

1. In the bromination reaction of alkanes at a certain temperature, the rate constants of substitution for primary, secondary, and tertiary hydrogen atoms are in the ratio of 1:4:5. For 3-ethylpentane, calculate the ratio of the following monosubstituted products (assuming only monosubstitution takes place): 1-bromo-3-ethylpentane, 2-bromo-3-ethylpentane, 3-bromo-3-ethylpentane.

- a. 1:4:5
- b. 1:4096:5
- c. 5:4:1
- d. 6:16:5
- e. 9:24:5

2. Does AgCl precipitate out of the solution with initial concentrations of AgNO₃ equal to 0.01 M and KCl equal to 0.1 M, if a) no NH₃ is added; b) 0.01 M NH₃ is present in the solution; c) 2 M NH₃ solution is present in the solution?

$$K_{sp}(\text{AgCl}) = 1.78 \times 10^{-10}$$

$$\text{For } [\text{Ag}(\text{NH}_3)_2]^+, \beta_1 = 2.09 \times 10^3, \beta_2 = 1.62 \times 10^7.$$

- a. no, no, no
- b. yes, no, no
- c. yes, no, yes
- d. yes, yes, no
- e. yes, yes, yes

3. Which form is dominant in the 0.01 M solution of Cd(NO₃)₂ in the presence of NaBr (0.01 M)? Assume no hydrolysis takes place.

$$\text{For } [\text{CdBr}_4]^{2-}, \lg \beta_1 = 2.23, \lg \beta_2 = 2.80, \lg \beta_3 = 3.60, \lg \beta_4 = 3.70.$$

- a. Cd²⁺
- b. [CdBr]⁺
- c. [CdBr₂]
- d. [CdBr₃]⁻
- e. [CdBr₄]²⁻

4. Amino acids and other optically active compounds in their pure enantiomeric form can racemize over time. Determine the signs of ΔH , ΔS , ΔG (in this order, left to right) for this process.

- a. =0, >0, <0
- b. =0, =0, =0
- c. <0, >0, <0
- d. <0, <0, >0
- e. >0, >0, =0

5. Determine the standard enthalpy of isomerization of gaseous cyclopropane to gaseous propylene ($\Delta_f H^\circ = 20.4 \text{ kJ/mol}$). The standard enthalpies of combustion (to CO₂(g) and H₂O(l)) are given below:

solid graphite	-393.5 kJ/mol
gaseous hydrogen	-285.8 kJ/mol
gaseous cyclopropane	-2091.2 kJ/mol

- a. -35.2 kJ/mol
- b. 82.5 kJ/mol
- c. -14.7 kJ/mol
- d. 39.3 kJ/mol
- e. -32.9 kJ/mol

6. To study the kinetics of isomerization of ammonium cyanate to urea, 22.9 g of ammonium cyanate was dissolved in water, and the volume of the solution was brought to 1.00 l. When measuring the urea content in the solution, the following data were obtained:

t, min	0	20.0	50.0	65.0	150
m (urea), g	0	7.0	12.1	13.8	17.7

Determine the order of the reaction.

- a. 0
- b. 1
- c. 2
- d. 3
- e. not enough data

7. Which compound is a Lewis acid but not a Brønsted acid?

- a. BF_3
- b. pyridine
- c. H_2SO_4
- d. NH_4^+
- e. any Lewis acid is also a Brønsted acid

8. A phosphate buffer solution was prepared in the laboratory by mixing 70 ml of $3 \times 10^{-3} \text{ M}$ sodium orthophosphate solution and 30 ml of $7 \times 10^{-3} \text{ M}$ phosphoric acid solution. Acidity constants of H_3PO_4 : $K_{a1} = 7.1 \times 10^{-3}$; $K_{a2} = 6.2 \times 10^{-8}$; $K_{a3} = 5.0 \times 10^{-13}$. Calculate the pH value of the resulting phosphate buffer solution.

- a. 6.2
- b. 6.9
- c. 7.2
- d. 8.1
- e. 8.6

9. The galvanic cell consists of two electrodes:

- a copper plate weighing 0.92 g, immersed in 0.1 L of a 0.09 M copper(II) nitrate solution;
- a silver plate weighing 3.84 g, coated with a layer of 2.38 g silver iodide in 0.2 L of a 0.2 M potassium iodide solution.

$$E^\circ_{\text{AgI/Ag, I}^-} = -0.152 \text{ V}$$

What is the final mass of the silver plate (without coating) after the reaction stops (emf = 0)?

- a. 0 g
- b. 1.25 g
- c. 1.49 g
- d. 1.90 g
- e. 4.92 g

10. In 1949, Willard Libby developed a method of radiometric analysis based on the decay of radioactive isotope ^{14}C to determine the age of objects of biological origin, for which he received the Nobel Prize in 1960. It allows one to determine the time that has passed since the death of a biological object and the cessation of carbon exchange with air. The isotope ^{14}C , whose concentration was previously maintained at a constant level due to this exchange, begins to decay in the first-order process. The half-life of this isotope is 5700 years.

The remains of a mammoth contain 7.25% of radioactive ^{14}C from its original amount in living tissue. Determine the geological age of the mammoth.

- a. 15330 years
- b. 20480 years
- c. 21580 years
- d. 78620 years

e. 85670 years

11. In two reactions of the same order, the difference in activation energy is $E_2 - E_1 = 40$ kJ/mol. At a temperature of 293 K, the ratio of rate constants is $k_1/k_2 = 2$. At what temperature will the rate constants be equal?

- a. 273 K
- b. 306 K
- c. 332 K
- d. 350 K
- e. 386 K

12. In the gas-phase reaction $A + B = D$, the initial rate was measured at different partial pressures of the reactants (at 300 K). The following data were obtained:

Experiment no.	p_A , Torr	p_B , Torr	rate, M/s
1	5.0	20	5.0×10^{-7}
2	25	4.0	2.5×10^{-6}
3	20	10	1.0×10^{-6}

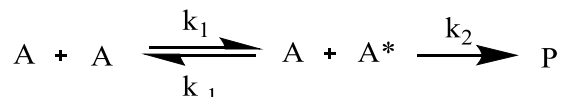
Determine the reaction partial orders for A and B, respectively.

- a. 0; -1
- b. $\frac{1}{2}$; 0
- c. 1; -1
- d. 1; 0
- e. 2; 1

13. Which of the following can **never** be true about a spontaneous process?

- a. The change in Gibbs energy is positive
- b. The change in Helmholtz energy is positive
- c. The internal energy of the system decreases
- d. The entropy of the universe decreases
- e. The change in enthalpy is positive

14. One of the theories of unimolecular reactions proposes the following mechanism for activating molecules (known as the Lindemann mechanism):



In this scheme, A collides with another molecule of A, and one of them forms a reactive, high-energy intermediate A^* , which then turns into product P in a monomolecular process.

Using steady-state approximation, determine the reaction order in A at low and high concentrations of A, respectively.

- a. 0; 1
- b. 1; 0
- c. 1; 1
- d. 1; 2
- e. 2; 1

Ammonia is the most widely produced product in the chemical industry, with more than 100 million tons produced annually. Its synthesis reaction is reversible: $N_2 + 3H_2 \rightleftharpoons 2NH_3$. At 200 °C and 1 atm, the equilibrium constant expressed in mole fractions is $K_x = 1$, and at 400 °C and the same pressure, $K_x = 0.01$.

Answer questions 15-17 using the data above.

15. Does the ammonia synthesis reaction occur with the release or absorption of heat?
- With the release, since the equilibrium constant gets smaller with higher temperature
 - With the absorption, since the equilibrium constant gets smaller with higher temperature
 - With the absorption, since the process is reversible
 - With the absorption, since the reaction proceeds at high temperatures
 - Not enough data
16. How many moles of ammonia can be formed at 200 °C from 1 mole of N₂ and 3 moles of H₂?
- 0.13 mol
 - 0.35 mol
 - 0.68 mol
 - 1 mol
 - 3 mol
17. An equilibrium mixture under certain conditions contains 0.65 mol N₂, 0.25 mol H₂, and 0.1 mol NH₃. In which direction will the equilibrium shift when 0.25 mol nitrogen is added to this mixture?
- To the left, since the equilibrium constant is smaller than 1
 - To the left, since further addition of N₂ is thermodynamically unfavorable
 - To the right, since the reagent is added to the mixture
 - To the right, since the equilibrium constant is bigger than 1
 - Not enough data

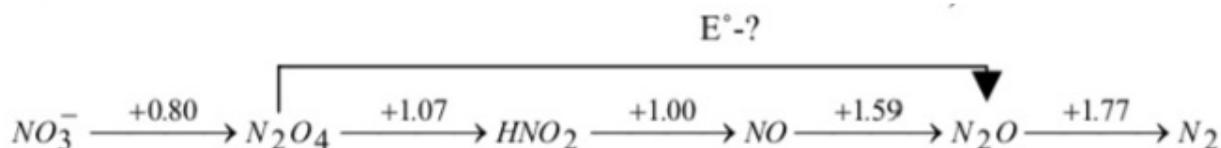
18. In the process $A + B \rightarrow C$, the time in which half of the final amount of C for a given experiment is formed was measured and its dependence on the initial concentrations of A and B was investigated. The results are given in the table:

Experiment no.	C (A), M	C (B), M	$\tau_{1/2}$, s
1	0.001	2	25
2	0.002	2	25
3	2	0.01	7200
4	2	0.02	3600

Determine the overall order of the reaction.

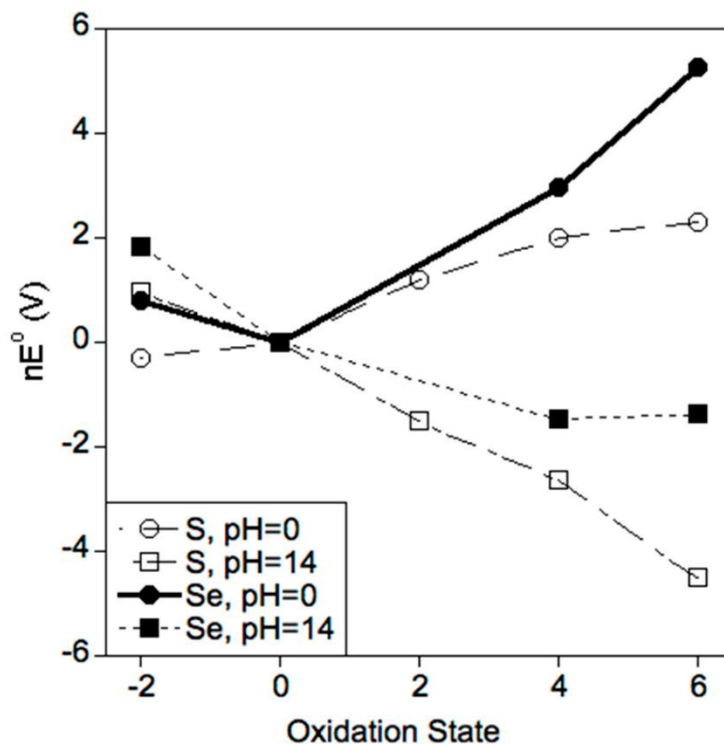
- 0
- 1
- 2
- 3
- 4

A Latimer diagram of a chemical element is a summary of the standard electrode potential data of that element. In a Latimer diagram, the most highly oxidized form of the element is on the left side, with successively lower oxidation states on the right side. The species are connected by arrows, and the numerical value of the standard potential (in volts) for the reduction is written at each arrow.



19. Find the value of E° for the diagram above (nitrogen-containing compounds at pH=0).
- 1.05 V
 - 1.22 V
 - 2.44 V
 - 3.66 V
 - 7.32 V

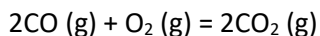
A Frost diagram of a chemical element is also a summary of the standard electrode potential data similar to the Latimer diagram described in question 19. The Frost diagram is a graph in which the x-axis represents the oxidation state of the element, and the y-axis shows the nE° value, where n is the oxidation state and E° is the standard reduction potential associated with interconversion between the free element and that oxidation state. The maxima and minima in the diagram can be used to predict stable and unstable forms of the element.



20. Which of the following statements is **FALSE**?
- All lines intersect at oxidation state 0 because it is a general property of all Frost diagrams.
 - The reaction of comproportionation H_2Se and H_2SeO_3 is favored thermodynamically.
 - SeO_3^{2-} is the most stable form of Se at basic conditions towards oxidation-reduction reactions.
 - If compared at the same pH, Se is easier to oxidize than S.
 - H_2SO_3 tends to undergo a disproportionation reaction.
21. Using data from the table in Supporting Information, calculate β_4 for AuCl_4^- complex.

- a. 10^{15} d. 10^{26}
 b. 10^{18} e. 10^{37}
 c. 10^{21}

22. Calculate the $\ln K_{eq}$ for the following reaction at 600 K (entropies and enthalpies are temperature-dependent):



Compound	$\Delta_f H^\circ_{298}$, kJ/mol	S°_{298} , J/mol*K	C_p , J/mol*K
CO (g)	-110.53	197.55	29.11
O ₂ (g)		205.04	29.83
CO ₂ (g)	-393.51	213.66	37.22

- a. ≈ 91.45 d. ≈ 92.66
 b. ≈ 91.89 e. ≈ 93.04
 c. ≈ 92.34

23. Calculate the solubility (in M) of a MgNH_4PO_4 in water at 25°C and pH=4 if its solubility product is equal to 6.8×10^{-14} (for H_3PO_4 $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 2.2 \times 10^{-13}$ and for NH_3 $K_b = 1.7 \times 10^{-5}$).

- a. 1.1×10^{-7} d. 0.88
 b. 0.041 e. 27
 c. 0.37

24. Using data from the table in Supporting Information, calculate the equilibrium constant for the reaction of KMnO_4 with H_2SO_3 at pH=0 and 298 K (use smallest integers coefficients).

- a. $\approx 10^{206}$ d. $\approx 10^{248}$
 b. $\approx 10^{220}$ e. $\approx 10^{350}$
 c. $\approx 10^{231}$

25. 400 mL KOH solution (0.5 M) and 600 mL H_3PO_4 solution (0.167 M) were mixed. Calculate the pH of the resulting solution (for H_3PO_4 $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 2.2 \times 10^{-13}$).

- a. ≈ 7.4 d. ≈ 9.5
 b. ≈ 8.6 e. ≈ 10.1
 c. ≈ 9.1

Supporting Information

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathcal{E}^\circ$ (V)	Half-reaction	$\mathcal{E}^\circ$ (V)
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	1.99	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.27
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{IO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{IO}_3^- + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.50
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.09	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.23
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.80	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52		

Useful equations:

Relationship between equilibrium constant, Gibbs energy, enthalpy, and entropy:

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

Nernst equation for electrochemical half-cell:

$$E = E^\circ + \frac{RT}{zF} \ln \frac{[Ox]}{[Red]}$$

Electromotive force:

$$Emf = - \frac{\Delta G}{zF}$$

Arrhenius equation:

$$k = Ae^{-\frac{E_A}{RT}}$$

Temperature-dependence of ΔH and ΔS :

$$\Delta_f H_T = \Delta_f H_{298} + C_p(T - 298); S_T = S_{298} + C_p \ln \frac{T}{298};$$