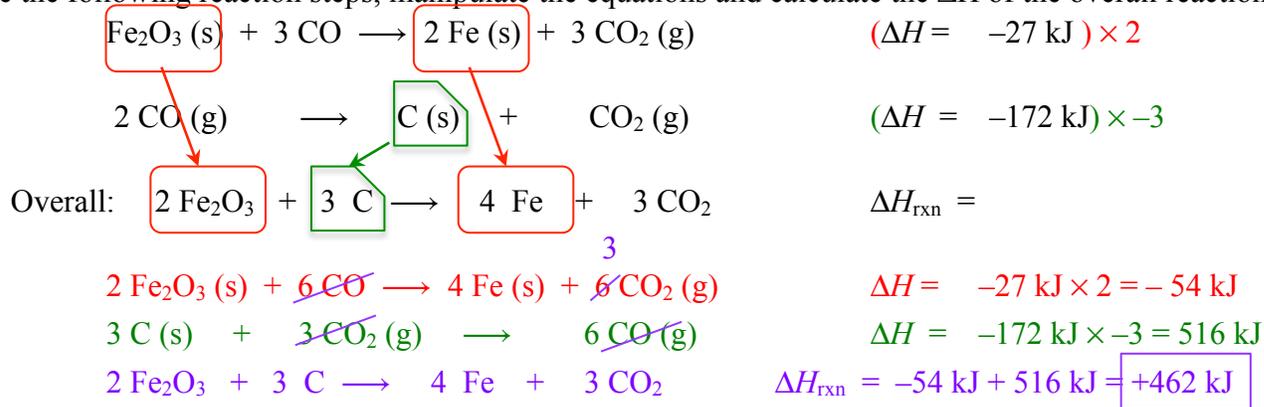


Topics:

- Enthalpy (ΔH): endothermic and exothermic reactions; Hess's Law (definition and modifying equations); Heat of formation reactions, using $\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum n\Delta H_f^{\circ}(\text{reactants})$
 - Is heat released or absorbed when bonds are broken? absorbed When bonds are formed? released.
- Definition of a state function and explanation of its relevance to Hess's Law.
- Analysis of heating and cooling curves: explain changes in temperature, why temperature plateaus, know phase changes
- Entropy (ΔS): identifying increasing or decreasing entropy changes.
- Spontaneity-- Gibbs Free Energy (ΔG), determining if spontaneous, using eq: $\Delta G = \Delta H - T \Delta S$
- Energy diagrams-- activation energy, ΔH , lowering E_a using a catalyst
- Conditions that effect rates (temp, concentration, surface area, catalyst), rates in terms of collisions
- Determining rate law from initial rate and initial concentration data
- Relationship between rate determining steps and rate law equations
- Questions similar to those in the Combustion Lab and Hess's Law Lab ($q = mc\Delta T$ and ΔH)

Practice Problems:

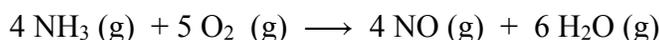
- 1) Use the following reaction steps, manipulate the equations and calculate the ΔH of the overall reaction:



- 2) Write the reaction showing the formation of 1 mole of KNO_3 and look up ΔH_f° of KNO_3 :



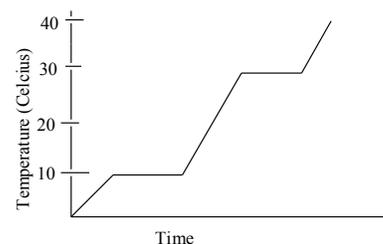
- 3) Given the ΔH_f° values shown below, calculate the ΔH_{rxn} for this reaction: (Use "products - reactants" method)



Substance	ΔH_f° (kJ/mole)
$\text{NH}_3(\text{g})$	-46.11
$\text{NO}(\text{g})$	+90.3
$\text{H}_2\text{O}(\text{g})$	-241.8

$$\begin{aligned}
 \Delta H_{\text{rxn}} &= [(4 \text{ mol})(90.3 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol})] \\
 &\quad - [(4 \text{ mol})(-46.11 \text{ kJ/mol}) + (5)(0)] \\
 &= [361.2 \text{ kJ} - 1450.8 \text{ kJ}] - [-184.4 \text{ kJ}] = -1089.6 \text{ kJ} + 184.4 \text{ kJ} \\
 &= \boxed{-905.2 \text{ kJ}}
 \end{aligned}$$

- 4) An unknown substance (initially a solid) is heated consistently and the heating curve to the right is obtained. Use the diagram to answer the questions:



- What is the condensation point of the unknown substance? 30°C
- At what temperature do the solid and liquid phases exist at the same time? 10°C
- Why does the temperature stay at 30° C for some time before rising again?

As energy is being added at the boiling point, all of the energy is being absorbed by the breaking of bonds to form the gas from the liquid, so the KE, hence the temperature, does not change.

- 5) Fill in this chart for the following three reactions.

	Endo or Exo	+ ΔS or $-\Delta S$
a. $\text{CaCO}_3(\text{s}) + 176 \text{ kJ} \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	Endo	+
b. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) + 44.02 \text{ kJ}$	Exo	-
c. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{ O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\text{g}) + 670 \text{ kcal}$	Exo	+

- 6) Given this decomposition reaction: $2 \text{KClO}_3(\text{s}) \rightarrow 2 \text{KCl}(\text{s}) + 3 \text{O}_2(\text{g})$

- What is the free energy change (ΔG) for this reaction if the reaction is carried out at 950°C?

$$\Delta H = -90.1 \text{ kJ/mol} \quad \Delta S = +492.2 \text{ J/mol}\cdot\text{K}$$

$$T = 950^\circ\text{C} + 273 = 1223 \text{ K}; \Delta S = 492.2 \text{ J/mol}\cdot\text{K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 0.4922 \text{ kJ/mol}\cdot\text{K}$$

$$\Delta G = \Delta H - T\Delta S = -90.1 \text{ kJ/mol} - (1223 \text{ K})(0.4922 \text{ kJ/mol}\cdot\text{K})$$

$$= -90.1 \text{ kJ/mol} - 602.0 \text{ kJ/mol} = \boxed{-692.1 \text{ kJ/mol}}$$

- Is this reaction spontaneous at 950°C? Yes How do you know? ΔG is negative
- Is the enthalpy change favorable? Yes How do you know? ΔH is negative
- Is the entropy change favorable? Yes How do you know? ΔS is positive
- Explain how you could answer question (d) without knowing the actual ΔS value.

Since the reaction produces 3 mol of gas and 2 mol of solid from 2 mol of solid, there is a net increase in the moles of gas. Since gas has such a large entropy, this will lead to an increase in entropy, or $\Delta S > 0$.

- 7) Given this reaction: $\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{CO}(\text{g}) \rightarrow 2 \text{Fe}(\text{s}) + 3 \text{CO}(\text{g})$

$$\Delta H = +24.7 \text{ kJ/mol} \quad \Delta S = +11.4 \text{ J/mol}\cdot\text{K}$$

- Use a calculation to verify that this reaction is not spontaneous at 25°C.

$$\Delta G = \Delta H - T\Delta S = +24.7 \text{ kJ/mol} - (298 \text{ K})(0.0114 \text{ kJ/mol}\cdot\text{K})$$

$$= 24.7 \text{ kJ/mol} - 3.40 \text{ kJ/mol} = \boxed{+21.3 \text{ kJ/mol}}$$

- However, it will become spontaneous if enough heat is applied. Why is it possible for this reaction to become spontaneous when heat is applied?

As T increases, the T ΔS term becomes more positive. Subtracting a larger positive number from ΔH eventually results in a negative ΔG (the sign changes when $\Delta G = 0$).

- At what temperature will this reaction become spontaneous?

$$\Delta G = 0 = +24.7 \text{ kJ/mol} - (T)(0.0114 \text{ kJ/mol}\cdot\text{K})$$

$$T = \frac{24.7 \text{ kJ/mol}}{0.0114 \text{ kJ/mol}\cdot\text{K}} = \boxed{2170 \text{ K or } 1890^\circ\text{C}}$$



- a. If 15.0 g of C_6H_6 reacts with O_2 , how much heat will be released?

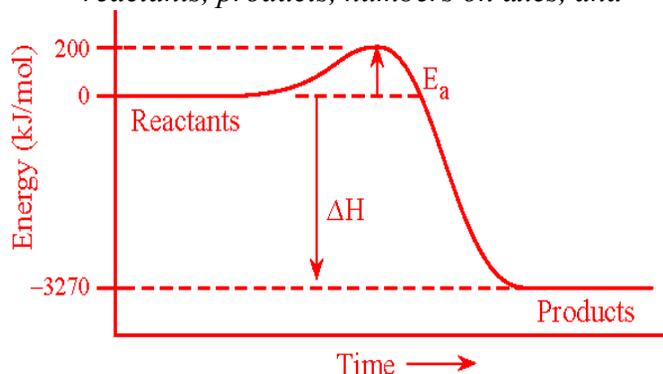
$$q = 15.0 \text{ g} \times \frac{1 \text{ mol}}{78.11 \text{ g}} \times \frac{-3270 \text{ kJ}}{1 \text{ mol}}$$

$$= \boxed{-628 \text{ kJ}} \text{ (- means released)}$$

- b. If all of this heat (that you just calculated) was used to heat up 5.00 kg of water, what would be the temperature change of the water?

$$\Delta T = \frac{q}{mc} = \frac{628,000 \text{ J}}{(5.00 \times 10^3 \text{ g})(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})} = \boxed{30.0^\circ\text{C}}$$

- c. This reaction is a spontaneous reaction; however a spark is needed to get C_6H_6 to start burning ($E_a = 200. \text{ kJ}$). Draw an energy diagram for this reaction. Label diagram with reactants, products, numbers on axes, and



- 9) Does every molecular collision lead to a reaction? No Why or why not?

An effective collision must have enough KE and the correct orientation. Only a small fraction of collisions will meet both of these requirements.

- 10) What is an activated complex? When is it formed? Why does it have high potential energy?

It is the species formed as reactants collide and start to form product bonds as reactant bonds are broken. It is formed during the collision, at the top of the "hill" and has high PE because KE is being converted to PE needed to break the reactant bonds.

- 11) Here are four ways to increase the rate of a reaction. Use collision theory, to explain how each way increases the rate. (more frequent collisions? harder collisions? change in activation energy?)

- a. Increase temperature

More frequent collisions and more with enough KE to obtain activated complex.

- c. Increase concentration

More collisions as the reactants become denser.

- b. Increase surface area

More collisions as reactants gain more access.

- d. use a catalyst

More collisions with enough KE to obtain activated complex as E_a decreases.

- 12) How is it possible for a catalyst to change the rate of a reaction without being consumed?

While the catalyst must participate in the reaction, it will be consumed in an early step (the RDS) to become part of an intermediate, which will subsequently react to release the catalyst in its original form.

- 13) Answer the following questions by using the mechanism at the right.

- a. Below the steps of the mechanism, fill in the balanced equation for the overall reaction.

- b. Which step is the rate-determining step? Step 2

- c. Which step forms an activated complex with the highest amount of potential energy? Step 2

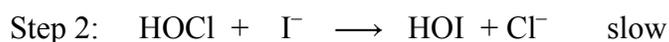
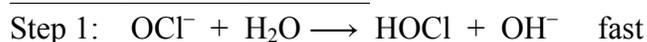
- d. Write the rate law equation for this reaction:

$$\text{Rate} = k [\text{HOCl}] [\text{I}^-]$$

- e. Identify any intermediates:



Mechanism for the reaction:



- f. Is there a catalyst? If so, what is it?

Yes: H_2O

14) The kinetics of the reaction: $2 X + Y \longrightarrow Z$ was studied and the results are:

Run	Initial [X] (M)	Initial [Y] (M)	Initial rate (M/s)
1	0.20	0.10	7.0×10^{-4}
2	0.20	0.20	1.4×10^{-3}
3	0.40	0.20	1.4×10^{-3}
4	0.60	0.60	4.2×10^{-3}

a. Deduce the rate law

Rate doubles from Run 1 to 2 as [Y] doubles and [X] stays the same, so 1st order in Y
 Rate is unchanged from Run 2 to 3 and [X] doubles and [Y] stays the same, so 0 order in X

$$\text{Rate} = k [Y]$$

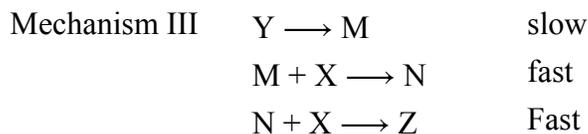
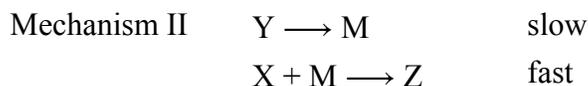
b. Determine the value of k with units.

$$\text{For run 1: } 7.0 \times 10^{-4} \text{ M/s} = k(0.10 \text{ M}); k = \frac{7.0 \times 10^{-4} \text{ M/s}}{0.10 \text{ M}} = 7.0 \times 10^{-3} \text{ s}^{-1}$$

c. What would the initial rate be if [X] = 0.35 M and [Y] = 0.55 M?

$$\text{Rate} = (7.0 \times 10^{-3} \text{ s}^{-1})(0.55 \text{ M}) = 3.9 \times 10^{-3} \text{ M/s}$$

d. The following 3 mechanisms have been proposed. What is the overall reaction for each mechanism? Which mechanism is consistent with the rate law from part a?



While Mechanisms II & III match the rate law and the RDS, of the two only Mechanism III also matches the overall reaction, thus only Mechanism III is completely consistent.

15) The rate law for the reaction, $\text{OH}^- (\text{aq}) + \text{H}_2\text{PO}_2^- (\text{aq}) \longrightarrow \text{HPO}_2^- (\text{aq}) + \text{H}_2 (\text{g})$, is

$$\text{Rate} = k [\text{OH}^-]^2 [\text{H}_2\text{PO}_2^-]$$

a) If the H_2PO_2^- concentration is doubled, what happens to the overall rate? Doubles

b) If the OH^- concentration is tripled, what happens to the rate? Increases 9x

16) How is it possible for a very spontaneous reaction to *seemingly* not occur? What must be true about the reaction? [Hint: other than being spontaneous, what does a reaction need in order to occur?]

Spontaneity is unrelated to kinetics. Thus, even an extremely spontaneous reaction can proceed so slowly as to be practically unobservable if the activation energy is sufficiently large.