

Recitation Worksheet Seven: Exam Two Review

Name:

Key

MyID:

Textbook:

Chemistry & Chemical Reactivity

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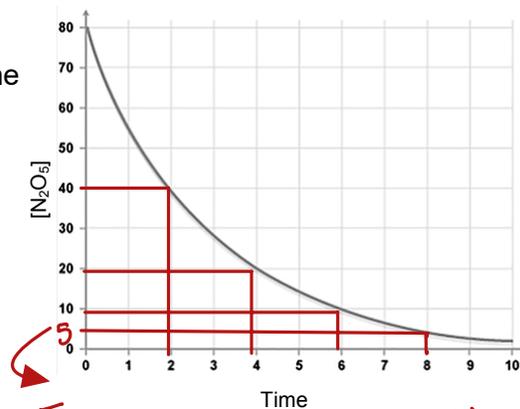
Instructions:

- This recitation worksheet is a review for Exam One.
- Exam coverage: Ch. 14.4-14.7, 18.1-18.5, 13.1-13.3
- You **do not** need to submit it to Gradescope.
- The answer key has been posted with this worksheet to eLC.
- The **recitation session during the exam week (October 7-10) is still mandatory**. Your attendance will be recorded.
- A periodic table and formula sheet are attached to the end of this worksheet.

1. Using the graphical representation below of the concentration of N_2O_5 versus time for the reaction $N_2O_5(g) \rightarrow NO_3(g) + NO_2(g)$, which of the statements is false?

A

- A. The decomposition of N_2O_5 follows zero order kinetics.
 B. It takes about 2 minutes for N_2O_5 to decrease to half of its original concentration.
 C. The half-life of this reaction is independent on the original concentration of N_2O_5 .
 D. The rate for this reaction can be expressed as rate = $k [N_2O_5]$



Choice B, C, D are correct
 & consistent with first-order kinetics

From this plot of $[N_2O_5]$ vs. time it takes 2 minutes for the conc of N_2O_5 to drop to half of its original concentration characteristic of first-order half-life

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$	$[A]$ vs Time t y-intercept = $[A]_0$ Slope = $-k$	$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$	$\ln[A]$ vs Time t y-intercept = $\ln[A]_0$ Slope = $-k$	$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$1/[A]$ vs Time t Slope = k y-intercept = $1/[A]_0$	$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

2. Carbon-14, which is present in all living tissue, radioactively decays via a first-order process. A one-gram sample of wood taken from a living tree gives a rate for carbon-14 decay of 13.6 counts per minute. If the half-life for carbon-14 is 5720 years, how old (in years) is a wood sample that gives a rate for carbon-14 decay of 11.9 counts per minute?

1.10×10^3

Years

$$\ln [A]_t = -kt + \ln [A]_0$$

$$\ln [11.9] = -1.21179577 \times 10^{-4} \times t + \ln [13.6]$$

$$\therefore t = 1.101929846 \times 10^3 \text{ yr}$$

$$\approx 1.10 \times 10^3 \text{ years}$$

$$[A]_0 = 13.6 \text{ counts/minute}$$

$$[A]_t = 11.9 \text{ counts/minute}$$

$$t = ?$$

k = determine from first order half-life

$$\therefore t_{1/2} = \frac{\ln 2}{k}$$

$$5720 = \frac{\ln 2}{k}$$

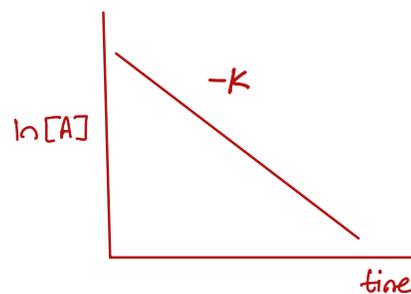
$$\therefore k =$$

$$1.21179577 \times 10^{-4} \text{ yr}^{-1}$$

3. When the reaction $A \rightarrow B + C$ is studied, a plot of $\ln[A]_t$ vs. time gives a straight line with a negative slope. What is the order of the reaction?

B

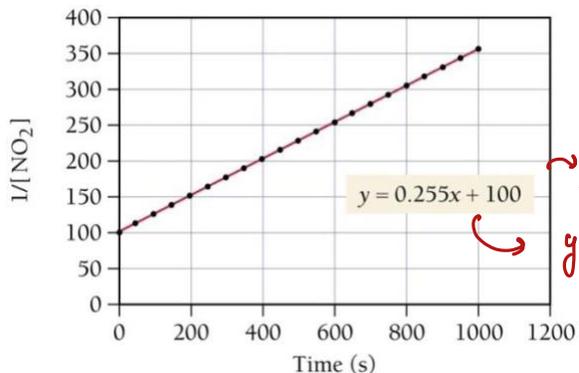
- A. Zero
 B. First
 C. Second
 D. Third
 E. More information is needed to determine the order.



Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	$\text{Rate} = k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$
1	$\text{Rate} = k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
2	$\text{Rate} = k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

→ You need to know the plot for each of the reaction orders

4. Consider the following graph, which depicts the change in the concentration of NO over time.



→ this graph represents second-order kinetics
 $y = mx + c$
 $m = \text{slope} = k = 0.255$

- If the initial concentration of NO_2 is 0.010 M, how long will it take for the NO_2 concentration to decrease to 10% of its initial concentration?

3500

 s

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$[A]_0 = 0.01 \text{ M}$
 Remaining $\leftarrow [A]_t = 10\% \times 0.01 = 0.0010$
 is 90% $t = ?$
 $k = 0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$

$$\frac{1}{0.0010} = 0.255t + \frac{1}{0.01 \text{ M}}$$

$$\therefore 900 = 0.255t$$

$$t = 3529.411765 \text{ sec}$$

$$\sim 3500 \text{ s}$$

5. In a second order reaction:

- I) the sum of the exponents in the rate law is equal to two.
- II) at least one of the exponents in the rate law is a two.
- III) the half-life is dependent on the initial concentration of the reactant species.
- IV) the half-life is independent of the initial concentration of the reactant species.
- V) k can be expressed as $M^{-2} s^{-1}$ or $M^{-2} min^{-1}$.

D

- A. I and IV
- B. II and IV
- C. I, III, and V
- D. I and III
- E. II and III

i) Rate = $[A][B]$ overall order = 2

Rate = $[A]^2$ overall order = 2

ii) Rate not necessarily 2

iii) $t_{1/2} = \frac{1}{k[A]_0}$ → dependent on initial conc

iv) this applies only for first-order half-life

v) Rate = $k[A]^2$

$M/s = k[M]^2 M$

$k = M^{-1} s^{-1}$

6. The second-order reaction $2 Mn(CO)_5 \rightarrow Mn_2(CO)_{10}$ has a rate constant equal to $3.0 \times 10^9 L/mol \cdot s$ at 25 °C. If the initial concentration of $Mn(CO)_5$ is $2.0 \times 10^{-5} mol/L$, how long will it take (in seconds) for 90.0% of the reactant to disappear?

1.5×10^{-4} s

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

→ 10.0% remaining

$k = 3.0 \times 10^9 L/mol \cdot s$
 $[A]_0 = 2.0 \times 10^{-5} mol/L$

$t = ?$

$[A]_t = 10.0\% \times 2.0 \times 10^{-5}$
 $= 2.0 \times 10^{-6} mol/L$

$$\frac{1}{[2.0 \times 10^{-6}]} = 3.0 \times 10^9 t + \frac{1}{[2.0 \times 10^{-5}]}$$

$$4.5 \times 10^5 = 3.0 \times 10^9 t$$

$$\therefore t = 1.5 \times 10^{-4} s$$

↪ means that $100 - 87.5 = 12.5\%$

7. A first order reaction is observed to be 87.5% complete in 1200 s. What is the half-life in seconds for this reaction?

4.0×10^2 s

$$\ln \frac{[A]}{[A]_0} = -kt$$

$[A]_t = 12.5\%$

$[A]_0 = 100\%$

$t = 1200$

$k = ?$

① $\ln \left(\frac{12.5}{100} \right) = -k(1200)$

$\therefore k = 1.732867951 \times 10^{-3} s^{-1}$ (2 sig figs)

② $t_{1/2} = \frac{\ln 2}{k}$

$\therefore t_{1/2} = \frac{\ln 2}{1.732867951 \times 10^{-3}} = 4.0 \times 10^2 \text{ sec}$

8. For question 45, a first-order reaction, how long does it take in seconds to reach 95% completion?

$$1.7 \times 10^3 \text{ s}$$

$$\ln\left(\frac{100-95}{100}\right) = -1.732867951 \times 10^{-3} t$$

$$\therefore t = 1728.771238 \text{ s}$$

$$\sim 1700 = 1.7 \times 10^3 \text{ s}$$

9. Experiment shows that the reaction below is first order: $A \rightarrow P$ Answer the questions based on the kinetic information in the table.

Time (s)	$\ln[A]$
1.0	-1.659
2.0	-2.209

Handwritten notes:
 - This conc. at $t=1.0$ sec can be considered as initial condition.
 - Note that this is the natural log of $[A]$ \therefore can be plugged directly into the equation.
 - This can be considered the condition after 2.0 seconds.

- A. What is the numerical value of the rate constant for this reaction?

$$0.55 \text{ s}^{-1}$$

$$\ln[A]_{2.0} = -kt + \ln[A]_{1.0}$$

$$-2.209 = -k(2.0 - 1.0) + (-1.659)$$

$$\therefore k = 0.55 \text{ s}^{-1}$$

- B. What was the initial concentration of A?

$$0.33 \text{ M}$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$-2.209 = -0.55 \text{ s}^{-1} (2.0 \text{ s}) + \ln[A]_0$$

$$\therefore \ln[A]_0 = -1.109 \rightarrow \text{take 'e' of both sides}$$

$$\therefore [A]_0 = 0.32988868 \sim 0.33 \text{ M}$$

- C. What would the concentration of A be after 4.0 seconds?

$$0.037 \text{ M}$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$\ln[A]_t = -0.55(4) + \ln[0.330]$$

$$\ln[A]_t = -3.30866 \rightarrow \text{take 'e' of both sides}$$

$$\therefore [A]_{4.0} = 0.036565 \text{ M}$$

$$\sim 0.037 \text{ M}$$

- D. What is the half-life (in seconds) for this reaction?

$$1.3 \text{ s}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.55 \text{ s}^{-1}} = 1.260267 \text{ sec}$$

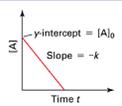
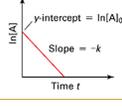
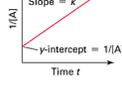
$$\sim 1.3 \text{ sec}$$

second order

10. Data is collected for the reaction $A \rightarrow B + C$, demonstrating a straight line with a positive slope when plotted as $1/[A]$ vs time. The reaction exhibits (select all the apply, use the letters with no commas):

BEH

- A. a half-life independent of concentration
- B. a half-life inversely proportional to concentration
- C. a half-life directly proportional to concentration
- D. a half-life proportional to k
- E. a half-life inversely proportional to k
- F. 0th order kinetics
- G. 1st order kinetics
- H. 2nd order kinetics

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

11. At a given temperature, a first-order reaction has a rate constant of $2.5 \times 10^{-3} s^{-1}$. How long will it take for the reaction to be 35% complete?

E

- A. 420 s
- B. 1600 s
- C. 1400 s
- D. 74 s
- E. 170 s

$$\ln \frac{[A]}{[A]_0} = -kt$$

$$\ln \left(\frac{65}{100} \right) = -2.5 \times 10^{-3} t$$

$$\therefore t = 172.3131664 s \approx 170 s$$

$$[A]_0 = 100\%$$

$$[A]_t (\text{remaining}) =$$

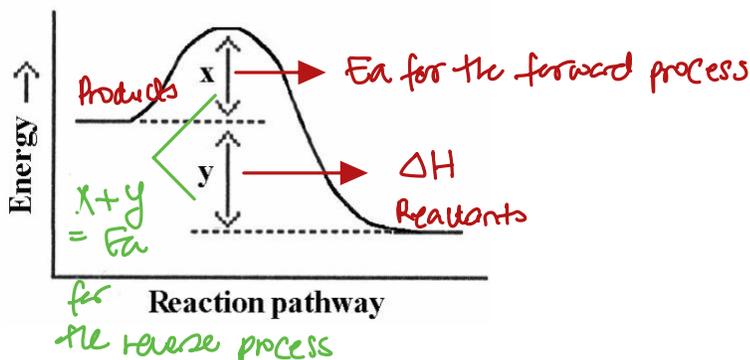
$$100 - 35 = 65\%$$

$$k = 2.5 \times 10^{-3} s^{-1}$$

$$t = ?$$

12. Which energy difference in the energy profile below corresponds to the activation energy for the forward reaction?

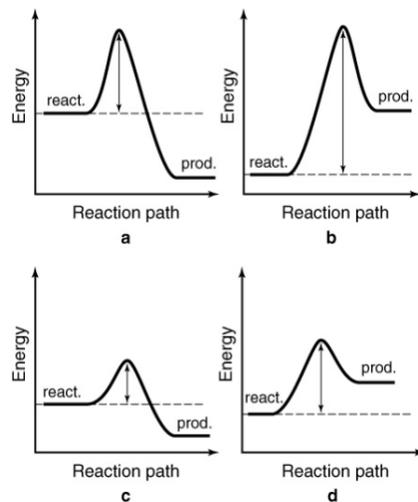
x



- A. x
- B. y
- C. x + y
- D. x - y
- E. y - x

13. The energy profiles for four different reactions are shown below. Which reaction requires the most energetic collisions to reach the transition state?

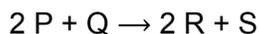
- b A. a
B. b
C. c
D. d



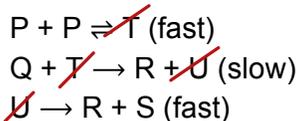
* Energetic collision indicates that the reactant molecules should have kinetic energy equal to or greater than the activation energy

* the potential energy plot with the highest activation energy requires the most energetic collisions.

14. Consider the reaction:

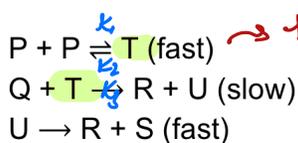


The mechanism is proposed for this reaction:



Substances T and U are unstable intermediates. What rate law is predicted by this mechanism?

- C A. Rate = $k [P]^2$
B. Rate = $k [P][Q]$
C. Rate = $k [P]^2[Q]$
D. Rate = $k [P][Q]^2$
E. Rate = $k [U]$



→ this mechanism has a fast first step and a slow second step
∴ the rate law cannot be written based on the slow step because the reactant is one of the intermediates
∴ we will have to write a derived rate law

step 1: From the fast equilibrium step

Rate forward = Rate reverse

$$k_1 [P]^2 = k_2 [T]$$

∴ rearrange in terms of intermediate T

$$\therefore [T] = \frac{k_1}{k_2} [P]^2$$

step 2: From the slow equilibrium step

$$\therefore \text{Rate} = k_3 [Q][T]$$

step 3: Substitute [T] from step 1 in step 2

$$\therefore \text{Rate} = k_3 [Q] \frac{k_1}{k_2} [P]^2$$

$$\therefore \text{Rate} = \frac{k_3 \times k_1}{k_2} [Q][P]^2$$

→ combined into k

step 4: Rate = $k [Q][P]^2$

15. The rate constant for a particular zero-order reaction is 0.075 M s^{-1} . If the initial concentration of reactant is 0.537 M it takes _____ s for the concentration to decrease to 0.100 M .

5.8

$$0.100 \text{ M} \leftarrow [A] = -kt + [A]_0 \rightarrow 0.537 \text{ M}$$

$$0.075 \text{ M/s}$$

$$0.100 = -0.075t + 0.537$$

$$\therefore t = 5.826666667 \text{ s} \approx 5.8 \text{ s}$$

16. A reaction occurs via the following sequence of elementary steps. What is the rate law based on this reaction mechanism?

D



1st step: A ⇌ B very fast

2nd step: B + C → D slow

3rd step: D + F → 2E fast

- A. Rate = $k [E]^2$
- B. Rate = $k [B][C]$
- C. Rate = $k [A][C][F]$
- D. Rate = $k [A][C]$
- E. Rate = $k [D]$

this mechanism has a fast first step & a slow second step
 \therefore the rate law cannot be written based on the slow step because the reactant is one of the intermediates
 \therefore we will have to write a derived rate law

Step 1: (From very fast first step)

Rate of forward = Rate of reverse

$$k_1 [A] = k_2 [B] \text{ (intermediate)}$$

rearrange in terms of [B]

$$\therefore \frac{k_1}{k_2} [A] = [B]$$

Step 2: (From second slow step)

$$\text{Rate} = k_3 [B][C]$$

Step 3: substitute [B] from step 1 in step 2

$$\therefore \text{Rate} = \frac{k_3 \times k_1}{k_2} [A][C]$$

\hookrightarrow combine all into k

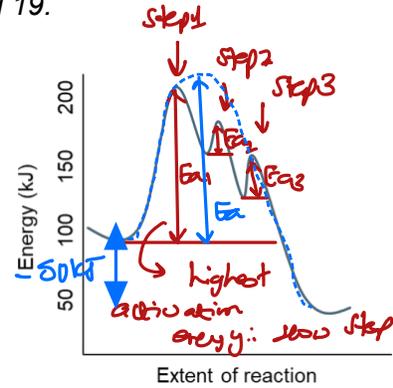
$$\therefore \text{Rate} = k [A][C]$$

Use the reaction coordinate below to answer questions 17, 18, and 19.

17. What type of mechanism would be consistent with this reaction coordinate? A ___ step mechanism with a slow ___ step.

D

- A. One, first
- B. One, third
- C. Three, third
- D. Three, first
- E. Two, first



18. What is the activation energy for the reaction? *for the overall process*

B

- A. 50 kJ/mol
- B. 100 kJ/mol
- C. 150 kJ/mol
- D. 175 kJ/mol
- E. 200 kJ/mol

19. What is the enthalpy for the reaction?

E

- A. 200 kJ/mol
- B. 100 kJ/mol
- C. -100 kJ/mol
- D. 50 kJ/mol
- E. -50 kJ/mol

→ the energy of the products is lower than the energy of the reactants ∴ it is an exothermic process

20. The active ingredient in an over-the-counter pain killer analgesic decomposes with a rate constant, $k = 9.05 \times 10^{-4} \text{ day}^{-1}$. How many days does it take for 15% of the original ingredient to decompose? *→ 85% remaining*

D

- A. 2096 days
- B. 414 days
- C. 365 days
- D. 180 days
- E. 78 days

this is a first order process

$$\ln \frac{[A]}{[A]_0} = -kt$$

*∴ [A] ≈ 85%
[A]₀ 100%
↳ 9.05 × 10⁻⁴*

$$\therefore \ln \left(\frac{0.85}{1} \right) = -9.05 \times 10^{-4} \times t$$

or
 $\frac{85}{100}$ (does not matter because it's a ratio)

$$\therefore t = 179.5789276 \text{ days}$$

$$\approx 180 \text{ days}$$

$$T_2 = 95.0 + 273.15 = 368.15 \text{ K}$$

 k_1

$$T_1 = 25.0 + 273.15 = 298.15 \text{ K}$$

21. A particular first-order reaction has a rate constant of $1.35 \times 10^2 \text{ s}^{-1}$ at 25.0°C . What is the value of k at 95.0°C if $E_a = 55.5 \text{ kJ/mol}$? $k_2 = ?$

$9.53 \times 10^3 \text{ s}^{-1}$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \rightarrow \text{two-point form Arrhenius equation}$$

$$\ln \left(\frac{k_2}{1.35 \times 10^2} \right) = -\frac{55.5 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}} \left(\frac{1}{368.15} - \frac{1}{298.15} \right)$$

$$\therefore k_2 = 9.532369632 \times 10^3 \text{ s}^{-1} \\ \approx 9.53 \times 10^3 \text{ s}^{-1}$$

$$k_1 = 4 \times k_2, T_1 = 40.0^\circ\text{C} + 273.15 = 313.15 \text{ K} \quad k_2, T_2 = 20.0^\circ\text{C} + 273.15 = 293.15 \text{ K}$$

22. The rate constant for a reaction at 40.0°C is exactly 4 times that at 20.0°C . Calculate the activation energy for the reaction.

B

- A. 36.36 kJ/mol
- B. 52.85 kJ/mol
- C. 15.25 kJ/mol
- D. 68.45 kJ/mol
- E. 28.26 kJ/mol

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

$$\therefore \ln \left(\frac{k_2}{4k_2} \right) = -\frac{E_a}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}} \left(\frac{1}{293.15} - \frac{1}{313.15} \right)$$

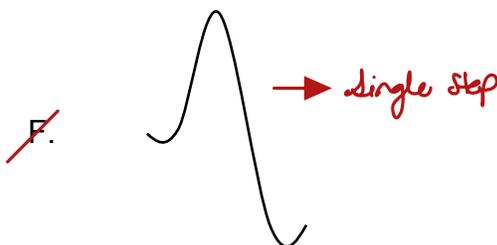
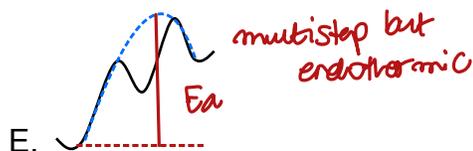
$$\therefore E_a = 52.90269489 \text{ kJ/mol}$$



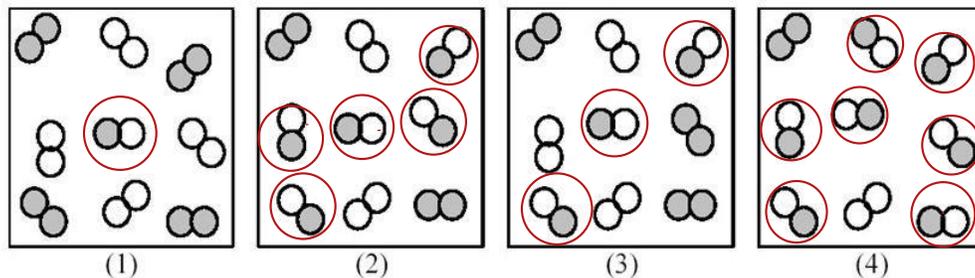
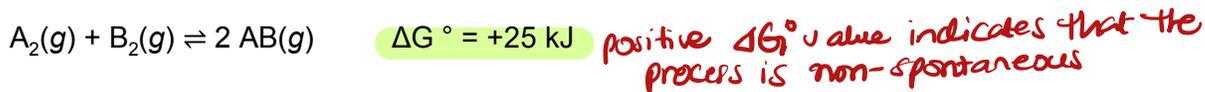
close to answer B

23. Which of the potential energy diagrams represents an exothermic chemical reaction with a high activation energy and multiple steps?

B



24. Consider the gas-phase reaction of A₂ (shaded spheres) and B₂ (unshaded spheres):

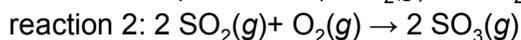


Which of the above reaction mixtures has the **least** spontaneous forward reaction?

- A**
- A. (1)
 - B. (2)
 - C. (3)
 - D. (4)

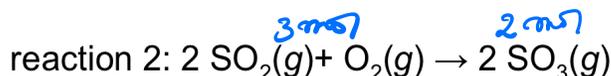
Strategy:
Examine pictures 1-4 & the picture that has the least amount of AB (product) will be the least spontaneous in the forward direction

25. Without doing any calculations, determine whether the standard entropy change, ΔS° is positive or negative for each of the following reactions.



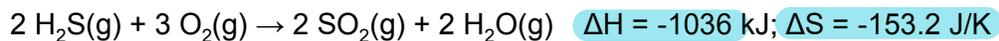
- B**
- A. ΔS° is positive for both reactions.
 - B. ΔS° is positive for reaction 1 but negative for reaction 2.
 - C. ΔS° is positive for reaction 2 but negative for reaction 1.
 - D. ΔS° is negative for both reactions.

*Although the number of moles of gas are equal on both sides, $SO_2(g)$ has a higher molecular complexity (compared to $O_2(g)$)
 $\therefore \Delta S^\circ > 0$ *3 mol* *2 mol**



the reaction results in a decrease in number of mol of gas

26. Above what temperature does this reaction change from spontaneous to nonspontaneous?



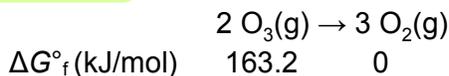
This reaction is spontaneous at low temperatures

A

- A. $6.762 \times 10^3 \text{ K}$
- B. 158.7 K
- C. 298 K
- D. This reaction is nonspontaneous at all temperatures.
- E. This reaction is spontaneous at all temperatures.

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \therefore \Delta H^\circ - T\Delta S^\circ &= 0 \\ \therefore T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-1036 \times 10^3 \text{ J}}{-153.2 \text{ J/K}} = 6.762 \times 10^3 \text{ K} \end{aligned}$$

27. What is $\Delta G^\circ_{\text{rxn}}$?



B

- A. 326.2 kJ
- B. -326.4 kJ
- C. -163.2 kJ
- D. 163.2 kJ
- E. 54.4 kJ

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [\sum G^\circ_f \text{ products} \times n_{\text{products}}] - [\sum G^\circ_f \text{ reactants} \times n_{\text{reactants}}] \\ &= [(3 \times 0)] - [(163.2 \times 2)] \\ &= -326.4 \text{ kJ} \end{aligned}$$

28. For the reaction, $\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$



what is $\Delta S^\circ_{\text{rxn}}$?

E

- A. -88.5 J/mol · K
- B. -176.7 J/mol · K
- C. 219 J/mol · K
- D. 176.7 J/mol · K
- E. -219.1 J/mol · K

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [\sum S^\circ \text{ products} \times n_{\text{products}}] - [\sum S^\circ \text{ reactants} \times n_{\text{reactants}}] \\ &= [(239.7 \times 1)] - [(197.6 \times 1) + (130.6 \times 2)] \\ &= -219.1 \text{ J/mol} \cdot \text{K} \end{aligned}$$

29. Suppose a chemical reaction is found to be spontaneous, but with $\Delta S_{\text{sys}} < 0$. Which of these statements is TRUE?

D

- As long as ΔS_{surr} is positive and of a larger magnitude than ΔS_{sys} $\therefore \Delta S_{\text{univ}} > 0$ \therefore Entropy of the process will be spontaneous*
- A. $\Delta S_{\text{surr}} < 0$ and its magnitude is $< \Delta S_{\text{sys}}$. In other words, the system loses entropy, and the surroundings also lose entropy. The loss by the surroundings is less than the loss by the system. *$\therefore \Delta S_{\text{univ}} < 0$ \therefore the process will be non-spontaneous*
- B. $\Delta S_{\text{surr}} < 0$ and its magnitude is $> \Delta S_{\text{sys}}$. In other words, the system loses entropy, and the surroundings also lose entropy. The loss by the surroundings is greater than the loss by the system. *similar to answer A*
- C. $\Delta S_{\text{surr}} > 0$ and its magnitude is $< \Delta S_{\text{sys}}$. In other words, the system loses entropy, but the surroundings gain entropy. The gain by the surroundings is less than the loss by the system. *If the magnitude of ΔS_{sys} is greater than ΔS_{surr} (+) $\therefore \Delta S_{\text{univ}} < 0$*
- D. $\Delta S_{\text{surr}} > 0$ and its magnitude is $> \Delta S_{\text{sys}}$. In other words, the system loses entropy, but the surroundings gain entropy, and the gain by the surroundings outweighs the loss by the system.
- E. An error has been made, as $S_{\text{sys}} > 0$ by necessity for a spontaneous process. *requires both system & surroundings*

According to the 2nd law of thermodynamics $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for a spontaneous process

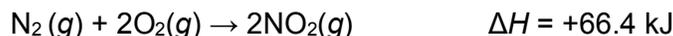
30. Which of these reactions will result in a positive ΔS_{sys} ? (Select all that apply).

ACE

- sys = reaction or process*
- A. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{g})$ *0 mol gas \rightarrow 5 mol gas*
- B. $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$ *solid produced*
- C. $14\text{O}_2(\text{g}) + 3\text{NH}_4\text{NO}_3(\text{s}) + \text{C}_{10}\text{H}_{22}(\text{l}) \rightarrow 3\text{N}_2(\text{g}) + 17\text{H}_2\text{O}(\text{g}) + 10\text{CO}_2(\text{g})$ *14 mol gas \rightarrow 30 mol gas*
- D. $\text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$ *3 mol \rightarrow 1 mol*
- E. $\text{SiCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{g})$ *4 mol \rightarrow 4 mol*

31. Nitrogen gas is allowed to react with oxygen to produce nitrogen dioxide gas at a constant temperature. Using the equation below and the information provided, what is the value of ΔS_{surr} at 298 K? Is this reaction spontaneous or non-spontaneous at this temperature?

B



3 mol 2 mol ∴ $\Delta S_{\text{sys}} < 0$

- A. $\Delta S_{\text{surr}} = +223 \text{ J/K}$, reaction is non-spontaneous
 B. $\Delta S_{\text{surr}} = -223 \text{ J/K}$, reaction is non-spontaneous
 C. $\Delta S_{\text{surr}} = -2656 \text{ J/K}$, reaction is spontaneous
 D. $\Delta S_{\text{surr}} = +66.4 \text{ kJ/K}$, reaction is non-spontaneous
 E. $\Delta S_{\text{surr}} = -223 \text{ J/K}$, it is not possible to predict the spontaneity of this reaction without more information

1) $\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} = -\frac{66.4 \times 10^3 \text{ J}}{298 \text{ K}} = -222.8187919 \text{ J/K} \approx -223 \text{ K}$

2) To determine if the reaction is spontaneous or non-spontaneous use

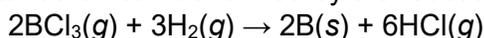
$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

(+) (-)

∴ the reaction is

non-spontaneous at all temperatures.

32. Elemental boron can be formed by the reaction of boron trichloride with hydrogen.



Substance	$\text{BCl}_3(\text{g})$	$\text{H}_2(\text{g})$	$\text{B}(\text{s})$	$\text{HCl}(\text{g})$
$S^\circ (\text{J/K}\cdot\text{mol})$?	130.6	5.9	186.8

If $\Delta S_{\text{rxn}}^\circ = 161.8 \text{ J/K}\cdot\text{mol}$, what is S° for $\text{BCl}_3(\text{g})$?

C

- A. $-18.2 \text{ J/K}\cdot\text{mol}$
 B. $18.2 \text{ J/K}\cdot\text{mol}$
 C. $289.5 \text{ J/K}\cdot\text{mol}$
 D. $370.4 \text{ J/K}\cdot\text{mol}$
 E. $579.0 \text{ J/K}\cdot\text{mol}$

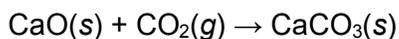
$$\Delta S_{\text{rxn}}^\circ = [\sum S^\circ_{\text{products}} \times n_{\text{products}}] - [\sum S^\circ_{\text{reactants}} \times n_{\text{reactants}}]$$

$$161.8 \text{ J/K}\cdot\text{mol} = [(2 \times 5.9) + (6 \times 186.8)] - [(2 \times S^\circ(\text{BCl}_3)) + 3(130.6)]$$

$$161.8 \text{ J/K}\cdot\text{mol} = [(1132.6 \text{ J/K}\cdot\text{mol})] - [(2 \times \text{BCl}_3) + 391.8 \text{ J/K}\cdot\text{mol}]$$

∴ $S^\circ = 289.5 \text{ J/mol}\cdot\text{K}$

33. Which statement is true about the formation of $\text{CaCO}_3(\text{s})$ from $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$ at 1.00 atm?



$$\Delta H^\circ = -178.7 \text{ kJ} \text{ and } \Delta S^\circ = -150.4 \text{ J/K}$$

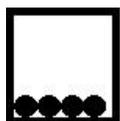
the reaction is spontaneous at low temperatures

C

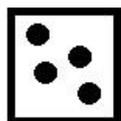
- A. The reaction is spontaneous at all temperatures.
- B. The reaction is spontaneous at high temperatures.
- C. The reaction is spontaneous at low temperatures.
- D. The reaction is not spontaneous at any temperature.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
this is an exothermic reaction ($\Delta H^\circ(-)$) that is entropically non-favorable ($\Delta S^\circ(-)$) so for a reaction to be spontaneous ($\Delta G^\circ < 0$) the enthalpy (ΔH°) has to be greater in magnitude compared to the term $+T\Delta S^\circ$

34. Which is true for this process?



add heat



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

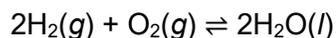
$(+)$ $(+)$

the entropy of the system increases $\Delta S^\circ(+)$ when the reaction is heated ($\Delta H^\circ(+)$) in order for the reaction to be spontaneous ($\Delta G^\circ(-)$) the term $-T\Delta S^\circ$ can be of a magnitude larger than $\Delta H^\circ(+)$ only at high temperatures

D

- A. It is spontaneous at all temperatures
- B. It is nonspontaneous at all temperatures
- C. It is spontaneous at low temperatures
- D. It is spontaneous at high temperatures
- E. More information is needed.

35. The formation of water from the reaction of H_2 and O_2 at 298 K is a spontaneous process. What do you predict about the rate of this reaction?



$$\Delta H_{\text{rxn}} = -285.8 \text{ kJ/mol} \quad \Delta S_{\text{rxn}} = -327 \text{ J/K}\cdot\text{mol}$$

E

- A. The reaction rate is higher because this is an exothermic reaction
- B. The reaction rate is lower because the entropy of the reaction is negative
- C. In general, spontaneous reactions show higher reaction rate
- D. The reaction rate is lower because both enthalpy and entropy changes of the reaction are negative.
- E. Based on the given information you cannot predict the rate of this reaction

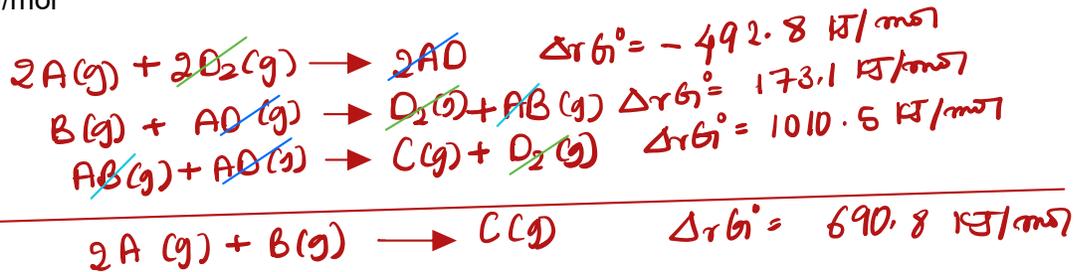
thermodynamics does not provide information about rates of reaction

36. Calculate Gibbs free energy for the reaction:



- ① $A(g) + D_2(g) \rightarrow AD(g)$ $\Delta_r G^\circ = -246.4 \text{ kJ/mol}$ *x2*
 ② $B(g) + AD(g) \rightarrow D_2(g) + AB(g)$ $\Delta_r G^\circ = 173.1 \text{ kJ/mol}$ *stays the same*
 ③ $C(g) + D_2(g) \rightarrow AB(g) + AD(g)$ $\Delta_r G^\circ = -1010.5 \text{ kJ/mol}$ *flip*

690.8 kJ/mol



37. At temperatures below 273 K, it is observed that liquid water spontaneously freezes to form solid ice. What are the signs (+ or -) of

ΔS_{sys} - ΔS_{surr} + ΔS_{univ} +



$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

This process is spontaneous at low temperatures $\therefore \Delta S_{\text{univ}}(+)$, H_2O changes state from solid to liquid $\therefore \Delta S_{\text{sys}}(-)$ & this is an exothermic process $\therefore \Delta S_{\text{surr}}(+)$

38. A sample of water is heated at a constant pressure of one atmosphere. At 260 K the sample is ice, and the sample consists of steam at 400 K. In which of the following 5 K temperature intervals would there be the greatest increase in the entropy of the sample?

- D
- A. From 260 K to 265 K
 B. From 275 K to 280 K
 C. From 360 K to 365 K
 D. From 370 K to 375 K

Note: water starts boiling at 373 K*

Entropy is affected by:

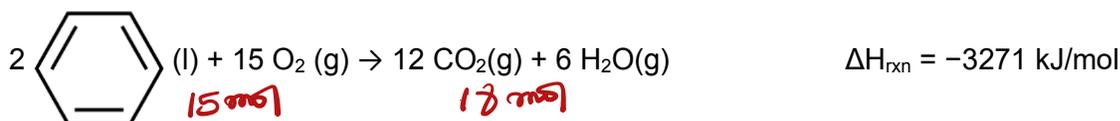
1) States of matter

solid \rightarrow liquid \rightarrow gas

Entropy increases \rightarrow

2) Increase in temperature: increases kinetic energy of the water molecules \therefore results in more microstates & greater entropy

39. Consider the combustion of benzene:



A. Calculate the entropy change (kJ/mol·K) in the surroundings associated with this reaction at 25.00 °C. Keep 4 significant figures. (1 point)

10.97 kJ/K

$$\Delta S_{\text{sur}} = -\frac{\Delta H_{\text{sys}}}{T} = -\frac{(-3271 \text{ kJ/mol})}{(25.00 + 273.15) \text{ K}}$$

$$= 10.97098776$$

$$\approx 10.97 \text{ kJ/mol}\cdot\text{K}$$

B. Determine the sign (+ or -) of the entropy change for the system. (1 point)

+ (increase in no. of mol of gas)

C. Determine the sign (+ or -) of the entropy change for the universe. (1 point)

+ $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$

\downarrow \downarrow
 (+) (+)

40. The dissolution of ammonium nitrate occurs spontaneously in water at 25°C. As NH_4NO_3 dissolves, the temperature of the water decreases. What are the signs of ΔH , ΔS , and ΔG for this process?

- C
- A. $\Delta H > 0$, $\Delta S < 0$, $\Delta G > 0$
 - B. $\Delta H > 0$, $\Delta S > 0$, $\Delta G > 0$
 - C. $\Delta H > 0$, $\Delta S > 0$, $\Delta G < 0$
 - D. $\Delta H < 0$, $\Delta S < 0$, $\Delta G < 0$
 - E. $\Delta H < 0$, $\Delta S > 0$, $\Delta G > 0$

- $\text{NH}_4\text{NO}_3(\text{s}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \therefore \Delta S > 0$

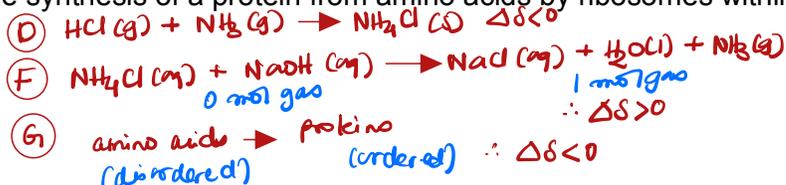
- If the temperature of the system (NH_4^+ & NO_3^- ions) \therefore the system absorbs heat from the surroundings $\therefore \Delta H > 0$

- the question indicates that NH_4NO_3 (soluble) dissolves $\therefore \Delta G < 0$

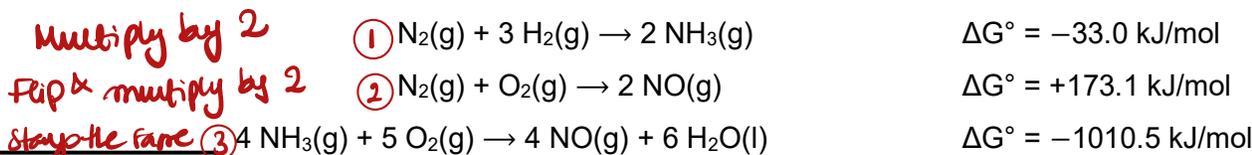
41. Which of these would result in a positive change in entropy? (Select all that apply)

B E F

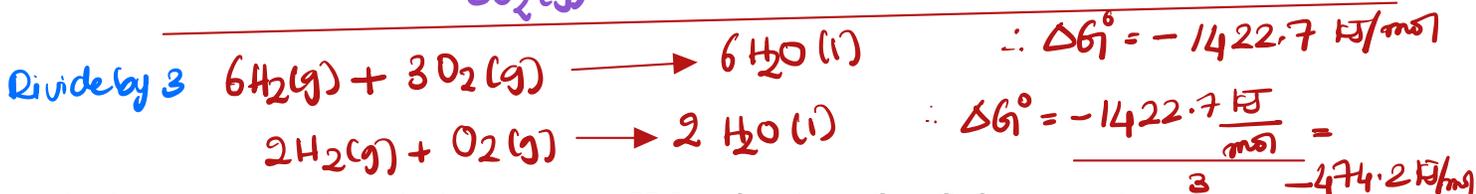
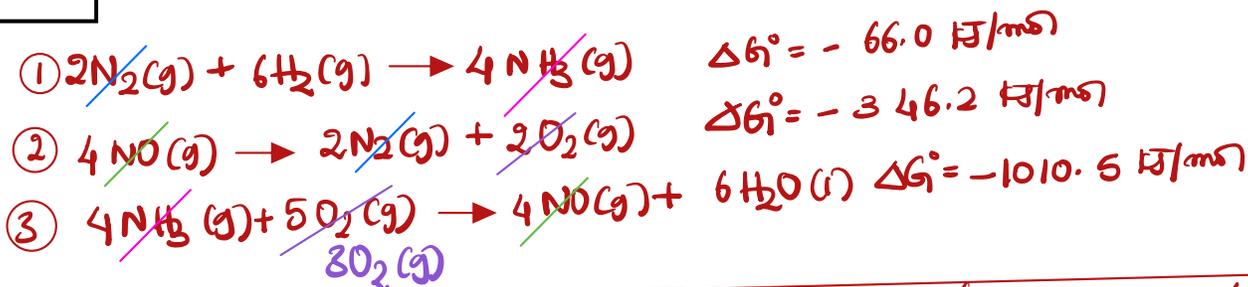
- A. Adding AgCl to water *insoluble in H₂O ∴ ΔS ≈ 0*
- B. Heating up a beaker of ethanol from 20 °C to 30 °C *ΔS > 0*
- C. Water vapor condensing on a cold surface *H₂O(g) → H₂O(l) ∴ ΔS < 0*
- D. Mixing HCl gas and NH₃ gas to form an ammonium chloride salt
- E. Adding NH₄NO₃ to water in an ice pack *NH₄NO₃ is H₂O soluble ∴ ΔS > 0*
- F. Adding NH₄Cl (aq) to a solution of NaOH(aq) and forming NaCl(aq), H₂O(l), and NH₃(g)
- G. The synthesis of a protein from amino acids by ribosomes within cells



42. Calculate the Δ°G value for the reaction $2 \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(l)}$ using the information provided below.

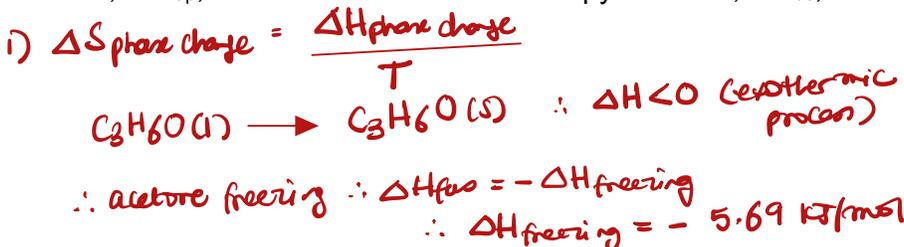


-474.2 kJ/mol



43. What is the change in entropy that occurs when 22.0 g of acetone (C₃H₆O) freezes at its melting point (-94.8 °C). The enthalpy of vaporization, ΔH_{vap}, is 32.0 kJ/mol and the enthalpy of fusion, ΔH_{fus}, is 5.69 kJ/mol for acetone.

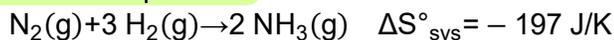
-12.1 J/K



2) $\Delta S_{\text{freezing}} = -5.69 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times 22.0 \text{ g C}_3\text{H}_6\text{O} \times \frac{1 \text{ mol C}_3\text{H}_6\text{O}}{58.09 \text{ g}}$

 $(-94.8 \text{ }^\circ\text{C} + 273.15)$
 $= -12.0826014$
 $\sim -12.1 \text{ J/K}$

44. At 298 K, the formation of ammonia has a negative $\Delta S^\circ_{\text{sys}}$. Calculate $\Delta S^\circ_{\text{univ}}$, and state whether the reaction occurs spontaneously at this temperature.



A. What is the $\Delta H^\circ_{\text{rxn}}$? ($\Delta H^\circ_f \text{NH}_3 = -45.9 \text{ kJ/mol}$)

91.8 kJ

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= \sum n H_f^\circ (\text{products}) - \sum n H_f^\circ (\text{reactants}) \\ &= [2 \times -45.9] - [(1 \times 0) + (3 \times 0)] \\ &= -91.8 \text{ kJ} \end{aligned}$$

B. What is the ΔS_{surr} ?

308 J/K

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{rxn}}}{T} = -\left(\frac{-91.8 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{298 \text{ K}}\right) = 308 \text{ J/K}$$

C. What is the calculated value of $\Delta S^\circ_{\text{univ}}$?

111 J/K

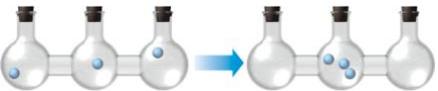
$$\begin{aligned} \Delta S^\circ_{\text{univ}} &= \Delta S^\circ_{\text{sys}} + \Delta S_{\text{surr}} \\ &= -197 \text{ J/K} + 308 \text{ J/K} \\ &= 111 \text{ J/K} \end{aligned}$$

D. Is the reaction spontaneous (A) or non-spontaneous (B)

A

45. Entropy usually increases when: $\Delta S > 0$

- I. A molecule decomposes into two smaller molecules
- II. A reaction that results in the increase in the number of moles of gas

III.  disordered \rightarrow ordered

IV. Vaporization of a liquid $\text{liquid} \rightarrow \text{gas}$


- A. I, II, III, and IV
- B. I, II, and III
- C. I, II, and IV
- D. I and II
- E. II only

C

46. If a chemical transformation is determined to be spontaneous, however no transformation is observed, which reasons could be valid for this observation? (Select all that apply)

AE

- A. The transformation has a high activation energy
 - B. The transformation has a low activation energy
 - C. The transformation is exothermic
 - D. The transformation is endothermic
 - E. The transformation is only spontaneous at very high or very low temperatures.
- if low E_a ∴ the reaction must occur
spontaneous processes can be endothermic or exothermic*

47. What is the percent by mass of a KCl solution prepared by dissolving 23.4 g of KCl in 10.5 mol water?

C

- A. 0.028%
- B. 1.59%
- C. 11.0%
- D. 12.4%
- E. None of the above

$$\% \text{ mass} = \frac{\text{mass of solute in g}}{\text{mass of solution in g}} \times 100$$

23.4g *23.4g KCl*

solute + solvent

$$10.5 \text{ mol H}_2\text{O} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol}} = 189.21 \text{ g H}_2\text{O}$$

$$\therefore \% \text{ by mass} = \frac{23.4 \text{ g KCl}}{23.4 \text{ g KCl} + 189.21 \text{ g H}_2\text{O}} \times 100 = 11.00606746\% \approx 11.0\%$$

A - thermodynamics gives me only information about spontaneity but does not give information about the speed of the reaction or how long it will take to transform from reactants to products ∴ the reaction must have a high activation energy

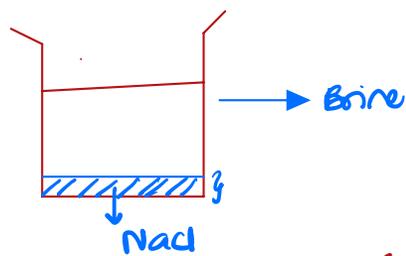
E - spontaneity can be temperature dependent based on the signs for ΔH & ΔS

F - Equilibrium reactions can be spontaneous or non-spontaneous

48. Brine is a common solution used in research labs, typically recognizable as having at least 1 inch of solid NaCl resting at the bottom of the container. Brine would be considered a _____ solution.

D

- A. Concentrated
- B. Dilute
- C. Unsaturated
- D. Saturated
- E. Supersaturated



If a solution that has reached its maximum solubility (no more solid dissolves) no matter how much you add ∴ the solution is saturated

49. Arrows in this energy diagram represent enthalpy changes occurring in the exothermic formation of a solution:

ΔH_{soln} = enthalpy of solution

$\Delta H_{\text{solute-solute}}$ = enthalpy change involving solute-solute interactions

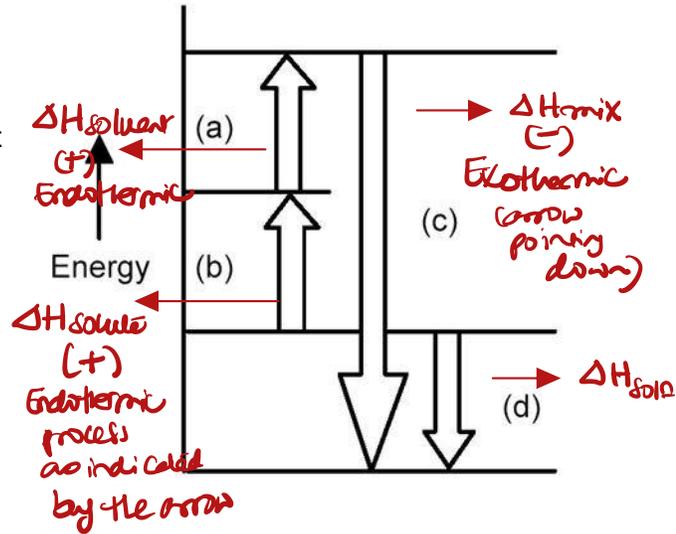
$\Delta H_{\text{solute-solvent}}$ = enthalpy change involving solute-solvent interactions

$\Delta H_{\text{solvent-solvent}}$ = enthalpy change involving solvent-solvent interactions

Which arrow represents ΔH_{soln} ?

- A. arrow (a)
- B. arrow (b)
- C. arrow (c)
- D. arrow (d)

D

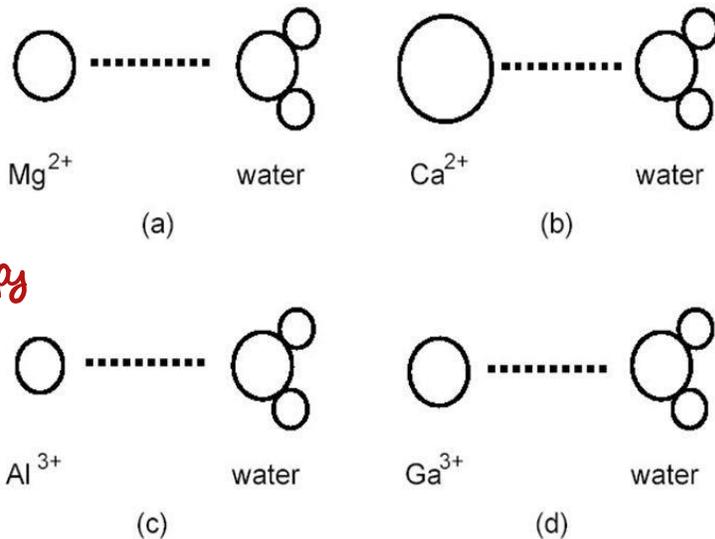


$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} (+) + \Delta H_{\text{solvent}} (+) + \Delta H_{\text{mix}} (-)$$

50. Which ion-dipole interaction results in the larger (more negative) hydration energy?

C

- A. diagram (a)
- B. diagram (b)
- C. diagram (c)
- D. diagram (d)



When considering the Enthalpy of hydration we reference the same factors pertaining to lattice energy

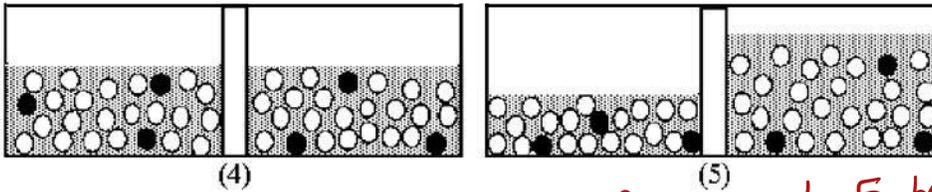
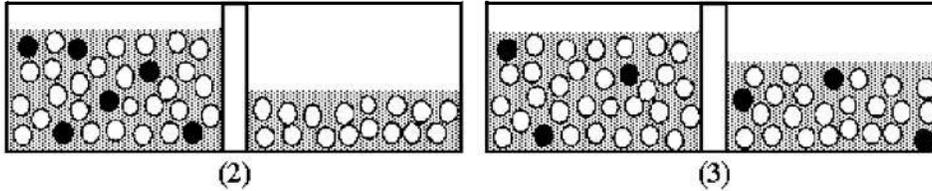
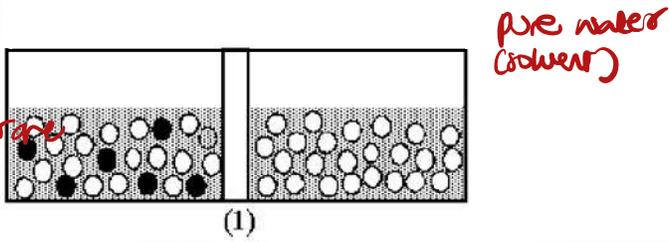
ionic charge (more important) ionic size

- Mg²⁺ & Ca²⁺ have a lower charge compared to Al³⁺ & Ga³⁺

- Al³⁺ is smaller in size than Ga³⁺ ∴ Al³⁺ will have the most negative enthalpy of hydration

51. Drawing (1) shows a nonequilibrium system comprised of pure water separated from an aqueous solution by a semipermeable membrane. Shaded spheres represent solute particles and unshaded spheres represent water molecules. Which drawing (2)-(5) represents this system after equilibrium is reached?

think osmotic pressure = movement of solvent particles from a dilute (less concentrated) to a concentrated solution through a semipermeable membrane
 semipermeable membrane only allows the passage of solvent particles only)



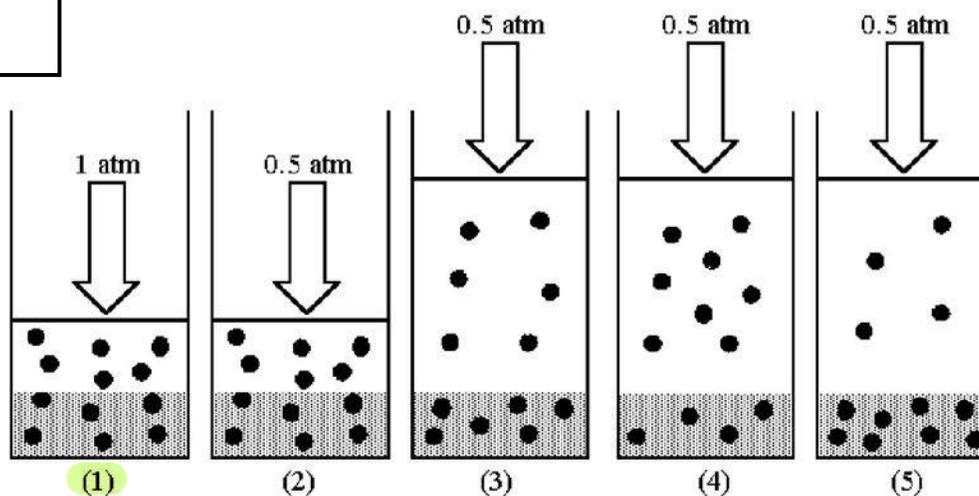
Drawings 3, 4, 5 have solute particles on both sides which cannot pass through a semipermeable membrane.

A

- A. drawing (2)
- B. drawing (3)
- C. drawing (4)
- D. drawing (5)

52. Drawing (1) shows a system in which an equilibrium exists between dissolved and undissolved gas particles at $P = 1$ atm. According to Henry's law, if the pressure is decreased to 0.5 atm and equilibrium is restored, which drawing (2)-(5) best represents the equilibrium at 0.5 atm?

C



- A. drawing (2)
- B. drawing (3)
- C. drawing (4)
- D. drawing (5)

Henry's law $C_{\text{gas}} = k_H \times P_{\text{gas}}$

Henry's law constant k_H

C_{gas} \downarrow solubility of gas in mol/L

P_{gas} \downarrow partial pressure of gas above the solution

According to Henry's law the solubility of the gas increases with increasing the partial pressure of the gas above the solvent & vice versa
 \therefore if $P_{\text{gas}} \downarrow$ C_{gas} should also \downarrow

53. Isoamyl salicylate (molar mass = 208.25 g/mol) has a pleasant aroma and is used in perfumes and soaps. What is the molality of the solution if 117.2 g of isoamyl salicylate is dissolved in 950.0 mL of ethyl alcohol? Density of ethyl alcohol is 0.7893 g/mL.

0.75 m

molality = $\frac{\text{mol of solute}}{\text{kg of solvent}}$

1) mol of solute = $117.2 \text{ g} \times \frac{1 \text{ mol}}{208.25 \text{ g}} = 0.562785114 \text{ mol}$ of isoamyl salicylate

2) kg of ethyl alcohol = $950 \text{ mL} \times \frac{0.7893 \text{ g}}{\text{mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.749835 \text{ kg}$

3) $m = \frac{0.562785114 \text{ mol}}{0.749835 \text{ kg}} = 0.750545272 \text{ m} \approx 0.75$

54. Which of the statements is **true** for aqueous solutions of 3.0 m KBr and 3.0 m Ni(NO₃)₂?

C

- A. The KBr solution has a ^{lower} freezing point and ^{higher} vapor pressure than the Ni(NO₃)₂ solution
- B. The KBr solution has a ^{higher} freezing point and ^{lower} vapor pressure than the Ni(NO₃)₂ solution
- C. The KBr solution has a higher freezing point and higher vapor pressure than the Ni(NO₃)₂ solution
- D. The KBr solution has a higher freezing point and ^{lower} vapor pressure than the Ni(NO₃)₂ solution
- E. None of the statements are true

Colligative properties are related to the number of solute particles in a solution

More solute particles =

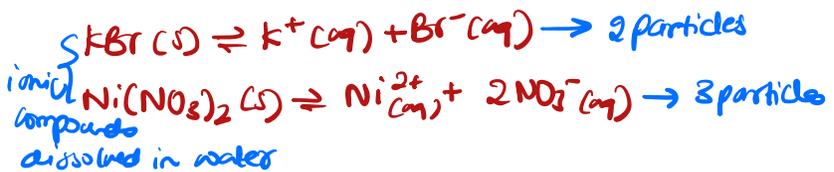
↑ boiling point

↑ osmotic pressure

↓ freezing point & ↓ vapor pressure

3.0 m KBr and 3.0 m Ni(NO₃)₂

↓
Same conc. of both salts



55. A handbook lists the value of the Henry's Law constant as 6.100 × 10⁻⁴ mol/L·atm for nitrogen, N₂, dissolved in water at 25 °C. Calculate the mole fraction of nitrogen in water at a nitrogen partial pressure of 292 torr. The density of this solution is 1.00 g/mL.

4.22 × 10⁻⁶

$$C_{gao} = K_H \times P_{N_2}$$

$$C_{gao} = 6.100 \times 10^{-4} \frac{\text{mol}}{\text{L} \cdot \text{atm}} \times 292 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}$$

$$= 2.343684211 \times 10^{-4} \text{ mol/L}$$

2) Convert from M to χ_{N_2}

$$\chi_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}}$$

$$\frac{2.343684211 \times 10^{-4} \text{ mol } N_2}{1 \text{ L solution} \rightarrow \text{solute} + \text{solvent}}$$

1 L solution → solute + solvent
∴ you can consider the 1L the solvent

1) Convert mol/L of N₂ to grams of N₂

$$2.343684211 \times 10^{-4} \text{ mol } N_2 \times \frac{28.00 \text{ g } N_2}{1 \text{ mol } N_2} = 6.562315791 \times 10^{-3} \text{ g}$$

ii) Mass of solution

$$1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.0 \text{ g}}{\text{mL}} = 1000 \text{ g}$$

$$\text{iii) Mass of } H_2O = 1000 \text{ g} - 6.562315791 \times 10^{-3} \text{ g} \approx 1000 \text{ g } H_2O$$

$$n_{H_2O} = 1000 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 55.49389567 \text{ mol}$$

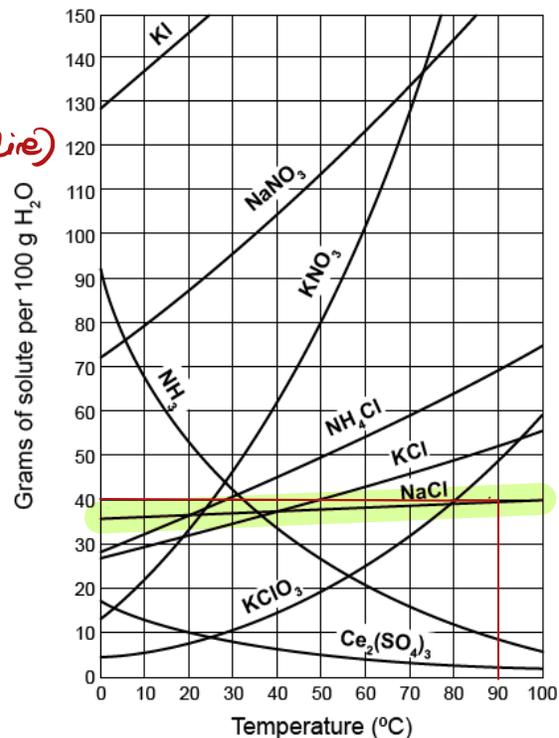
3) $\chi_{N_2} =$

$$\frac{2.343684211 \times 10^{-4}}{2.343684211 \times 10^{-4} + 55.49389567} = 4.223301112 \times 10^{-6}$$

56. Which of these statements is true, after 40. g of NaCl is added to 100. g of water at 90 °C? (Select all that apply)

- A. The solution is ~~supersaturated~~ at this temperature *saturated (the temperature & solubility fall along the line)*
- B. The solution is saturated at this temperature *correct*
- C. The change in the Gibbs free energy of the dissolution of the solute at this temperature is zero *true (dynamic equilibrium $\Delta G=0$)*
- D. The concentration of the solution increases when more NaCl is added at this temperature *doesn't change because this is a saturated solution*

B C



57. A sample of homemade whiskey from a cheap backyard still has a mole fraction of ethanol of 0.350. What would be the mole fraction of the ethanol in the vapor of this sample at 40.0 °C? At 40.0 °C the vapor pressure of H₂O is 55.0 mm Hg and ethanol is 135 mm Hg.

0.569

① Using Raoult's law to determine the partial pressures of ethanol & H₂O in the vapor

$$P_{\text{ETOH}} = \chi_{\text{ETOH}} \times P_{\text{ETOH}}^{\circ} = 0.35 \times 135 = 47.25 \text{ mmHg}$$

$$P_{\text{H}_2\text{O}} = \chi_{\text{H}_2\text{O}} \times P_{\text{H}_2\text{O}}^{\circ} = (1 - 0.35) \times 55 = 31.75 \text{ mmHg}$$

② Using Dalton's law of partial pressures

$$\chi_{\text{ETOH}} = \frac{n_{\text{ETOH}}}{n_{\text{ETOH}} + n_{\text{H}_2\text{O}}} = \frac{P_{\text{ETOH}}}{P_{\text{ETOH}} + P_{\text{H}_2\text{O}}}$$

$$= \frac{47.25}{47.25 + 31.75} = 0.599277$$

Indicates that is a saturated solution

58. A solution of sucrose (sugar) in water is in equilibrium with solid sucrose. If more solid sucrose is now added, with stirring,

C

- A. the concentration of the solution will increase.
- B. the concentration of the solution will decrease.
- C. the concentration of the solution will remain the same.
- D. the volume of solution will increase.
- E. a supersaturated solution will be produced.

If a solution is saturated its concentration would never change because the solute in the solution is in dynamic equilibrium with the solid

59. What is the molarity of a solution that is 26.0% by mass phosphoric acid (H_3PO_4) and that has a density of 1.155 g/mL? Molar mass of H_3PO_4 is 97.994 g/mol.

D

- A. $2.30 \times 10^{-3} M$
- B. 2.30 M
- C. 2.65 M
- D. 3.06 M
- E. 0.265 M

1) $\frac{26.0g H_3PO_4}{100.0g \text{ solution}} \rightarrow \frac{\text{mass of } H_3PO_4}{1L \text{ solution}}$

2) Moles of H_3PO_4
 $26.0g H_3PO_4 \times \frac{1 \text{ mol } H_3PO_4}{97.994 g H_3PO_4} = 0.2653223667 \text{ mol}$

3) Liter of solution
 $100.0g \times \frac{1 \text{ mL}}{1.155g} \times \frac{1L}{1000 \text{ mL}} = 8.658008658 \times 10^{-2} L$

4) Molarity of the solution = $\frac{0.2653223667 \text{ mol}}{8.658008658 \times 10^{-2} L} = 3.064473335 M \approx 3.06 M$

60. What is the percent $CdSO_4$ by mass in a 1.00 molal aqueous $CdSO_4$ solution? Molar mass of $CdSO_4$ is 208.47 g/mol.

C

- A. 0.001%
- B. 0.10%
- C. 17.2%
- D. 20.8%
- E. 24.4%

$\frac{1.00 \text{ mol } CdSO_4}{1 \text{ kg of } H_2O \text{ (solvent)}} \rightarrow \frac{g \text{ of } CdSO_4}{g \text{ of solution}} \times 100$
 ($\frac{1}{g} CdSO_4 + g H_2O$)

1) Convert mol of $CdSO_4$ to g
 $1.00 \text{ mol } CdSO_4 \times \frac{208.47g CdSO_4}{1 \text{ mol}} = 208.47g CdSO_4$

2) Mass of solution:
 $208.47g CdSO_4 + 1000g H_2O = 1208.47g \text{ solution}$

3) % by mass of $CdSO_4$ solution
 $= \frac{208.47g}{1208.47g} \times 100 = 17.25073854 \approx 17.2\%$

61. Below is a list of various solutes dissolved in water to give solutions with different molal concentrations.

Which of the solutions below has the **lowest** freezing point?

D

- A. 0.60 m CH₂O $i=1$ $\therefore 1 \times 0.60 = 0.60$ mol particles
 B. 0.010 m Cd(NO₃)₂ $i=3$ $3 \times 0.010 = 0.030$ mol particles
 C. 0.30 m HC₂H₃O₂ $i=1$ $1 \times 0.30 = 0.30$ mol particles
 D. 0.50 m MgCl₂ $i=3$ $3 \times 0.50 = 1.50$ mol particles
 E. 0.20 m Ca₃(PO₄)₂ $i=5$ $5 \times 0.20 = 1.0$ mol particles

*colligative property
 \therefore depends on number of
 solute particles &
 determined by
 Van't Hoff factor*

$i=5$ $\therefore 5 \times 0.20 = 1.0$ mol particles

62. A solution of potassium hydroxide is in equilibrium with undissolved solute at 45 °C. What will happen if the temperature is raised to 50 °C? The solubility of potassium hydroxide increases as temperature increases.

B

- A. the mass of undissolved KOH will increase. *true if the solubility decreases with temperature*
 B. the mass of undissolved KOH will decrease.
 C. the mass of undissolved KOH will be unchanged. *true if solubility does not change with temperature*
 D. the mass of water in the solution will increase.
 E. the entropy of the system will decrease.

\downarrow
 Entropy always increases with an increase in temperature

Determined by the Van't Hoff factor (i)

63. You have just discovered the new compound "Funorium", and you want to determine if "Funorium" is an electrolyte or a non-electrolyte. You start by dissolving 0.941 g of "Funorium" in 29.88 mL of ethanol (C₂H₅OH) and determine that the boiling point of the solution is 79.87 °C. Is "Funorium" an electrolyte or a non-electrolyte? (The density of pure ethanol is 0.7892 g/cm³, the boiling point is 78.37 °C, and K_b ethanol = 1.2 °C/m. The molar mass of "Funorium" is 70.01 g/mol)

- A. Funorium is an electrolyte because its Van't Hoff factor is greater than 1
 B. Funorium is a non-electrolyte because its Van't Hoff factor is 1
 C. More information is needed

A

$$\Delta T_b = K_b \times m \times i \rightarrow ?$$

$T_b(\text{solution}) - T_b(\text{solvent})$

$$-\Delta T_b = 79.87^\circ\text{C} - 78.37^\circ\text{C} = 1.5^\circ\text{C}$$

$$-m = \frac{0.941 \text{ g Funorium}}{29.88 \text{ mL C}_2\text{H}_5\text{OH}} \times \frac{1 \text{ mol Funorium}}{70.01 \text{ g Funorium}} \times \frac{1 \text{ mL}}{0.7892 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}}$$

$$= 0.5699829648 \text{ m}$$

$$- \text{solve for } i = \frac{\Delta T_b}{K_b \times m} = \frac{1.5^\circ\text{C}}{1.2^\circ\text{C/m} \times 0.5699829648}$$

$$= 2.193047998 \approx 2 \therefore \text{Funorium is an electrolyte}$$

64. Gatorade contains 2.70 g of NaCl and 3.10 g sucrose ($C_{12}H_{22}O_{11}$) in 236.6 ml of the drink. What are the mole fractions of the NaCl and sucrose in the sports drink?

Note: assume that the density of Gatorade is 1.08 g/mL, molar mass: NaCl 58.44 g/mol, sucrose 342.3 g/mol, water 18.02 g/mol.

1. Mole fraction NaCl:

0.00332

$$x_{NaCl} = \frac{n_{NaCl}}{n_{NaCl} + n_{sucrose} + n_{H_2O}}$$

$$1) n_{NaCl} = 2.70 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.04620123203 \text{ mol}$$

$$2) n_{sucrose} = 3.10 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} = 0.00905638329 \text{ mol}$$

3) n_{H_2O} :

- Mass of solution (Gatorade):

$$236.6 \text{ mL} \times \frac{1.08 \text{ g}}{\text{mL}} = 255.528 \text{ g solution}$$

- Mass of H_2O :

$$255.528 - (2.70 + 3.10) = 249.728 \text{ g}$$

$$- n_{H_2O} = 249.728 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 13.85837958$$

2. Mole fraction sucrose:

0.000651

$$4) n_{NaCl} = \frac{0.0462}{0.0462 + 0.00906 + 13.9} = 0.00332$$

$$5) n_{sucrose} = \frac{0.00906}{0.00906 + 0.0462 + 13.9}$$

$$= 0.000651$$

65. Cinnamaldehyde (molar mass = 132.15 g/mol) is used as a flavoring agent. What mass of cinnamaldehyde must be added to 175 g of ethanol to give a solution whose boiling point is 82.7°C? ($K_b = 1.22^\circ\text{C}/m$, boiling point of pure ethanol = 78.5°C.)

E

- A. 62.4 g
- B. 67.8 g
- C. 76.2 g
- D. 78.5 g
- E. 79.6 g

$$1) \Delta T_b = K_b \times m \times i$$

$$(82.7 - 78.5)^\circ\text{C} = 1.22^\circ\text{C}/m \times m \times 1$$

$$\therefore m = 3.442622951$$

$$2) \frac{\text{mol of Cinnamaldehyde}}{175 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \text{ Ethanol}} = 3.442622951$$

$$3) \text{ mol of Cinnamaldehyde} = 0.6024590164 \text{ mol}$$

$$4) \text{ Mass of Cinnamaldehyde} = 0.6024590164 \text{ mol} \times \frac{132.15 \text{ g}}{1 \text{ mol}} = 79.61495902 \text{ g} \sim 79.6 \text{ g}$$

moles mass of
→ Cinnamaldehyde

Formula Sheet

Length

1 kilometer = 0.62137 mile
1 inch = 2.54 centimeters (exactly)
1 Ångstrom = 1×10^{-10} meter

Energy

1 joule = $1 \text{ kg}\cdot\text{m}^2/\text{s}^2$
1 calorie = 4.184 joules
1 Calorie = 1 kilocalorie = 1000 calories
1 L·atm = 101.325 joules

Pressure

1 pascal = $1 \text{ N}/\text{m}^2 = 1 \text{ kg}/\text{m}\cdot\text{s}^2$
1 atmosphere = 101.325 kilopascals = 760 mm Hg = 760 torr = 14.70 lb/in²
1 bar = 1×10^5 Pa (exactly)

Temperature

0 K = -273.15°C
K = $^\circ\text{C} + 273.15$
 $^\circ\text{C} = (5/9)(^\circ\text{F} - 32)$

Mass

1 kg = 2.205 lbs

Volume

1 mL = $1 \text{ cm}^3 = 1 \text{ cc}$

Constants

$c = 2.998 \times 10^8 \text{ m}/\text{sec}$
 $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{sec}^{-1}$
 $R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K}$
Specific heat of water = 4.184 J/g·K
Mass of an electron: $9.109 \times 10^{-31} \text{ kg}$
Mass of a proton: $1.673 \times 10^{-27} \text{ kg}$
 $RH = 2.18 \times 10^{-18} \text{ J}$
Specific heat of water = 4.184 J/g·K
STP = 273.15 K and 1 atm
Avogadro's number: 6.022×10^{23}

Equations

d (density) = m/V

$P_1V_1 = P_2V_2$

$V_1/T_1 = V_2/T_2$

$P_1V_1/n_1T_1 = P_2V_2/n_2T_2$

$PV = nRT$

$(P + a(n^2/V^2))\cdot(V - nb) = nRT$

molar mass (M) = mRT/PV

density (d) = MP/RT

$x_A = n_A/n_{\text{tot}} = P_A/P_{\text{tot}} = V_A/V_{\text{tot}}$

$P_{\text{tot}} = P_A + P_B + \dots$

$n_{\text{tot}} = n_A + n_B + \dots$

$$\mu_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\frac{\text{Rate of effusion A}}{\text{Rate of effusion B}} = \sqrt{\frac{MW_B}{MW_A}}$$

$$Q = C \times \Delta T = c_{\text{specific}} \times m \times \Delta T$$

$$Q = n \times \Delta H \text{ (kJ/mol)} = m \times \Delta H \text{ (kJ/g)}$$

$$w = -P\Delta V$$

$$\Delta E = q + w$$

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$$

$$\Delta H^\circ = \sum n\Delta H^\circ(\text{bonds broken}) - \sum n\Delta H^\circ(\text{bonds formed})$$

$$E = hv$$

$$c = \lambda\nu$$

$$\lambda = h/mv$$

$$\Delta E = -2.18 \times 10^{-18} J \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$C_g = kP_g$$

$$P_{\text{solution}} = P_{\text{solvent}} X_{\text{solvent}}$$

$$P_{\text{solution}} = \sum P_j = \sum P_j X_j$$

$$\Delta T_b = K_b m_i$$

$$\Delta T_f = K_f m_i$$

$$\pi = MRT_i$$

Thermodynamic and Electrochemistry

$$S = k_b \times \ln(W)$$

$$k_b = 1.381 \times 10^{-23} \text{ J/K}$$

$$\Delta S = q_{\text{rev}}/T$$

$$\Delta S_{\text{surr}} = q_{\text{surr}}/T = -q_{\text{rev}}/T$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S^\circ_{\text{rxn}} = \sum \nu S^\circ_{\text{products}} - \sum \nu S^\circ_{\text{reactants}}$$

$$\Delta H^\circ_{\text{rxn}} = \sum \nu H^\circ_{\text{products}} - \sum \nu H^\circ_{\text{reactants}}$$

$$\Delta G^\circ_{\text{rxn}} = \sum \nu G^\circ_{\text{products}} - \sum \nu G^\circ_{\text{reactants}}$$

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

$$\Delta G = \Delta G^\circ + RT \cdot \ln Q$$

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

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

$$\Delta G = -nFE_{\text{cell}}$$

$$F = 96485 \text{ J/(V}\cdot\text{mol e}^-)$$

$$E^\circ_{\text{cell}} = RT/nF \ln K$$

$$E^\circ_{\text{cell}} = (0.0257/n) \ln K = (0.0592/n) \log K$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/nF) \ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0257/n) \ln Q$$

$$\text{Electrolysis: } Q \text{ (total charge)} = I \times t = n \times F$$

Integrated Rate Laws & half-life

$$\ln \frac{[A]}{[A]_0} = -kt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$[A] = -kt + [A]_0$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

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

Equilibrium and Acid / Base

$$K_p = K_c \times (RT)^{\Delta n}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$$

$$K_w = K_a \times K_b$$

$$\text{p}K_a = -\log[K_a]$$

$$\text{Buffer: pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Periodic Table of the Elements

1																		2												
1 H 1.01	2																2 He 4.00													
3 Li 6.94	4 Be 9.01															5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18									
11 Na 22.99	12 Mg 24.31															13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95									
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80													
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [97]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29													
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97																
87 Fr [223]	88 Ra [226]															104 Rf [267]	105 Db [268]	106 Sg [269]	107 Bh [270]	108 Hs [269]	109 Mt [277]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Nh [286]	114 Fl [290]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]																