USNCO Coaching Session
Local Exam Preparation Tutorial Notes:
Thermodynamics

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U.S. National Chemistry Olympiad

EXAM STRUCTURE

60 Multiple Choice questions · 110 minutes
Scientific Calculator · Some reference provided

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THERMODYNAMICS TOPICS

1. 0th Law of Thermodynamics
   a. Changes in Temperature: Calorimetry
   b. Changes in State of Matter

2. 1st Law of Thermodynamics
   a. Changes in Internal Energy
   b. Enthalpy
      i. Enthalpy of Formation
      ii. Experimental Determination
      iii. Average Bond Energy
      iv. Hess’s Law

3. 2nd Law of Thermodynamics
   a. Entropy
   b. Gibbs Free Energy
   c. Spontaneity
   d. Van’t Hoff Equation
# U.S. National Chemistry Olympiad

## Abbreviations and Symbols

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<th>Amount of Substance</th>
<th>Symbol</th>
<th>Faraday Constant</th>
<th>Frequency</th>
<th>Reaction Quotient</th>
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<tr>
<td>n</td>
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<td>Pressure</td>
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<td>Rate Constant</td>
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<td>Speed of Light</td>
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<td>Temperature, K</td>
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<td>Time</td>
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<td>Volt</td>
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<td>Volume</td>
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<tr>
<td>Year</td>
<td>y</td>
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</tbody>
</table>

## Equations

### Van't Hoff Equation

\[
E = E^o - \frac{RT}{nF} \ln Q
\]

\[
\ln K = \frac{-\Delta H}{RT} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \text{constant}
\]

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E}{RT} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]
Laws of Thermodynamics

0th Law | Thermal Equilibrium
Two systems are in thermodynamic equilibrium if they have the same temperature.

1st Law | Conservation of Energy
Energy can be converted from one form to another, but it cannot be created nor destroyed. The internal energy of a system can be changed by heat and work.

2nd Law | Spontaneity
The total entropy of an isolated system (universe) can never decrease.

3rd Law | Absolute Zero
The entropy of a perfect crystal at zero Kelvin is zero.
Changes in Temperature (Calorimetry)

Specific Heat ($C_p$) [$J\cdot g^{-1}\cdot K^{-1}$]
- Describes a substance’s resistance to change in temperature.
- Energy required to increase 1 g of a substance by 1 K.
- Specific Heat of Water $= 1 \text{ cal} \cdot g^{-1} \cdot K^{-1}$
  $= 4.184 \text{ J} \cdot g^{-1} \cdot K^{-1}$

2021 Local #20
Two metal samples, labeled A and B, absorb the same amount of heat. Sample A has a mass of 10.0 g, and its temperature increases by $\frac{3}{8}$ °C. Sample B has a mass of 20.0 g, and its temperature increases by $\frac{2}{3}$ °C. Which sample has the greater specific heat capacity?

(A) Sample A
(B) Sample B
(C) Both samples have the same specific heat capacity.
(D) It is impossible to determine from the information given.
Changes in Temperature (Calorimetry)

Heat ($q$) \[\text{[J] or [cal]}\]

- Transfer of energy that involves a temperature change
- $q > 0$ Process is endothermic
- $q < 0$ Process is exothermic

Calorimetry

- $q = m \cdot C_p \cdot \Delta T$
- $+q_{sys} = -q_{surr}$

2019 Local #19

The specific heat capacity of iron is 0.461 J g$^{-1}$ K$^{-1}$ and that of titanium is 0.544 J g$^{-1}$ K$^{-1}$. A sample consisting of a mixture of 10.0 g Fe and 10.0 g Ti at 100.0 °C loses 200. J of heat to the environment. What is the final temperature of the sample?

- (A) 89.9 °C
- (B) 80.1 °C
- (C) 60.2 °C
- (D) 39.8 °C
Changes in State of Matter

Heat of Fusion ($\Delta H_{\text{fus}}$) [kJ·mol$^{-1}$]
- Energy required to melt 1 mole of a solid

Heat of Vaporization ($\Delta H_{\text{vap}}$) [kJ·mol$^{-1}$]
- Energy required to vaporize 1 mole of a liquid

Changes in State
- Solid $\rightarrow$ Liquid $\rightarrow$ Gas  Endothermic (+)
- Gas $\rightarrow$ Liquid $\rightarrow$ Solid  Exothermic (−)
- $q = n \cdot \Delta H$

2020 Local #20
A 2.00 g sample of ice at 0.0 ºC is placed in 50.0 g of water initially at 25.0 ºC in an insulated container. What is the final temperature after the system has achieved equilibrium? (For ice, $\Delta H^\circ_{\text{fusion}} = 6.01$ kJ mol$^{-1}$.)

(A) 21.0 ºC  (B) 21.8 ºC
(C) 22.5 ºC  (D) 24.0 ºC
Changes in State

![Diagram showing phase changes of water](image-url)
1st Law | Changes in Internal Energy

Internal Energy ($\Delta E$ or $\Delta U$) [J]
- The sum of all the kinetic energy (motion of particles) and potential energy (attractions) of the particles in a system.
- $\Delta E_{\text{int}} = q + w$ (Generally $q = \Delta H$)

Work ($w$) [J]
- Energy gained by a system when it is compressed.
- $w = -P \cdot \Delta V$
  (Note: 1 J = 1 kPa·L)

2019 Local #22
For a constant-pressure process, what is the difference between the internal energy change ($\Delta U$) and the enthalpy change ($\Delta H$)?
(A) Heat  (B) Work
(C) Entropy  (D) Gibbs free energy
Enthalpy | Types

Enthalpy ($\Delta H$) [kJ·mol$^{-1}$]
- Flow of heat due to a physical or chemical process.
- **Enthalpy of Reaction ($\Delta H_{\text{rxn}}$):** Energy involved in any physical or chemical process.
- **Enthalpy of Formation ($\Delta H_f$):** Energy involved in forming 1 mole of a compound from elements at standard state.
  \[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \]
- **Enthalpy of Fusion ($\Delta H_{\text{fus}}$):** Energy required to melt 1 mole of a solid substance.
  \[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \]
- **Enthalpy of Vaporization ($\Delta H_{\text{vap}}$):** Energy required to vaporize 1 mole of a liquid substance.
  \[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \]
- **Enthalpy of Combustion ($\Delta H_{\text{comb}}$):** Energy released when 1 mole of a substance undergoes combustion (burning).
  \[ \text{C}_2\text{H}_6(g) + \frac{7}{2} \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(l) \]
- **Enthalpy of Solution ($\Delta H_{\text{soln}}$):** Energy involved in dissolving 1 mole of a solute.
  \[ \text{CaCl}_2(s) \rightarrow \text{CaCl}_2(aq) \]
- **Enthalpy of Neutralization ($\Delta H_{\text{neut}}$):** Energy involved in forming 1 mole of water when an acid and a base are combined.
  \[ \text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) \]
Enthalpy | Enthalpy of Formation

Enthalpy of Formation (Δ\(H_f\)) [kJ·mol\(^{-1}\)]
- Energy involved in forming one mole of a substance from elements at standard state.
- Δ\(H_f\) of an element at standard state = 0.

2020 Local #19
For which reaction is \(\Delta H^\circ_{\text{rxn}}\) equal to \(\Delta H^\circ_f\) of CaSO\(_3\)(s)?

(A) Ca(s) + 1/8 S\(_8\)(s) + 3/2 O\(_2\)(g) → CaSO\(_3\)(s)
(B) 8 Ca(s) + S\(_8\)(s) + 12 O\(_2\)(g) → 8 CaSO\(_3\)(s)
(C) 8 Ca(s) + S\(_8\)(g) + 12 O\(_2\)(g) → 8 CaSO\(_3\)(s)
(D) CaO(s) + SO\(_2\)(g) → CaSO\(_3\)(s)
2019 Local #23
The standard enthalpy of reaction for the
dissolution of silica in aqueous HF is 4.6 kJ mol\(^{-1}\). What is the standard enthalpy of formation of SiF\(_4\)(g)?

\[
\text{SiO}_2(s) + 4 \text{HF(aq)} \rightarrow \text{SiF}_4(g) + 2 \text{H}_2\text{O(ℓ)}
\]
\[
\Delta H^\circ_{\text{rxn}} = 4.6 \text{ kJ mol}^{-1}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO(_2)(s)</th>
<th>HF(aq)</th>
<th>H(_2)O(ℓ)</th>
<th>SiF(_4)(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H^\circ_f) kJ mol(^{-1})</td>
<td>-910.9</td>
<td>-320.1</td>
<td>-285.8</td>
<td>???</td>
</tr>
</tbody>
</table>

(A) -1624.3 kJ mol\(^{-1}\)  (B) -1615.1 kJ mol\(^{-1}\)
(C) -949.8 kJ mol\(^{-1}\)  (D) -940.6 kJ mol\(^{-1}\)
Enthalpy | Experimental Determination

Experimental Determination

- \( \Delta H_{\text{rxn}} = q_{\text{rxn}} / n_{\text{rxn}} \)
- \( n_{\text{rxn}} = \) moles of reaction based on the limiting reactant

2016 Local #20

40.0 mL of 0.200 M aqueous NaOH is added to 200.0 mL of 0.100 M aqueous NaHCO\(_3\) in a flask maintained at 25 °C. Neglecting the effects of dilution, what is \( q \) for this reaction?

<table>
<thead>
<tr>
<th>( \Delta H^\circ ), kJ mol(^{-1})</th>
<th>( \Delta H_{\text{rxn}} ), kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^-)(aq)</td>
<td>–230</td>
</tr>
<tr>
<td>HCO(_3)^- (aq)</td>
<td>–692</td>
</tr>
<tr>
<td>CO(_3)^2- (aq)</td>
<td>–677</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>–286</td>
</tr>
</tbody>
</table>

(A) -41 J  (B) -74 J  (C) -330 J  (D) -820 J
Enthalpy | Average Bond Energy

Average Bond Energy, Bond Dissociation Energy

- Typical energy required to break a covalent bond
- Break Bond = endo  Form Bond = exo
- $\Delta H_{rxn} = (+$ bonds broken) + ($- bonds formed)
- Draw out structures first.

2017 Local #22
Given the bond dissociation enthalpies (BDE) below, what is the approximate $\Delta H^\circ_f$ for $\text{H}_2\text{O}(g)$?

<table>
<thead>
<tr>
<th>Bond</th>
<th>BDE, kJ mol$^{-1}$</th>
<th>Bond</th>
<th>BDE, kJ mol$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>H–H</td>
<td>432</td>
<td>O–O</td>
<td>146</td>
</tr>
<tr>
<td>O–H</td>
<td>467</td>
<td>O=O</td>
<td>495</td>
</tr>
</tbody>
</table>

(A) -934 kJ mol$^{-1}$  (B) -510 kJ mol$^{-1}$
(C) -429 kJ mol$^{-1}$  (D) -255 kJ mol$^{-1}$
Hess’ Law

- Because enthalpy is a state function and the process of the reaction does not matter, the enthalpy of a reaction is the sum of the enthalpies of other processes that combine to the reaction.

\[ \Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \ldots \]

2017 Local #20

Given the standard enthalpy changes for the reactions:

\[
\begin{align*}
\text{P}_4 (s) + 3 \text{O}_2 (g) & \rightarrow \text{P}_4 \text{O}_6 (s) \quad \Delta H^\circ = -1640 \text{ kJ mol}^{-1} \\
\text{P}_4 (s) + 5 \text{O}_2 (g) & \rightarrow \text{P}_4 \text{O}_{10} (s) \quad \Delta H^\circ = -2940 \text{ kJ mol}^{-1}
\end{align*}
\]

Calculate the standard enthalpy change \( \Delta H^\circ \) for the following reaction:

\[
\text{P}_4 \text{O}_6 (s) + 2 \text{O}_2 (g) \rightarrow \text{P}_4 \text{O}_{10} (s)
\]

(A) \(-4.58 \times 10^3 \text{ kJ mol}^{-1}\)

(B) \(-1.30 \times 10^3 \text{ kJ mol}^{-1}\)

(C) \(1.79 \text{ kJ mol}^{-1}\)

(D) \(4.82 \times 10^6 \text{ kJ mol}^{-1}\)
Entropy

Entropy (S) \([\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]\)
- Measure of energy dispersion, microstates, or disorder of a system.
- \(S_{\text{solid}} < S_{\text{liquid}} << S_{\text{gas}}\)
- \(\Delta S > 0\) entropy/disorder increases
- \(\Delta S < 0\) entropy/disorder decreases

2018 Local #24
Which of the following reactions takes place with an increase in entropy under standard conditions?

(A) \(\text{NH}_4^+(aq) + \text{CH}_3\text{COO}^-(aq) \rightarrow \text{NH}_3(aq) + \text{CH}_3\text{COOH}(aq)\)
(B) \(\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s)\)
(C) \(\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq)\)
(D) \(\text{C}_2\text{H}_4(g) + \text{Br}_2(\ell) \rightarrow \text{C}_2\text{H}_4\text{Br}_2(\ell)\)
2nd Law | Spontaneity

Driving Forces of the Universe
- Minimize enthalpy: \( \Delta H < 0 \)
- Maximize entropy: \( \Delta S > 0 \)

Gibbs Free Energy (\( \Delta G \)) [kJ·mol\(^{-1}\)]
- \( \Delta G = \Delta H - T \cdot \Delta S \)
  - \(-\) + Always spont.
  - + - Never spont.
  + + + Spont. at high temp
  - - - Spont. at low temp

- \( \Delta G < 0 \) Process is spontaneous
- \( \Delta G > 0 \) Process is non-spontaneous
- \( \Delta G = 0 \) Process is at equilibrium
- Be careful with units!
- Spontaneity is unrelated to kinetics.

2019 Local #21
For an endothermic reaction to be spontaneous under standard conditions at constant pressure at some temperature \( T \), which must be true?

(A) The entropy change \( \Delta S^\circ \) must be positive and greater than \( \Delta H^\circ / T \).

(B) The entropy change \( \Delta S^\circ \) must be positive and less than \( \Delta H^\circ / T \).

(C) The entropy change \( \Delta S^\circ \) must be negative and greater than \( -\Delta H^\circ / T \).

(D) The entropy change \( \Delta S^\circ \) must be negative and less than \( -\Delta H^\circ / T \).
2nd Law | Spontaneity

2nd Law of Thermodynamics: Entropy of the universe cannot decrease.

\[ \Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \]

\[ \Delta S_{\text{total}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} > 0 \]

\[ (-\frac{\Delta H_{\text{sys}}}{T}) + \Delta S_{\text{sys}} > 0 \]

\[ \Delta H_{\text{sys}} - T \cdot \Delta S_{\text{sys}} < 0 \]

\[ \Delta G_{\text{sys}} < 0 \]

2017 Local #23
Which of the following are true for a spontaneous process in a system at constant temperature and pressure?

I. \( \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \)
II. \( \Delta G_{\text{sys}} < 0 \)

(A) I only            (B) II only
(C) Both I and II    (D) Neither I nor II
What is the standard Gibbs free energy of formation, \( \Delta G^\circ_f \), of \( \text{NH}_3(\text{g}) \) at 298 K?

(A) \(-104\) kJ mol\(^{-1}\)  \hspace{1cm} (B) \(-16\) kJ mol\(^{-1}\)

(C) \(-7\) kJ mol\(^{-1}\)  \hspace{1cm} (D) \(13\) kJ mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H^\circ_f ), kJ mol(^{-1})</th>
<th>( S^\circ ), J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2(\text{g}) )</td>
<td>0</td>
<td>131</td>
</tr>
<tr>
<td>( \text{N}_2(\text{g}) )</td>
<td>0</td>
<td>192</td>
</tr>
<tr>
<td>( \text{NH}_3(\text{g}) )</td>
<td>(-46)</td>
<td>193</td>
</tr>
</tbody>
</table>
Spontaneity & Equilibrium

\[ \Delta G^\circ = -R \cdot T \cdot \ln K_{eq} \]
- \( R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \)
  (Be careful with units!)
- \( K_{eq} = \frac{\text{[products]}_{eq}}{\text{[reactants]}_{eq}} \)

2019 Local #24
The \( K_{sp} \) of \( \text{BaSO}_4 \) at 298 K is \( 1.1 \times 10^{-10} \). What is \( \Delta G^\circ \) at 298 K for the following reaction?

\[
\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightleftharpoons \text{BaSO}_4(s)
\]

(A) -57 kJ mol\(^{-1}\)    (B) -25 kJ mol\(^{-1}\)
(C) 25 kJ mol\(^{-1}\)    (D) 57 kJ mol\(^{-1}\)
Van’t Hoff Equation

\[ \Delta G^° = -R \cdot T \cdot \ln K_{eq} = \Delta H^° - T \cdot \Delta S^° \]

\[ \ln K_{eq} = (-\Delta H^°/R)(1/T) + (\Delta S^°/R) \]

2020 Local #21
Ethanol has a normal boiling point of 78.3°C and a standard heat of vaporization (\( \Delta H_{vap}^° \)) of 38.6 kJ mol\(^{-1}\). What is the vapor pressure of ethanol at 45.0 °C?

(A) 0.25 atm  
(C) 0.87 atm  
(B) 0.57 atm  
(D) 0.91 atm
Summary

**0th Law of Thermodynamics · Thermal Equilibrium**

Changes in Temperature
\[ q = m \cdot C_p \cdot \Delta T \]

Changes in State of Matter
\[ q = n \cdot \Delta H_{\text{fus}} \text{ or } q = n \cdot \Delta H_{\text{vap}} \]

Heat Transfer
\[ +q_{\text{sys}} = -q_{\text{surr}} \]

**1st Law of Thermodynamics · Energy Conservation**

Internal Energy
\[ \Delta E_{\text{internal}} = q + w \]

Expansion Work (by system)
\[ w = -P \cdot \Delta V \]

(1 J = 1 kPa·L)

Enthalpy of Reaction
\[ \Delta H_{\text{rxn}} = q_{\text{rxn}} / n_{\text{rxn}} \]

Enthalpy of Formation
\[ \Delta H_{\text{rxn}} = \Delta H_{f, \text{products}} - \Delta H_{f, \text{reactants}} \]

Bond Energies
\[ \Delta H_{\text{rxn}} = +\text{formed} - \text{broken} \]

Hess’ Law
\[ \Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 + ... \]

**2nd Law of Thermodynamics · Spontaneity**

Gibbs’ Free Energy
\[ \Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \]

Free Energy and Equilibrium
\[ \Delta G^\circ = -R \cdot T \cdot \ln K_{\text{eq}} \]

Van’t Hoff Equation
\[ \ln K_{\text{eq}} = -(\Delta H^\circ / R)(1 / T) + (\Delta S^\circ / R) \]

<table>
<thead>
<tr>
<th>Positive</th>
<th>( \Delta H )</th>
<th>Positive</th>
<th>( \Delta S )</th>
<th>Positive</th>
<th>( \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>endo</td>
<td>incr disorder</td>
<td>non-spont.</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>exo</td>
<td>decor disorder</td>
<td>spontaneous</td>
<td></td>
<td></td>
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