

American Chemical Society



# USNCO Coaching Session Local Exam Preparation Tutorial Notes: Thermodynamics

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28 Jan 2022

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# U.S. National Chemistry Olympiad

## EXAM STRUCTURE

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

<u>Questions</u>	<u>Topics</u>
1–6	Stoichiometry / Solutions
7–12	Descriptive / Laboratory
13–18	States of Matter
<b>19–24</b>	<b>Thermodynamics</b>
25–30	Kinetics
31–36	Equilibrium
37–42	Oxidation - Reduction
43–48	Atomic Structure / Periodicity
49–54	Bonding / Molecular Structure
55–60	Organic / Biochemistry



## THERMODYNAMICS TOPICS

- 0th Law of Thermodynamics
  - Changes in Temperature: Calorimetry
  - Changes in State of Matter
- 1st Law of Thermodynamics
  - Changes in Internal Energy
  - Enthalpy
    - Enthalpy of Formation
    - Experimental Determination
    - Average Bond Energy
    - Hess's Law
- 2nd Law of Thermodynamics
  - Entropy
  - Gibbs Free Energy
  - Spontaneity
  - Van't Hoff Equation

# U.S. National Chemistry Olympiad



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ABBREVIATIONS AND SYMBOLS			
amount of substance	$n$	Faraday constant	$F$
ampere	A	free energy	$G$
atmosphere	atm	frequency	$\nu$
atomic mass unit	u	gas constant	$R$
Avogadro constant	$N_A$	gram	g
Celsius temperature	$^{\circ}\text{C}$	hour	h
centi- prefix	c	joule	J
coulomb	C	kelvin	K
density	d	kilo- prefix	k
electromotive force	$E$	liter	L
energy of activation	$E_a$	measure of pressure mm Hg	
enthalpy	$H$	milli- prefix	m
entropy	$S$	molal	$m$
equilibrium constant	$K$	molar	M
		Faraday constant	$F$
		mole	mol
		Planck's constant	$h$
		pressure	$P$
		rate constant	$k$
		reaction quotient	$Q$
		second	s
		speed of light	$c$
		temperature, K	$T$
		time	$t$
		vapor pressure	VP
		volt	V
		volume	$V$
		year	y

CONSTANTS
$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$
$F = 96,500 \text{ C mol}^{-1}$
$F = 96,500 \text{ J V}^{-1} \text{ mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J s}$
$c = 2.998 \times 10^8 \text{ m s}^{-1}$
$0^{\circ}\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 1.013 \text{ bar} = 760 \text{ mm Hg}$
Specific heat capacity of $\text{H}_2\text{O} = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$

EQUATIONS		
$E = E^{\circ} - \frac{RT}{nF} \ln Q$	<p style="text-align: center;"><b>Van't Hoff Equation</b></p> $\ln K = \left( \frac{-\Delta H^{\circ}}{R} \right) \left( \frac{1}{T} \right) + \text{constant}$	$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

# 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 ( $C_p$ )**  $[\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}]$
- 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  $= 1 \text{ cal}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$   
 $= 4.184 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$

## 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 38 °C. Sample B has a mass of 20.0 g, and its temperature increases by 23 °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 ( $q$ ) [J] or [cal]

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

Calorimetry

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

2019 Local #19

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

(A)  $89.9 \text{ }^\circ\text{C}$

(B)  $80.1 \text{ }^\circ\text{C}$

(C)  $60.2 \text{ }^\circ\text{C}$

(D)  $39.8 \text{ }^\circ\text{C}$

# Changes in State of Matter



Heat of Fusion ( $\Delta H_{fus}$ ) [kJ·mol<sup>-1</sup>]

- Energy required to melt 1 mole of a solid

Heat of Vaporization ( $\Delta H_{vap}$ ) [kJ·mol<sup>-1</sup>]

- Energy required to vaporize 1 mole of a liquid

Changes in State

- Solid → Liquid → Gas Endothermic (+)
- Gas → Liquid → Solid Exothermic (-)
- $q = n \cdot \Delta H$

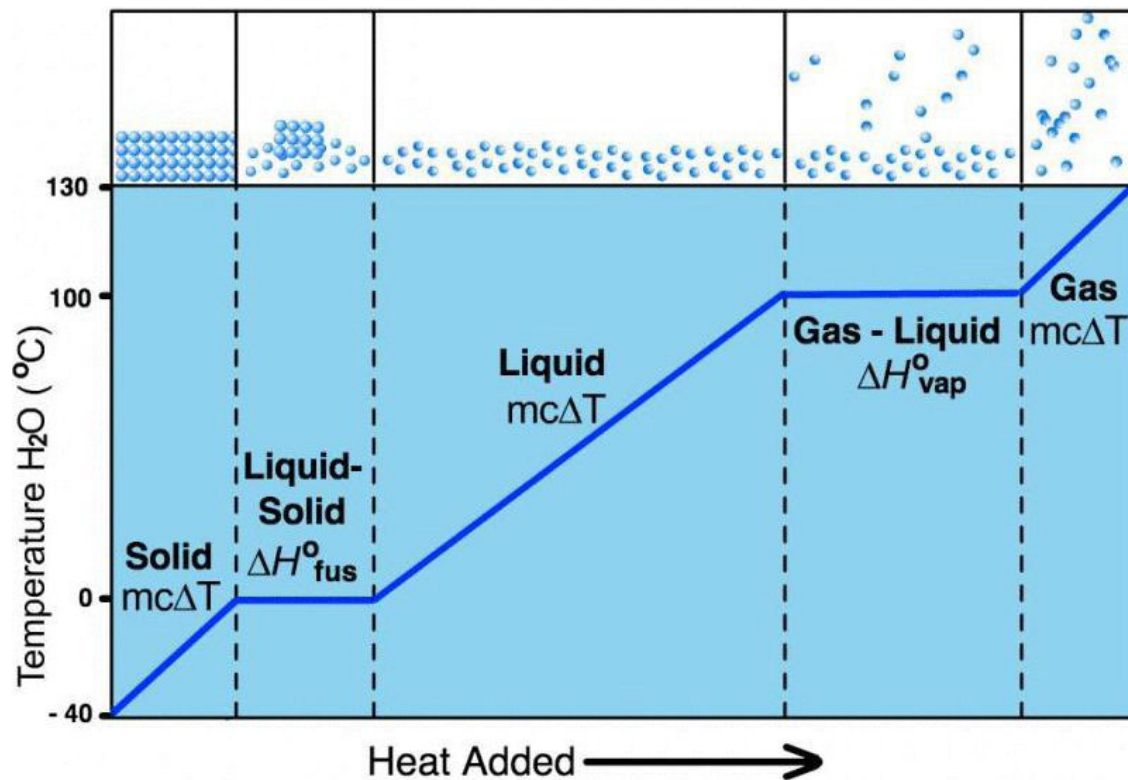
2020 Local #20

A 2.00 g sample of ice at 0.0 °C is placed in 50.0 g of water initially at 25.0 °C in an insulated container. What is the final temperature after the system has achieved equilibrium? (For ice,  $\Delta H_{fusion}^{\circ} = 6.01$  kJ mol<sup>-1</sup>.)

- (A) 21.0 °C                      (B) 21.8 °C  
(C) 22.5 °C                      (D) 24.0 °C



# Changes in State



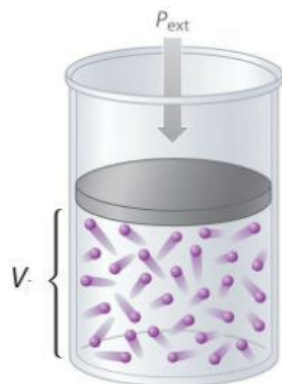
# 1st Law | Changes in Internal Energy

## 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<sup>-1</sup>]

- 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.



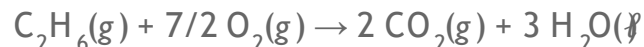
- **Enthalpy of Fusion ( $\Delta H_{\text{fus}}$ ):** Energy required to melt 1 mole of a solid substance.



- **Enthalpy of Vaporization ( $\Delta H_{\text{vap}}$ ):** Energy required to vaporize 1 mole of a liquid substance.



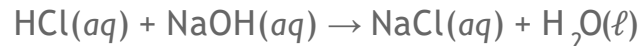
- **Enthalpy of Combustion ( $\Delta H_{\text{comb}}$ ):** Energy released when 1 mole of a substance undergoes combustion (burning).



- **Enthalpy of Solution ( $\Delta H_{\text{soln}}$ ):** Energy involved in dissolving 1 mole of a solute.



- **Enthalpy of Neutralization ( $\Delta H_{\text{neut}}$ ):** Energy involved in forming 1 mole of water when an acid and a base are combined.



# Enthalpy | Enthalpy of Formation

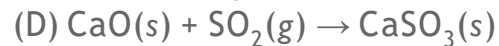


Enthalpy of Formation ( $\Delta H_f$ ) [kJ·mol<sup>-1</sup>]

- Energy involved in forming one mole of a substance from elements at standard state.
- $\Delta H_f$  of an element at standard state = 0.

2020 Local #19

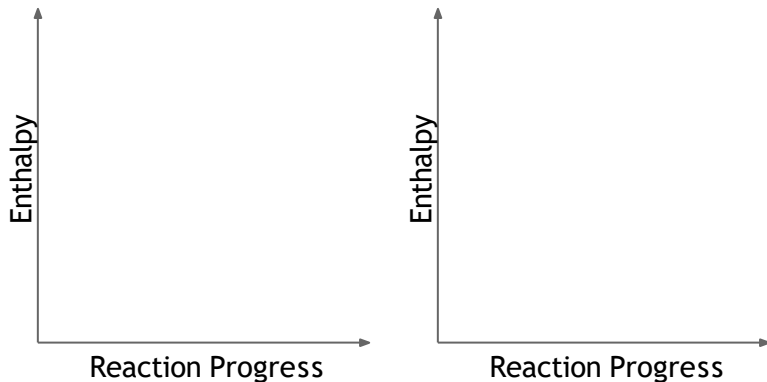
For which reaction is  $\Delta H_{\text{rxn}}^\circ$  equal to  $\Delta H_f^\circ$  of  $\text{CaSO}_3(\text{s})$ ?



# Enthalpy | Enthalpy of Formation

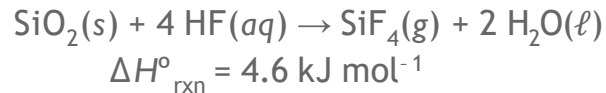


$$\Delta H_{rxn}^{\circ} = \sum \Delta H_{f,products}^{\circ} - \sum \Delta H_{f,reactants}^{\circ}$$



## 2019 Local #23

The standard enthalpy of reaction for the dissolution of silica in aqueous HF is  $4.6 \text{ kJ mol}^{-1}$ . What is the standard enthalpy of formation of  $\text{SiF}_4(\text{g})$ ?



Compound	$\text{SiO}_2(\text{s})$	$\text{HF}(\text{aq})$	$\text{H}_2\text{O}(\ell)$	$\text{SiF}_4(\text{g})$
$\Delta H_f^{\circ}, \text{ kJ mol}^{-1}$	-910.9	-320.1	-285.8	???

- (A)  $-1624.3 \text{ kJ mol}^{-1}$       (B)  $-1615.1 \text{ kJ mol}^{-1}$   
(C)  $-949.8 \text{ kJ mol}^{-1}$       (D)  $-940.6 \text{ kJ mol}^{-1}$

# 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<sub>3</sub> in a flask maintained at 25 °C. Neglecting the effects of dilution, what is  $q$  for this reaction?

	$\Delta H_{\text{f}}^{\circ}$ , kJ mol <sup>-1</sup>
OH <sup>-</sup> (aq)	-230
HCO <sub>3</sub> <sup>-</sup> (aq)	-692
CO <sub>3</sub> <sup>2-</sup> (aq)	-677
H <sub>2</sub> O(l)	-286

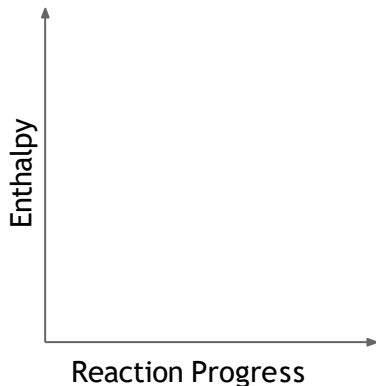
- (A) -41 J    (B) -74 J    (C) -330 J    (D) -820 J

# Enthalpy | Average Bond Energy



## Average Bond Energy, Bond Dissociation Energy

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



## 2017 Local #22

Given the bond dissociation enthalpies (BDE) below, what is the approximate  $\Delta H_f^\circ$  for  $\text{H}_2\text{O}(g)$ ?

Bond	BDE, $\text{kJ mol}^{-1}$	Bond	BDE, $\text{kJ mol}^{-1}$
H-H	432	O-O	146
O-H	467	O=O	495

(A)  $-934 \text{ kJ mol}^{-1}$   
(C)  $-429 \text{ kJ mol}^{-1}$

(B)  $-510. \text{ kJ mol}^{-1}$   
(D)  $-255 \text{ kJ mol}^{-1}$

# Enthalpy | Hess's Law



## Hess' Law

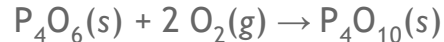
- Because enthalpy is a state function and the process of the reaction does not matter, the enthalpy of a reaction is the sum of the enthalpies of other processes that combine to the reaction.
- $\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \dots$

## 2017 Local #20

Given the standard enthalpy changes for the reactions:



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



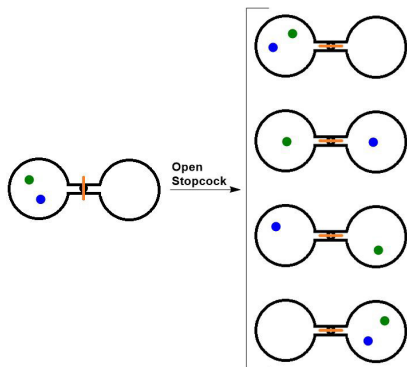
- (A)  $-4.58 \times 10^3 \text{ kJ mol}^{-1}$       (B)  $-1.30 \times 10^3 \text{ kJ mol}^{-1}$   
(C)  $1.79 \text{ kJ mol}^{-1}$       (D)  $4.82 \times 10^6 \text{ kJ mol}^{-1}$



# Entropy

Entropy (S) [J·mol<sup>-1</sup>·K<sup>-1</sup>]

- Measure of energy dispersion, microstates, or disorder of a system.
- $S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$
- $\Delta S > 0$  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)  $\text{NH}_4^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq})$
- (B)  $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$
- (C)  $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- (D)  $\text{C}_2\text{H}_4(\text{g}) + \text{Br}_2(\text{l}) \rightarrow \text{C}_2\text{H}_4\text{Br}_2(\text{l})$

# 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<sup>-1</sup>]

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

-	+	Always spont.
+	-	Never spont.
+	+	Spont. at high temp
- $\Delta G < 0$  Process is spontaneous **Spont. at low temp**
- $\Delta G > 0$  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.

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$$

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

$$(-\Delta H_{\text{sys}}/T) + \Delta S_{\text{sys}} > 0$$

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

$$\Delta G_{\text{sys}} < 0$$

## 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

# Gibbs Free Energy

## 2018 Local #22

What is the standard Gibbs free energy of formation,  $\Delta G^\circ_f$ , of  $\text{NH}_3(\text{g})$  at 298 K?

Substance	$\Delta H^\circ_f$ , $\text{kJ mol}^{-1}$	$S^\circ$ , $\text{J mol}^{-1} \text{K}^{-1}$
$\text{H}_2(\text{g})$	0	131
$\text{N}_2(\text{g})$	0	192
$\text{NH}_3(\text{g})$	-46	193

- (A)  $-104 \text{ kJ mol}^{-1}$       (B)  $-16 \text{ kJ mol}^{-1}$   
(C)  $-7 \text{ kJ mol}^{-1}$       (D)  $13 \text{ kJ mol}^{-1}$

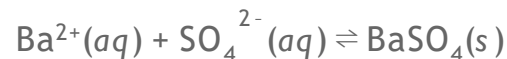
# Spontaneity & Equilibrium

$$\Delta G^\circ = -R \cdot T \cdot \ln K_{eq}$$

- $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$   
(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?

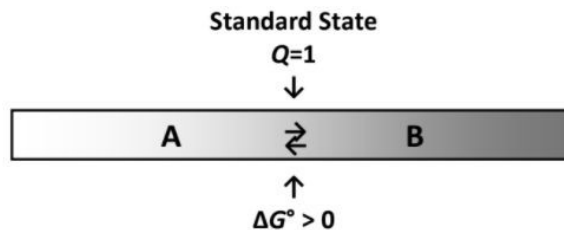
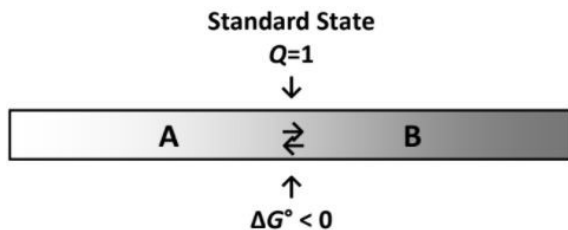


(A)  $-57 \text{ kJ mol}^{-1}$

(B)  $-25 \text{ kJ mol}^{-1}$

(C)  $25 \text{ kJ mol}^{-1}$

(D)  $57 \text{ kJ mol}^{-1}$



# Van't Hoff Equation

$$\Delta G^\circ = -R \cdot T \cdot \ln K_{\text{eq}} = \Delta H^\circ - T \cdot \Delta S^\circ$$

$$\ln K_{\text{eq}} = (-\Delta H^\circ/R)(1/T) + (\Delta S^\circ/R)$$

## 2020 Local #21

Ethanol has a normal boiling point of 78.3°C and a standard heat of vaporization ( $\Delta H^\circ_{\text{vap}}$ ) of 38.6 kJ mol<sup>-1</sup>. What is the vapor pressure of ethanol at 45.0 °C?

(A) 0.25 atm

(B) 0.57 atm

(C) 0.87 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  $q = n \cdot \Delta H_{fus}$  or  $q = n \cdot \Delta H_{vap}$

Heat Transfer  $+q_{sys} = -q_{surr}$

## 1st Law of Thermodynamics · Energy Conservation

Internal Energy  $\Delta E_{internal} = q + w$   
Expansion Work (by system)  $w = -P \cdot \Delta V$   
(1 J = 1 kPa·L)

Enthalpy of Reaction  $\Delta H_{rxn} = q_{rxn} / n_{rxn}$   
Enthalpy of Formation  $\Delta H_{rxn} = \Delta H_{f,products} - \Delta H_{f,reactants}$   
Bond Energies  $\Delta H_{rxn} = +\text{formed} - \text{broken}$   
Hess' Law  $\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \dots$

## 2nd Law of Thermodynamics · Spontaneity

Gibbs' Free Energy  $\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$

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

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

	<u><math>\Delta H</math></u>	<u><math>\Delta S</math></u>	<u><math>\Delta G</math></u>
Positive	endo	incr disorder	non-spont.
Negative	exo	decr disorder	spontaneous

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