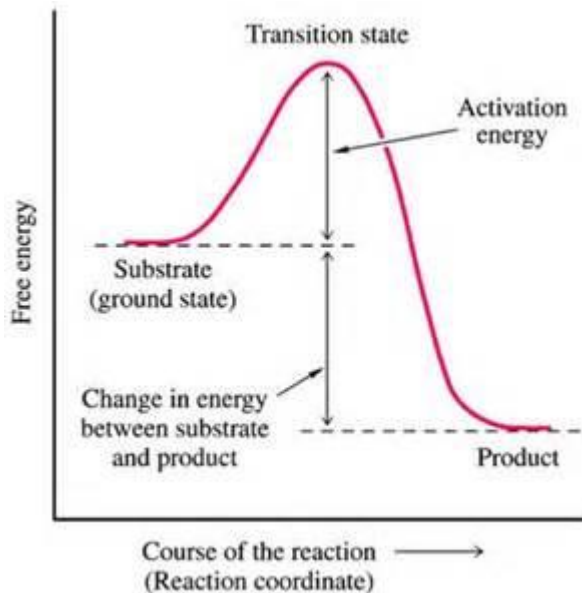
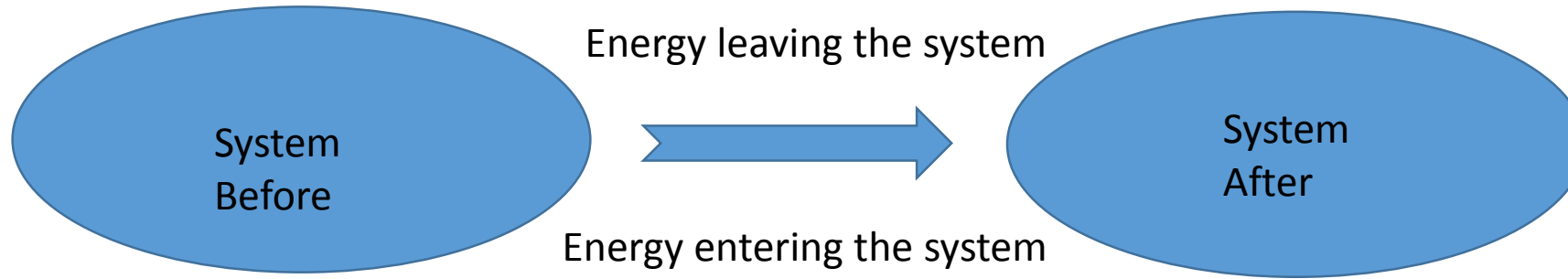
How much energy does a reaction give off?

- Physically collect the energy using lab technique calorimetry.
- Crude example but, energy lost = energy gained.
- $q = m * T * C$



How much energy does a substance give off?

Final – Initial



+ ΔH : System is gaining energy; surroundings get colder

- ΔH : System is losing energy; surroundings get hotter

This is the basis for the mathematical relationships below.

$$\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

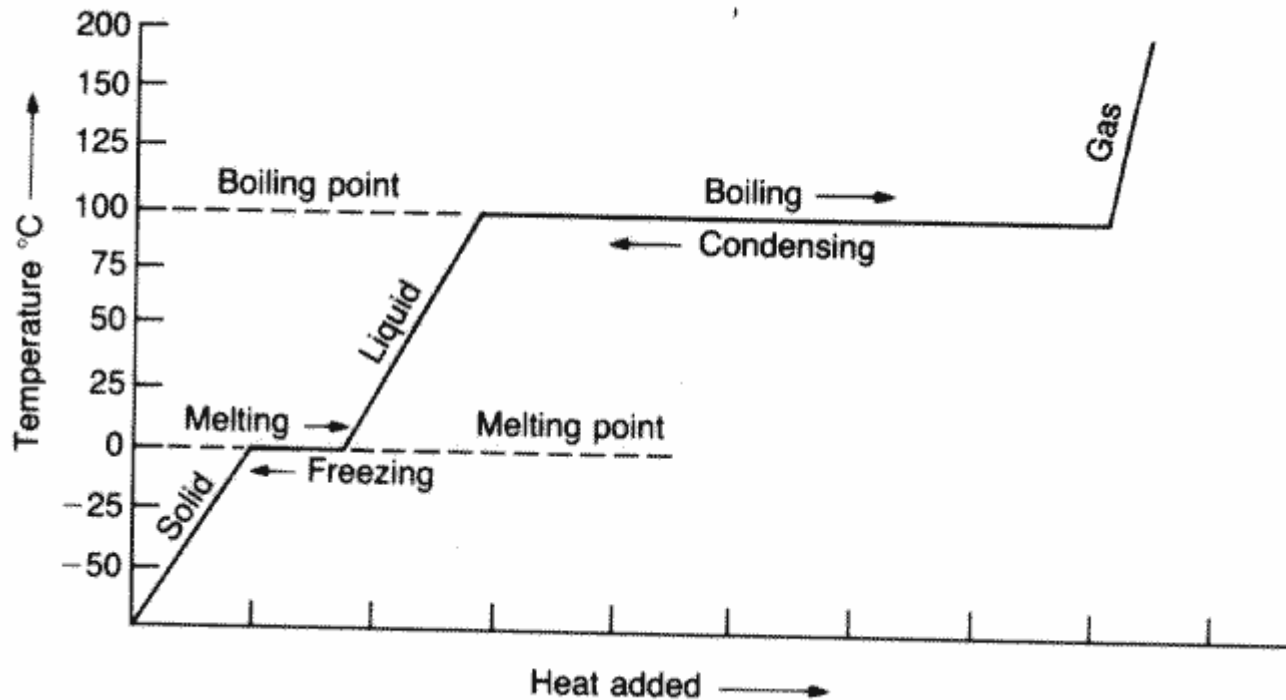
$$\Delta S_{\text{rxn}} = S_{\text{products}} - S_{\text{reactants}}$$

$$\Delta G_{\text{rxn}} = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

How do I quantify the amount of energy given off?

- Depends,
 - $q = \text{mass} * \Delta T * c$ (specific heat)
 - This will tell us how much energy is absorbed from another substance.
 - From a chemical reaction?
 - $\text{C}_3\text{H}_8 + 5\text{O}_2 \Rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \quad \Delta H = \text{XkJ/rxn}$
 - If 50 grams of propane can you determine how much energy is given off?

Heating curve (adding or removing energy)



- Endothermic
 - $S = L = G$
 - Energy added
- Exothermic
 - $G = L = S$
- Changing temperature
 - $q = m\Delta Tc$
- Changing phase
 - Energy/kg
 - ΔH_{fusion} $\Delta H_{\text{vaporization}}$

Heat capacity vs. specific heat

- Specific heat: amount of energy needed to change 1 gram of a substance 1 C. (4.18J = 1 calorie for water)
- Heat capacity:
 - Amount of energy it takes to raise 1 gram of a substance 1C. The mass in these situations is locked.
 - Example: a calorimeter cup has a Heat capacity constant. (energy/C) The mass of the cup will not change.

Enthalpy: What is it and how do I calculate?

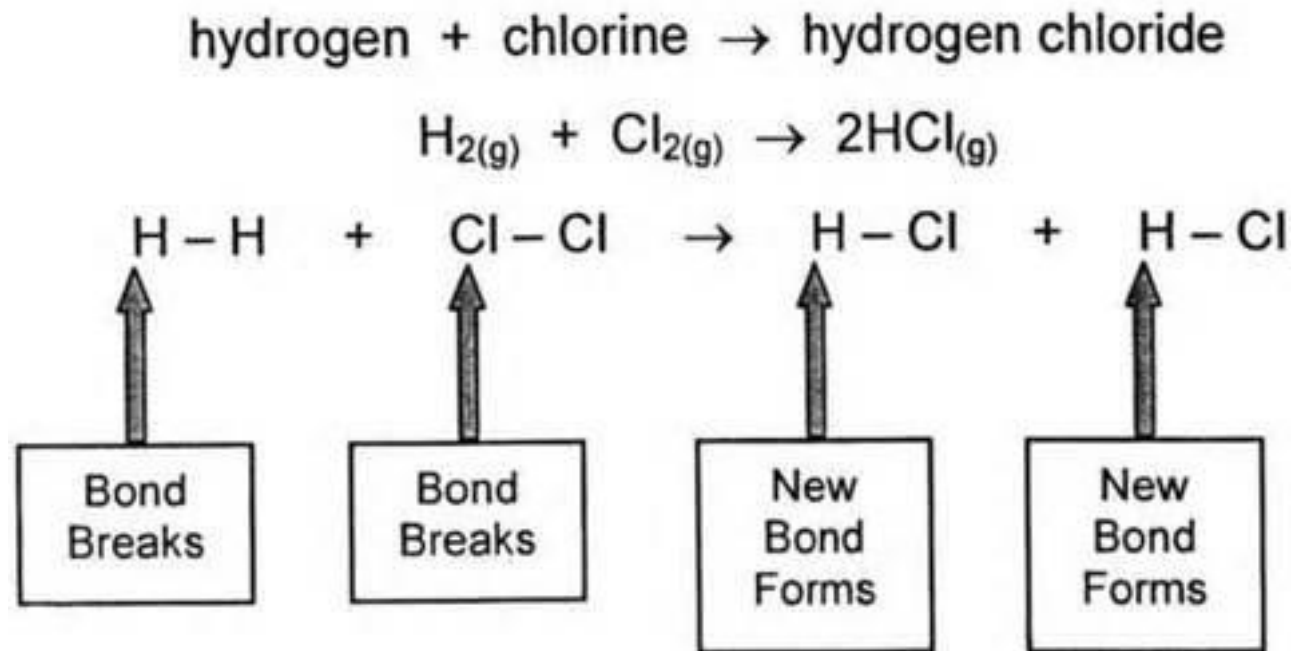
- Enthalpy = KJ/reaction cycle
- $1A + 2B = 2C + 1D \quad \Delta H = \text{KJ/rxn}$

$$\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

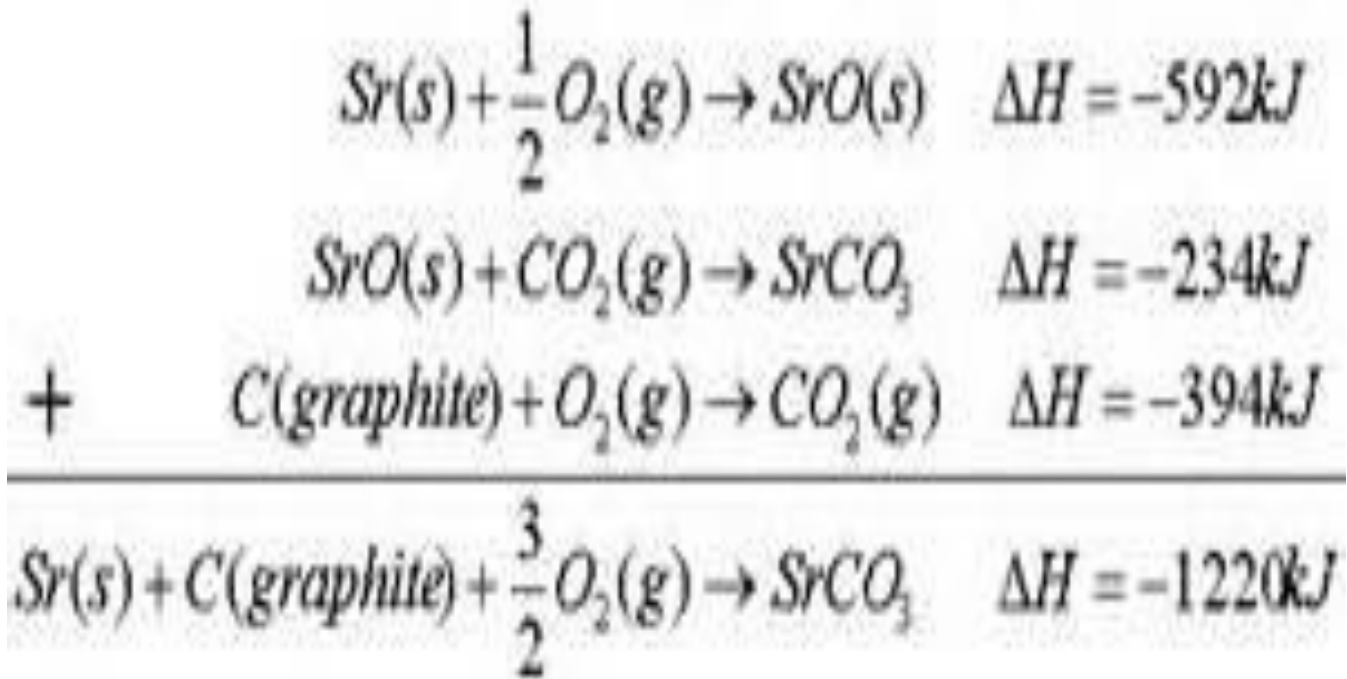
- Using thermodynamic tables
- Based upon relative scale of formation from elements
- Elements equal zero

Enthalpy: Bond Energies

- $\Delta H_{\text{rxn}} = \text{Bonds Broken} - \text{Bonds formed}$



Hess's law



- When manipulating reactions so to add up.
 - Flip reaction flip sign
 - Multiply coefficients multiply enthalpy

Entropy: Quantity of disorder

- Calculating Entropy:

$$\Delta S_{\text{rxn}} = S_{\text{products}} - S_{\text{reactants}}$$

-

- Must be able to estimate the ΔS_{rxn} simply by increase/decrease of movement.

- Note:

- Zero entropy is a perfect crystal at zero kelvin.
- Gases > liquids > solids
- Producing gases usually is an increase in entropy.
- $A(s) \Rightarrow B(g)$

Spontaneous or not spontaneous?

- Spontaneous: Reaction will proceed toward designated products (to the right)
- Non-spontaneous: Reaction will proceed to the reactants (to the left)

In both cases no energy will be needed to be invested for a reaction to flow.

Gibbs Free Energy

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

- Exergonic: A reaction will be flowing toward products.
- $-\Delta G$: Net loss of energy and will be spontaneous.
- $+\Delta G$: Net gain of energy and will need to be fed energy constantly
- Factors affecting
 - ΔS : $+\Delta S$ will be a spontaneous factor
 - ΔH : $-\Delta H$ will be a spontaneous factor
 - T: Affects Entropy

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

- Useful mathematical formula
 - Calculate ΔG°
 - Calculate ΔG at an alternate temperature.
 - Calculate ΔH°
 - Calculate ΔS°
 - Remember: $^{\circ}$ means calculated at STP (25C and 1atm)

Temperature a reaction becomes spontaneous?

$\Delta G > 0$ Then reaction is non-spontaneous

$\Delta G < 0$ Then reaction is spontaneous

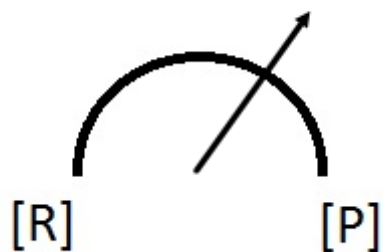
$\Delta G = 0$ reaction is just becoming or stopping the process of being spontaneous.

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

Set $\Delta G = 0$ and solve for temperature.

ΔG° vs. K vs. E°

- How does ΔG° relate?
 - - ΔG° means the reaction will proceed to products without energy investment
 - This correlates to a $K > 1$ and $E^\circ > 1$



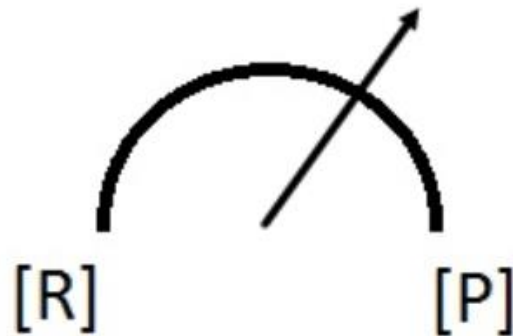
ΔG° vs. ΔG or E° vs. E

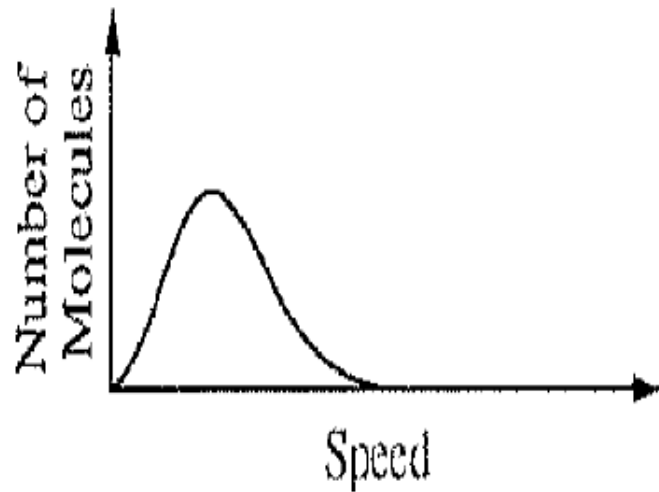
At STP: ΔG° & E° have a calculated value and that won't change.

Changing conditions: $\Delta G^\circ \Rightarrow \Delta G$ and $E^\circ \Rightarrow E$

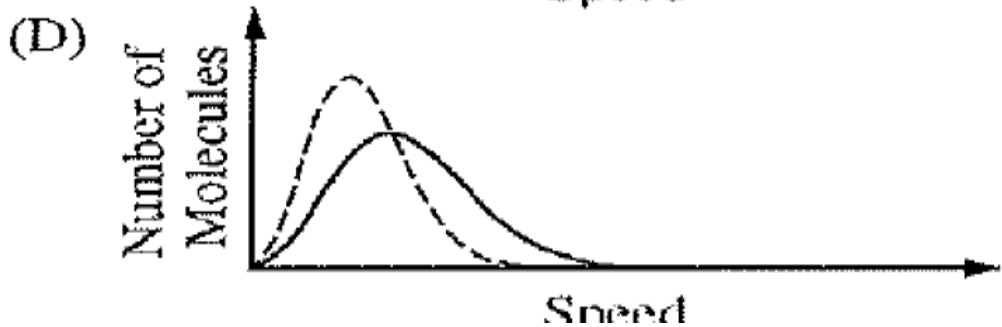
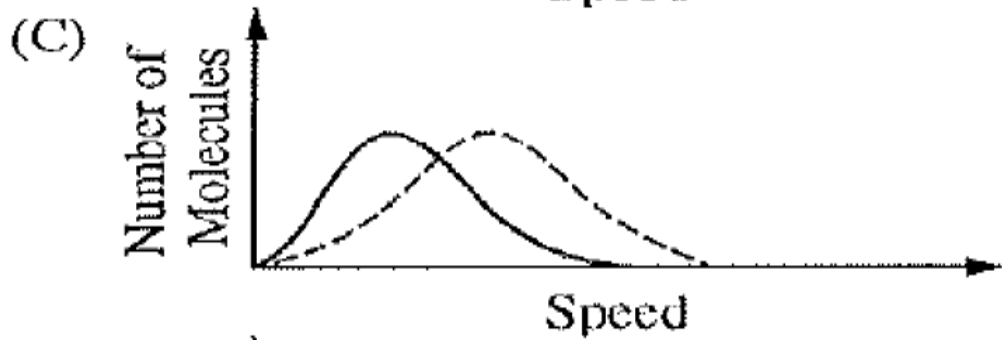
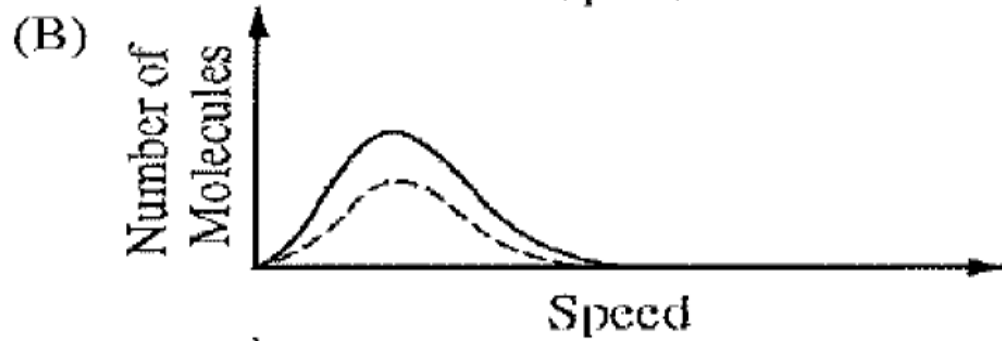
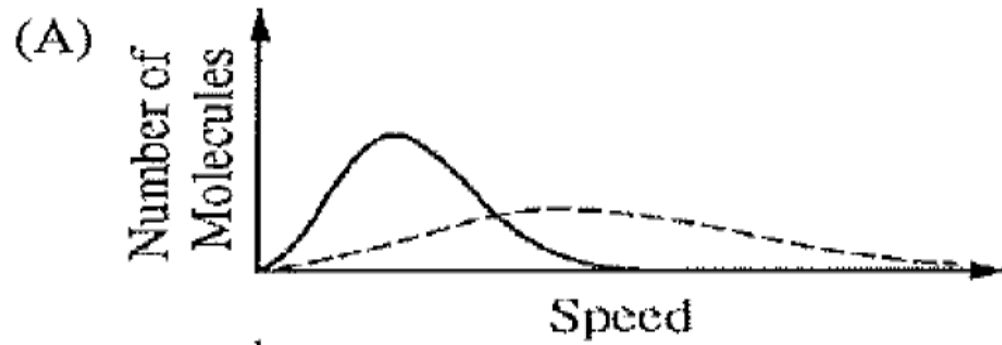
- This could be a result of concentrations changing as reaction proceeds to the endpoint.

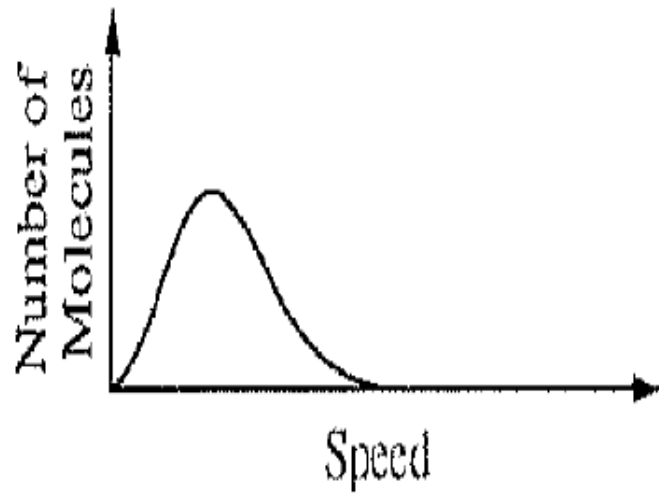
At equilibrium: ΔG & $E = \text{zero}$



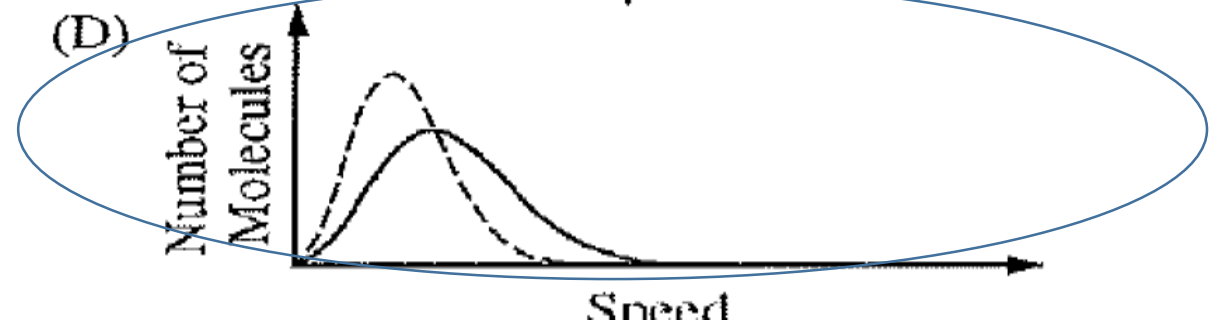
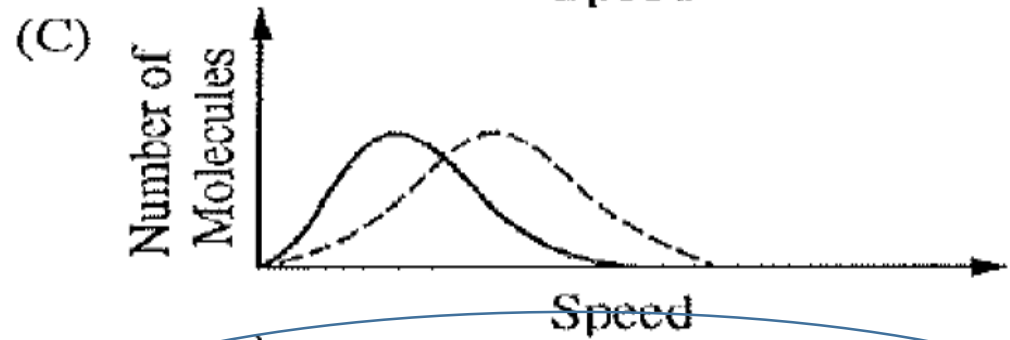
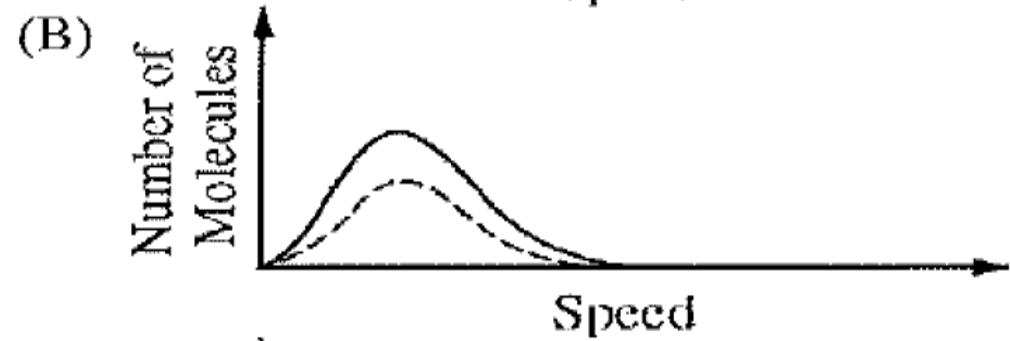


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9. A 100 g sample of a metal was heated to 100°C and then quickly transferred to an insulated container holding 100 g of water at 22°C . The temperature of the water rose to reach a final temperature of 35°C . Which of the following can be concluded?
- (A) The metal temperature changed more than the water temperature did; therefore the metal lost more thermal energy than the water gained.
 - (B) The metal temperature changed more than the water temperature did, but the metal lost the same amount of thermal energy as the water gained.
 - (C) The metal temperature changed more than the water temperature did; therefore the heat capacity of the metal must be greater than the heat capacity of the water.
 - (D) The final temperature is less than the average starting temperature of the metal and the water; therefore the total energy of the metal and water decreased.

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$$q = M * \Delta T * c$$

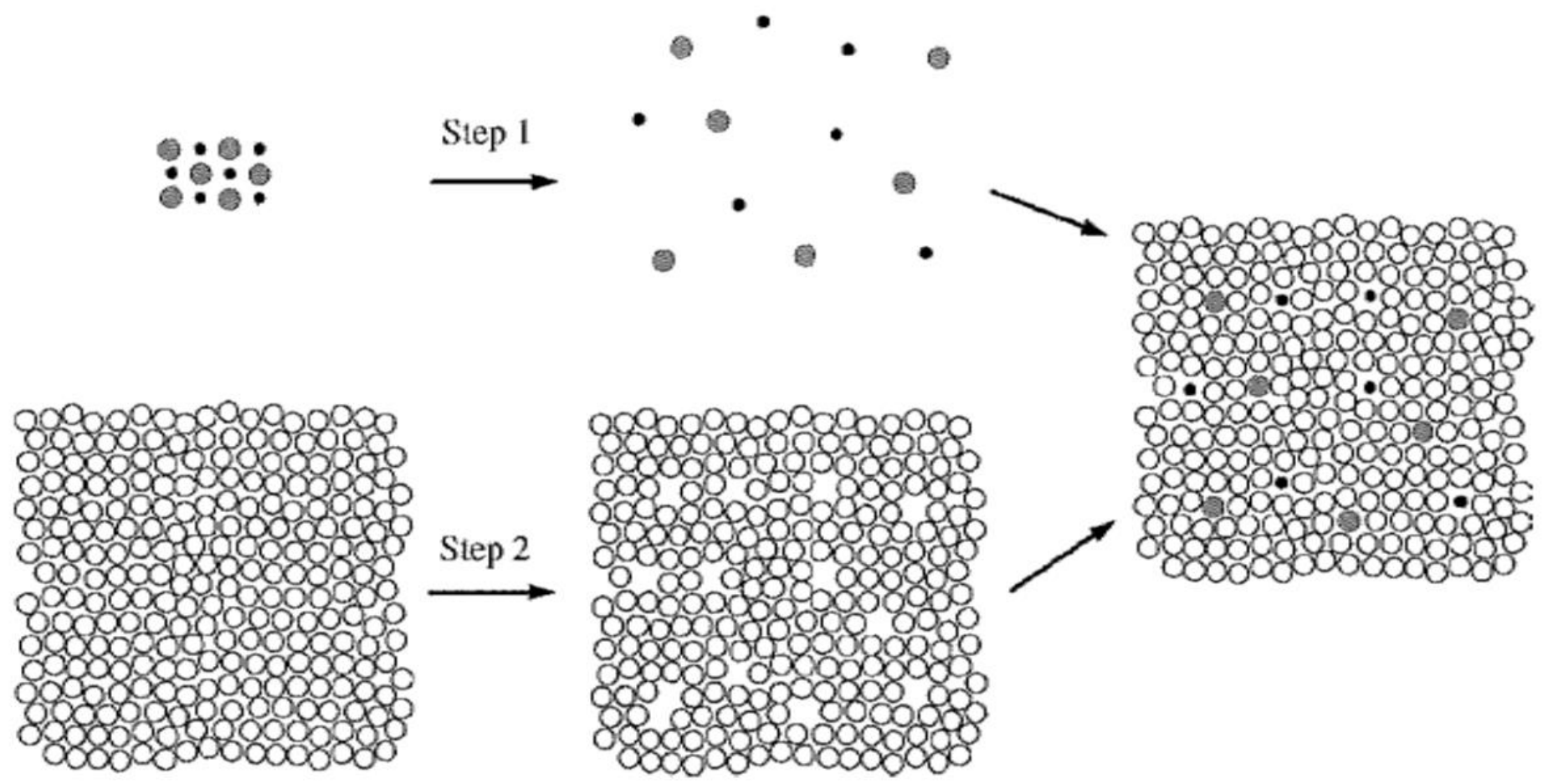
This problem is reflecting equal q transferred Between two objects but a different specific Heat " c " will cause a difference in temperature.

Container	A	B	C
Gas	Methane	Ethane	Butane
Formula	CH_4	C_2H_6	C_4H_{10}
Molar mass (g/mol)	16	30	58
Temperature ($^{\circ}\text{C}$)	27	27	27
Pressure (atm)	2.0	4.0	2.0

18. The average kinetic energy of the gas molecules is

- (A) greatest in container A
- (B) greatest in container B
- (C) greatest in container C
- (D) the same in all three containers





27. The dissolution of an ionic solute in a polar solvent can be imagined as occurring in three steps, as shown in the figure above. In step 1, the separation between ions in the solute is greatly increased, just as will occur when the solute dissolves in the polar solvent. In step 2, the polar solvent is expanded to make spaces that the ions will occupy. In the last step, the ions are inserted into the spaces in the polar solvent. Which of the following best describes the enthalpy change, ΔH , for each step?

- (A) All three steps are exothermic.
- (B) All three steps are endothermic.
- (C) Steps 1 and 2 are exothermic, and the final step is endothermic.
- (D) Steps 1 and 2 are endothermic, and the final step is exothermic.

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1st and 2nd step require an investment of energy. (endo)

3rd step will be bringing together particles that are attracting together forming a solution. This attraction is exothermic.

No energy is required to be invested.

D = answer



The elements K and Cl react directly to form the compound KCl according to the equation above. Refer to the information above and the table below to answer the questions that follow.

Process	ΔH° (kJ/mol _{rxn})
$\text{K}(s) \rightarrow \text{K}(g)$	v
$\text{K}(g) \rightarrow \text{K}^+(g) + e^-$	w
$\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$	x
$\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)$	y
$\text{K}^+(g) + \text{Cl}^-(g) \rightarrow \text{KCl}(s)$	z

34. How much heat is released or absorbed when 0.050 mol of $\text{Cl}_2(g)$ is formed from $\text{KCl}(s)$?

- (A) 87.4 kJ is released
- (B) 43.7 kJ is released
- (C) 43.7 kJ is absorbed
- (D) 87.4 kJ is absorbed



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(D) 87.4 kJ is absorbed

- Lets to the math proportions
- $\frac{1}{2}$ or .5 mol of $\text{Cl}_2 = 437 \text{ KJ}$ released.
- Since we have 1/10 of that we will get 1/10 of the energy.
- 43.7KJ release due to the “-” But Read carefully they are reversing the reaction!
- +43.7KJ C = is correct answer



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$\text{K}^+(g) + \text{Cl}^-(g) \rightarrow \text{KCl}(s)$	z

36. Which of the values of ΔH° for a process in the table is (are) less than zero (i.e., indicate(s) an exothermic process) ?

- (A) z only
- (B) y and z only
- (C) x , y , and z only
- (D) w , x , y , and z



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Acquiring Kinetic energy, Energy needs to be added

Pulling an e⁻ away from a +, Energy needs to be added

Breaking a bond, Energy needs to be added

e⁻ attract to + nucleus automatically, Exothermic

+ & - attract automatically, Exothermic
 OR
 Bond formation = energy released

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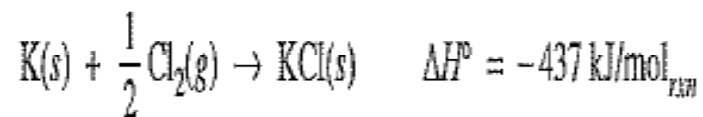
37. It is observed that the reaction producing KCl from its elements goes essentially to completion. Which of the following is a true statement about the thermodynamic favorability of the reaction?
- (A) The reaction is favorable and driven by an enthalpy change only.
- (B) The reaction is unfavorable and driven by an entropy change only.
- (C) The reaction is favorable and driven by both enthalpy and entropy changes.
- (D) The reaction is unfavorable due to both enthalpy and entropy changes.



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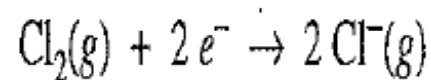
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- $\Delta G = \Delta H - T\Delta S$
- ΔG “-” due to the fact the reaction is running (favorable)
- ΔH “-” reaction is exothermic as listed and this is a spontaneous driving factor.
- ΔS “-” reaction is losing movement and therefore losing disorder. Not a driving factor in this reaction.



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38. Which of the following expressions is equivalent to ΔH° for the reaction represented above?

(A) $x + y$

(B) $x - y$

(C) $x + 2y$

(D) $\frac{x}{2} - y$



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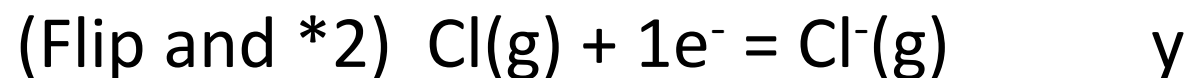
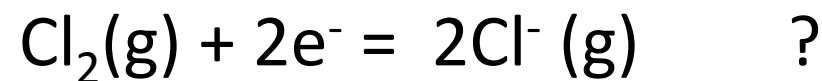
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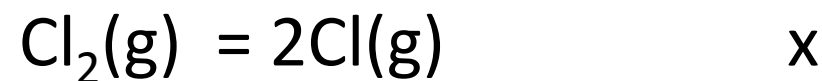
- This is a Hess's Law problem.

- Note:

- This is a half reaction.

- Answers only include x & z

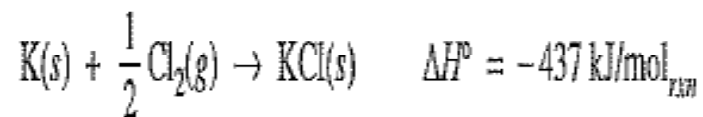




$$? - 2Y = x$$

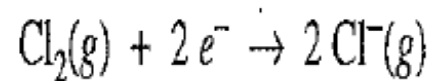
$$? = x + 2Y$$

Answer = C



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