

Solutions

1. The intermolecular attractive forces would be greatest in which of the following molecules: CH_4 , CH_2Cl_2 and CO_2 .

- (A) CH_4
- (B) CH_2Cl_2
- (C) CO_2
- (D) the same in all three molecules
- (E) no way to predict this property

CH_2Cl_2 is the only one that is polar, the others are nonpolar

2. The melting point of the halogens (Group VII: F_2 , Cl_2 , Br_2 , I_2) increases as you move down the column. This is because:

- (A) *Induced dipole effects increase with molecular weight.*
- (B) The smaller molecules have more hydrogen bonding.
- (C) I_2 is a solid at room temperature.
- (D) The larger molecules are more polar.
- (E) both A and D above.

All of these are nonpolar and have no hydrogen bonding. C is true, but doesn't explain why, so it's A (which is true and explains why)

3. The predominant intermolecular attractive force in solid xenon is:

- (A) ionic
- (B) covalent
- (C) metallic
- (D) dipole-dipole
- (E) *induced dipole-induced dipole*

Xenon is a nonmetal, so the only force in this atom is induced dipole-induced dipole

4. Urea, $\text{O}=\text{C}(\text{NH}_2)_2$ would be predicted to be most soluble in which solvent:

- (A) H_2O
- (B) CCl_4
- (C) CCl_3H
- (D) CH_4
- (E) C_3H_8

Urea has hydrogen bonding and is polar, so it would be most soluble in a solvent that is also polar and hydrogen bonding: H_2O

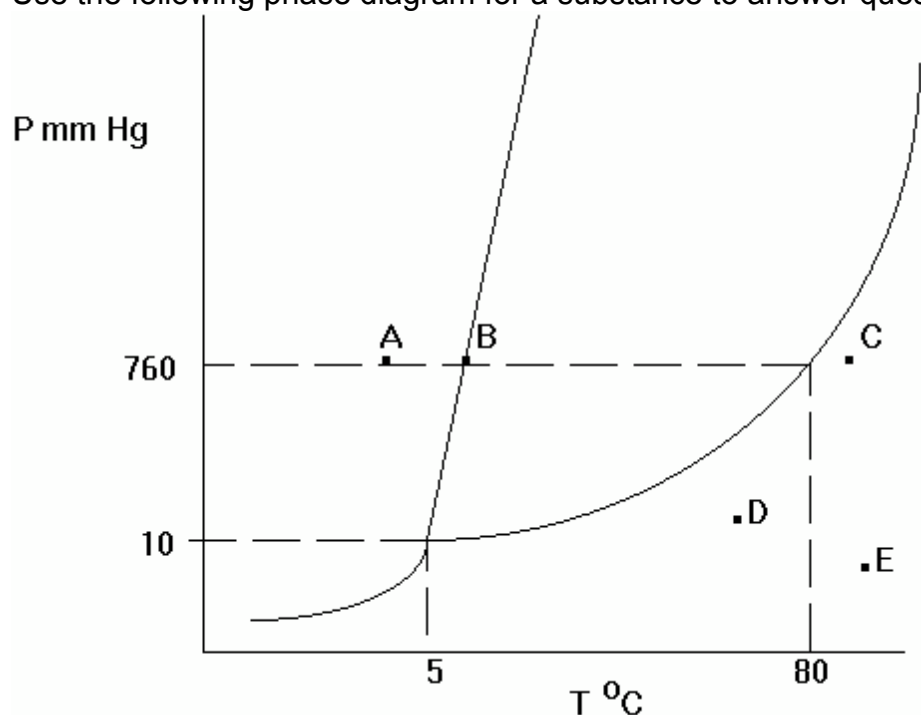
5. Calculate the energy, in kJ, required to convert a 36.00 g sample of solid water at 0°C to liquid water at 0°C . The molecular weight of water is 18.00 g/mol. For water, $\Delta H_{\text{vap}}=40.7$ kJ/mol and $\Delta H_{\text{fusion}}=6.0$ kJ/mol.

- (A) 6.0
- (B) **12.0**
- (C) 20.4
- (D) 40.7
- (E) 81.4

Melt water at its normal melting point, so $\Delta H = \Delta H_{\text{fusion}} \times \text{moles water}$

$\Delta H = 6.0 \text{ kJ/mol} \times (36.00 \text{ g water}) \times (1 \text{ mol water}/18.00 \text{ g}) = 12.0 \text{ kJ}$

Use the following phase diagram for a substance to answer questions 6 and 7.



6. A sample of the substance is placed in a container at a temperature of 85°C and the pressure is fixed at 10 mm Hg. Under these conditions what phase(s) exist?

- (A) solid only (D) solid and liquid
(B) liquid only (E) liquid and gas

(C) gas only

Near label "E" above : gas only

7. The substance is placed in a container at the same original conditions as in problem number 6. The substance is then cooled to 0 °C at *constant pressure*. What phase(s) will be present at the final conditions?

(A) solid only

(B) liquid only

(C) gas only

(D) solid in equilibrium with liquid

(E) solid in equilibrium with gas

Constant pressure, so move left on the graph to where it is a solid

8. The heat of vaporization of water is 40.7 kJ/mol. It boils at 100 °C at 1 atm. At what temperature does water boil at the top of Mt. Washington, where the atmospheric pressure is 0.80 atm?

- (A) 89°C *(B) 94 °C* (C) 97 °C (D) 99.5 °C (E) 105 °C

$$\ln\left(\frac{P_2}{P_1}\right) = \left(\frac{\Delta H_{vap}^0}{R}\right)\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Use $T_1=100+273=373\text{ K}$, $P_1=1\text{ atm}$, $P_2=0.8\text{ atm}$, $\Delta H_{\text{vap}}=40.7\text{ kJ/mol}$ and $R=8.314\times 10^{-3}\text{ kJ/(mol K)}$

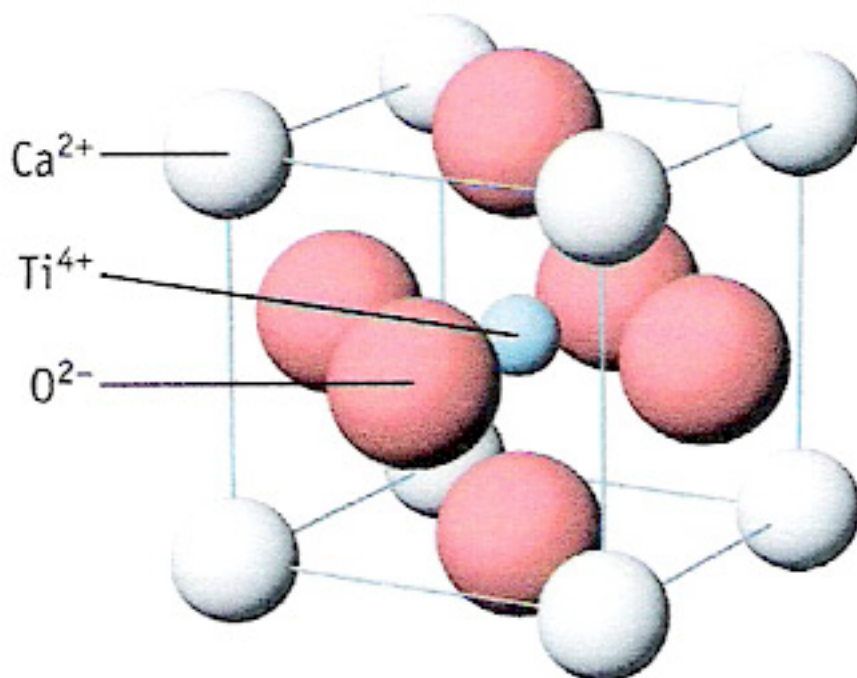
$$\ln\left(\frac{0.8}{1.0}\right) = \left(\frac{40.7\text{ kJ/mol}}{8.314\times 10^{-3}\text{ kJ/(mol K)}}\right)\left[\frac{1}{373\text{ K}} - \frac{1}{T_2}\right]$$

$$-0.2231 = (4895.4\text{ K})\left[0.00268097\frac{1}{\text{K}} - \frac{1}{T_2}\right]$$

$$-0.00004557\frac{1}{\text{K}} = \left[0.00268097\frac{1}{\text{K}} - \frac{1}{T_2}\right]$$

$$-0.00272654\frac{1}{\text{K}} = -\frac{1}{T_2}$$

$$T_2 = 366.8\text{ K} = 93.8^\circ\text{C}$$



9. The unit cell of the mineral perovskite is shown above. The unit cell described by the Ca^{2+} ions is _____.

- (A) *simple cubic*
- (B) face centered cubic
- (C) body centered cubic
- (D) hexagonal close packing
- (E) tetrahedral

10. The formula of perovskite is _____.

(A) CaTiO_3

(B) CaTiO_6

(C) Ca_2TiO_3

(D) Ca_2TiO_6

(E) Ca_8TiO_6

Unit cell: 8 Ca^{2+} at corners (each 1/8 atom) = 1 atom Ca^{2+}

1 Ti^{4+} at center (1 atom) = 1 atom Ti^{4+}

6 O^{2-} on faces (1/2 atom each) = 3 atoms O^{2-}

11. The decomposition of SO_2Cl_2 is a first-order reaction:



The rate constant is 0.17 1/sec. What is the rate of the reaction at an initial concentration $[\text{SO}_2\text{Cl}_2] = 1.2 \times 10^{-3} \text{ mol/L}$? The rate is in units of mol/(L sec).

(A) 2.0×10^{-4} (B) 6.3×10^{-4} (C) 1.2×10^{-3} (D) 7.1×10^{-3} (E) 3.2×10^{-2}

Rate = $k[\text{SO}_2\text{Cl}_2] = (0.17 \text{ 1/sec})(1.2 \times 10^{-3} \text{ mol/L}) = 2.0 \times 10^{-4} \text{ mol/(L sec)}$

12. The reaction



is second order in $[\text{NO}]$ and first order in $[\text{H}_2]$. If the rate of the reaction is 0.55 M s^{-1} when $[\text{NO}] = 0.90 \text{ M}$ and $[\text{H}_2] = 0.45 \text{ M}$, what is the rate constant in $\text{M}^{-2}\text{s}^{-1}$?

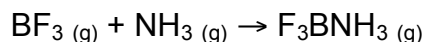
(A) 0.68 (B) 1.36 (C) 1.51 (D) 2.72 (E) 8.90

Rate = $k[\text{NO}]^2[\text{H}_2]$, so

$0.55 \text{ M s}^{-1} = k(0.90 \text{ M})^2(0.45 \text{ M}) = (0.3645 \text{ M}^3) k$

so, $k = (0.55 \text{ M s}^{-1}) / (0.3645 \text{ M}^3) = 1.51 \text{ M}^{-2}\text{s}^{-1}$

The following data were collected for the rate of disappearance of NH_3 in the reaction:



Experiment	$[\text{BF}_3](\text{M})$	$[\text{NH}_3](\text{M})$	Initial rate M/s
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0250	1.13×10^{-1}
3	0.0252	0.0125	5.64×10^{-2}

13. What is the rate law for the reaction?

(A) Rate = $k[\text{BF}_3][\text{NH}_3]$

(D) Rate = $k[\text{BF}_3]$

(B) Rate = $k[\text{BF}_3]^2[\text{NH}_3]$

(E) Rate = $k[\text{BF}_3]^2[\text{NH}_3]^2$

(C) Rate = $k[\text{BF}_3][\text{NH}_3]^2$

Expt 1 vs 3, $[\text{NH}_3]$ unchanged, $[\text{BF}_3]$ increased 2x, and the rate increases 4x (this is 2^2), so second order in $[\text{BF}_3]$.

Expt 3 vs 2, $[\text{BF}_3]$ unchanged, $[\text{NH}_3]$ increased 2x, and the rate increases 2x (this is 2^1), so first order in $[\text{NH}_3]$. Rate = $k[\text{BF}_3]^2[\text{NH}_3]$

14. In a study of the gas phase decomposition of dimethyl ether at 500 °C,



the concentration of CH_3OCH_3 was followed as a function of time. It was found that a graph of $\ln[\text{CH}_3\text{OCH}_3]$ versus time in seconds gave a straight line with a slope of $-6.00 \times 10^{-4} \text{ s}^{-1}$ and a y-intercept of -1.99

Based on this plot, the reaction is _____ order in CH_3OCH_3 and the rate constant for the reaction is _____ s^{-1} .

(A) zero, 6.00×10^{-4}

(B) first, 6.00×10^{-4}

(C) first, -7.42

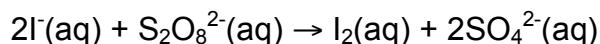
(D) second, 6.00×10^{-4}

(E) second, -7.42

For a first order reaction, $\ln[R] = \ln[R]_0 - kt$,

so a plot of $\ln[R]$ vs time gives a straight line with slope $-k$

15. The reaction



was studied at 25°C. The following results were obtained where

$$\text{Rate} = - \frac{d[\text{S}_2\text{O}_8^{2-}]}{dt}$$

$[\text{I}^-]_0$ (mol/L)	$[\text{S}_2\text{O}_8^{2-}]_0$ (mol/L)	Initial rate (mol/L s)
0.080	0.040	12.50×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.01×10^{-6}
0.060	0.030	7.02×10^{-6}

The rate equation for this reaction is:

(A) $R = k[\text{I}^-][\text{S}_2\text{O}_8^{2-}]$

(B) $R = k[\text{I}^-]^2[\text{S}_2\text{O}_8^{2-}]$

(C) $R = k[\text{I}^-][\text{S}_2\text{O}_8^{2-}]^2$

(D) $R = k[\text{I}^-]^2[\text{S}_2\text{O}_8^{2-}]^2$

(E) $R = k[\text{I}^-]$

Row 2 vs row 1, $[S_2O_8^{2-}]$ unchanged, $[I^-]$ increased 2x, rate increases 2x, so first order in $[I^-]$.

Row 3 vs row 1, $[I^-]$ unchanged, $[S_2O_8^{2-}]$ increased 2x, rate increases 2x, so first order in $[S_2O_8^{2-}]$. Rate = $k[I^-][S_2O_8^{2-}]$

The half life for the radioactive decay of ^{14}C is 5720 years.

16. What is the first order rate constant for this process?

- (A) 5720 year (D) $8.25 \times 10^3 \text{ year}^{-1}$
 (B) $1.75 \times 10^{-4} \text{ year}^{-1}$ (E) not enough information
 (C) $1.21 \times 10^{-4} \text{ year}^{-1}$

$$t_{1/2} = \frac{0.693}{k}, \text{ so } k = 0.693/(t_{1/2}) = 0.693/(5720 \text{ years}) = 1.21 \times 10^{-4} \text{ year}^{-1}$$

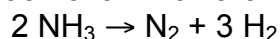
17. If a 1.000 g sample of ^{14}C were to sit for 3000 years, how much ^{14}C would remain?

- (A) 0.524 g (D) 0.363 g
 (B) 0.784 g (E) 0.696 g
 (C) 0.250 g

First order decay, so $[R] = [R]_0 e^{-kt}$, with $[R]_0 = 1.000 \text{ g}$, $k = 1.21 \times 10^{-4} \text{ year}$ (see #16) and $t = 3000 \text{ years}$. So, $kt = 0.363$ and $[R] = 1.000 e^{-(0.363)} = 0.696 \text{ grams}$.

Note: I would probably give you a problem where you were given k , rather than using k from the previous problem.

18. The decomposition of ammonia on a platinum surface at 856 °C



is zero order in NH_3 with a rate constant of $1.50 \times 10^{-6} \text{ Ms}^{-1}$.

If the initial concentration of NH_3 is 0.00116 M, the concentration of NH_3 will be 0.000213 M after _____ seconds have passed.

- (A) 142 (D) 1.02×10^6
 (B) 631 (E) 1.13×10^6
 (C) 773

Zero order, so $[R] = [R]_0 - kt$
 $0.000213 \text{ M} = 0.00116 \text{ M} - (1.50 \times 10^{-6} \text{ Ms}^{-1})t$
 $-0.000947 \text{ M} = -(1.50 \times 10^{-6} \text{ Ms}^{-1})t$
 $t = 631 \text{ seconds}$

19. The gas phase decomposition of nitrosyl chloride at 500 K
 $2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$
 is second order in NOCl with a rate constant of $5.90 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$.

If the initial concentration of NOCl is 0.080 M, the concentration of NOCl will be 0.020 M after _____ seconds have passed.

- (A) 0.34 (D) 636
 (B) 1.02 (E) 847
 (C) 212

Second order, so

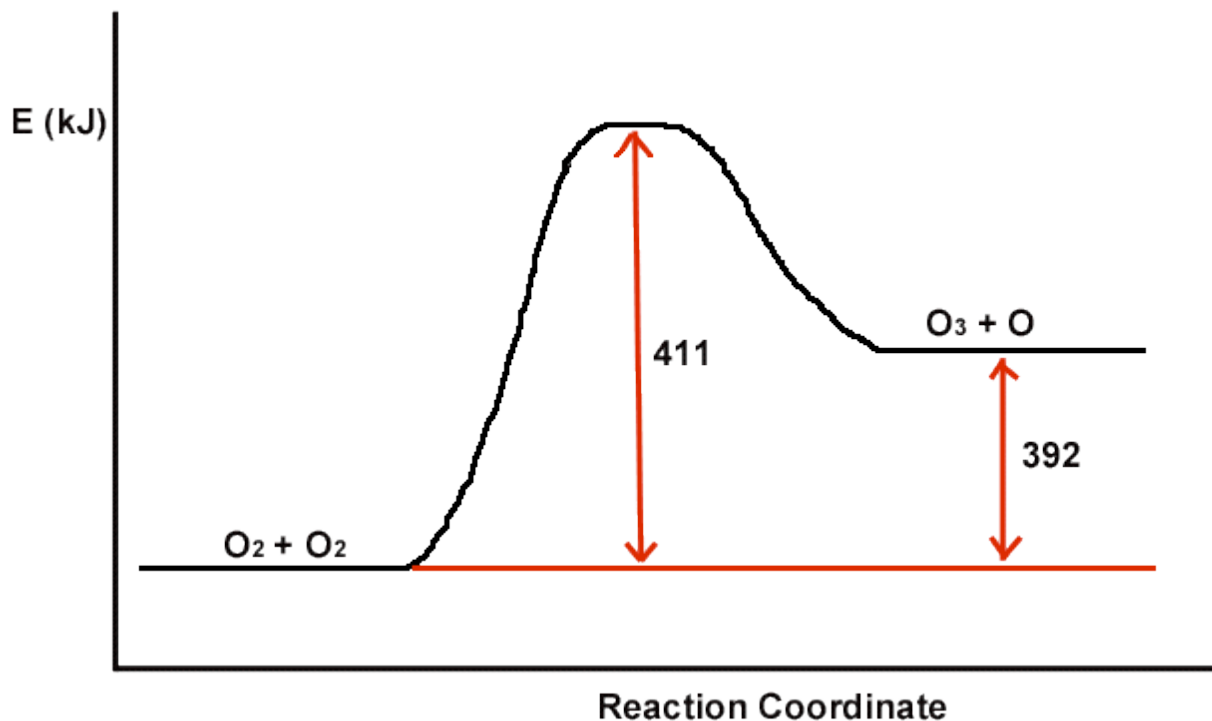
$$1/[R] = 1/[R]_0 + kt$$

$$1/(0.020 \text{ M}) = 1/(0.080 \text{ M}) + (5.90 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1})t$$

$$50 \text{ M}^{-1} = 12.5 \text{ M}^{-1} + (5.90 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1})t$$

$$37.5 \text{ M}^{-1} = (5.90 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1})t$$

$$t = 636 \text{ seconds}$$



20. A reaction profile for the reaction $2 \text{O}_2 \rightarrow \text{O}_3 + \text{O}$ is shown above. Which of the following is true (choose only one)

- (A) This reaction is endothermic, the value of the activation energy is 392 kJ, and ΔE is +411 kJ.
 (B) This reaction is endothermic, the value of the activation energy is 803 kJ, and ΔE is +392 kJ.
 (C) This reaction is endothermic, the value of the activation energy is 411 kJ, and ΔE is +392 kJ.
 (D) This reaction is exothermic, the value of the activation energy is 411 kJ, and ΔE is

-392 kJ.

(E) This reaction is exothermic, the value of the activation energy is 392 kJ, and ΔE is -411 kJ.

The reaction is endothermic (the products are higher in energy than the reactants). It is endothermic by 392 kJ, so ΔE is +392 kJ and the activation energy is 411 kJ.