**Chemistry 12, Exam III, Form A, April 4, 2001**

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**In all questions involving gases, assume that the ideal-gas laws hold, unless the question specifically refers to the non-ideal behavior.**

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1. It takes 21.3 s for $N_2$ (g) to effuse from a 1.0 L container at 30 °C. In a separate experiment, it takes 25.4 s for an unknown gas to effuse under identical conditions. Which of the following gases can be the unknown gas?

    a. $Cl_2$
    b. $O_2$
    c. Kr
    d. Ar
    e. Ne

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The rate of effusion is related to the molecular weight by Graham's law:

$r_1/r_2 = (M_2/M_1)^{0.5}$ from which $M_2 = M_1\,(r_1/r_2)^2$

The rates of effusion are inversely proportional to the times it takes for a given quantity of gas to escape. Therefore: $r_1/r_2 = t_2/t_1$, where $t_1$ and $t_2$ are the times for $N_2$ and the unknown gas, respectively.

Substituting the data from the problem ($M_1$ = 28.0 g/mol for $N_2$):
$M_2 = M_1\,(r_1/r_2)^2 = M_1\,(t_2/t_1)^2 = 28.0\,(25.4/21.3)^2 =$ 39.8 g/mol, very close to the molecular weight of Ar (39.9 g/mol from the periodic table). (answer d)

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2. If a 20.0 L sample of $NH_3$ (g) at STP is dissolved in methanol to yield a total volume of 845 mL, what is the molarity of the resulting $NH_3$/methanol solution?

    a. 1.06 M
    b. 0.947 M
    c. 10.6 M
    d. 9.47 M
    e. 16.9 M

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1 mol of gas at STP occupies 22.41 L (see constants at the end of the exam).
Therefore, 20.0 L corresponds to 20.0/22.41 = 0.982 mole of $NH_3$. The resulting concentration is equal n/V = 20.0/(22.41·0.845) = 1.06 M, since V = 0.845 L (answer a)

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3. Which of the following elements is primarily responsible for the photochemical smog?

    a. N
    b. S
    c. C
    d. Cl
    e. F

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Nitrogen (oxides) are mainly responsible for smog. (answer a)

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4. How many electron-pair domains are around the central atom of $NH_3$?

    a. 1
    b. 2
    c. 3
    d. 4
    e. 5

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Lewis structure of $NH_3$ (8-valence electrons) has three shared electron pairs (to three hydrogen atoms) and one lone pair. Total of 4 domains. (answer d)

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5. In which of the following species does the central atom obey the octet rule?

    a. $SF_4$
    b. $XeF_2$
    c. $BrF_5$
    d. $ClF_3$
    e. $CCl_3^-$

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Counting electrons in preparation for drawing Lewis structures is one way to figure it out:

a) $SF_4$ (S = 6 e, 4 *x* F = 28 e; total 34 e); S has four bonds to fluorines (8 e) and 2 e above the octet after each fluorine gets its three pairs.
b) $XeF_2$ (Xe = 8 e, 2 *x* F = 14 e; total 22 e); Xe has two bonds to fluorines (4 e) and 6 e as lone pairs, i.e. 2 e above the octet after each fluorine gets its three pairs.
c) $BrF_5$ (Br = 7 e, 3 *x* F = 21 e; total 28 e); Br has three bonds to fluorines (6 e) and 4 e as lone pairs, i.e. 2 e above the octet after each fluorine gets its three pairs.
d) $ClF_3$ (Cl = 7 e, 3 *x* F = 21 e; total 28 e); Cl has three bonds to fluorines (6 e) and 4 e as lone pairs, i.e. 2 e above the octet after each fluorine gets its three pairs.
e) $CCl_3^-$ (C = 4 e, 3 *x* Cl = 21 e; charge = 1 e, total 26 e); C has three bonds to chlorines (6 e) and one lone pairs, i.e. nothing above the octet after each chlorine gets its three pairs.

**Cont.**

The question can be solved quickly without counting all electrons, if one notices that in all cases the "outside" atoms have 7 valence electrons, and will need to share only one of their electrons (i.e. they will form only one bond) with the central atom to get their own octet. It means that the central atom to satisfy the octet rule (i.e. do not go over eight electrons) must have number of valence electrons that is equal to (or less than) [8 - n], where n is the number of atoms attached to the central atom. Sulfur has 6e plus 4 atoms attached (>8), Xe has 8e plus two atoms attached (>8), Br has 7e plus three atoms attached (>8), and Cl has 7e plus 3 atoms attached (>8). Only C has 4e plus 3 atoms attached, plus charge (1e) that makes the number equal to eight. (answer e)

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6. Which of the following gases has a density of 4.42 g/L at 125 $^{o}$C and 714 torr?

a. $H_2$
b. $CH_4$
c. He
d. $O_3$
e. $CCl_4$

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The density of gas is $d$= P$M$/(RT). Therefore, $M$ = dRT/P, and inserting the values given:

$M$ = dRT/P = [4.42 (g/L) · 0.0821 L·atm/(mol·K) · (273+125) K]/(714/760) atm = 153.7 g/mol, close to $M$ of $CCl_4$ (153.8 g/mol). (answer e)

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7. A study of the effects of certain gases on plant growth requires a synthetic atmosphere. Such an atmosphere was prepared by mixing 3.00 moles of $CO_2$(g), 36.0 moles of $O_2$(g), and 161 moles of Ar(g). What is the partial pressure of $O_2$(g), if the total pressure of this synthetic atmosphere is 745 torr?

a. 0.980 atm
b. 1.76 atm
c. 134 torr
d. 20.7 torr
e. 41.4 torr

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Partial pressure of gas is $P_i = X_i P_{tot}$, where Xi is the molar fraction.
X($O_2$) = 36/(3+36+161) = 0.18, and P($O_2$) = X($O_2$) · $P_{tot}$ = 0.18 · 745 torr = 134 torr
(answer c)

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8. Which of the following statements based on the kinetic theory of gases is true?

a. At a given temperature, different gases have different average kinetic energy.
b. At a given temperature, different gases have the same average kinetic energy.
c. At a given temperature, different gases have the same root-mean-square speeds.
d. At a given temperature, all molecules of a given gas have the same speed.
e. As the temperature of the gas increases, the volume of that gas must increase, because molecules need more space to keep the number of collisions constant.

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In the kinetic theory, the temperature is defined as the average kinetic energy of the gases (multiplied by a constant). Therefore, all gases of the same temperature must have the same average kinetic energy (answer b). Since gases may have different molecular masses, their rms speed must vary (k.e. = 0.5m$u^2$), to keep k.e. constant at a given temperature. At a given temperature, there will be always distribution of speeds. The last statement (e) makes no sense at all. (answer b)

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9. CFC's are responsible for ozone depletion in the atmosphere. The process of depletion of $O_3$ begins with the photodissociation of carbon-chlorine bonds in the CFC's. If the typical C-Cl bond energy in CFC's is 328 kJ/mol, what is the minimum wavelength of light needed to break this bond?

a. 453 nm
b. 426 nm
c. 398 nm
d. 365 nm
e. 274 nm

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Since energy of one mole of photons of the electromagnetic wave required to break one mole of C-Cl bonds is E = $N_A h\nu$, where $N_A$ is Avogadro's number, h is the Planck constant, and $\nu$ is the frequency of light $\nu = c/\lambda$.

E = $N_A \cdot h \cdot \nu$, = $N_A \cdot h \cdot c/\lambda$ from which: $\lambda = N_A \cdot h \cdot c/E = 6.02 \cdot 10^{23} \cdot 6.63 \cdot 10^{-34} \cdot 3 \cdot 10^{8}/328 \cdot 10^{3}$ =
= $3.65 \cdot 10^{-7}$ m = 365 nm

(all in SI units) (answer d)

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10. What are the electron-pair and the molecular geometries of $SnCl_3^-$?

| | **electron-pair** | **molecular** |
|---|---|---|
| a. | trigonal pyrimidal | tetrahedral |
| b. | trigonal planar | trigonal pyramidal |
| c. | tetrahedral | tetrahedral |
| d. | tetrahedral | trigonal pyramidal |
| e. | trigonal planar | trigonal planar |

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Sn has 4 valence electrons, three Cl's contribute 21 valence electrons, and one electron has to be added because of the negative charge. Total number of electrons is 26. Sn is the central atom with three chlorines bonded to it (total 6 electrons). Each chlorine has three lone pairs (18 electrons) the remaining two electrons are on Sn (lone pair). Thus, there are four electron domains around Sn. The electron pair geometry is tetrahedral. There are only three bonded atoms (the fourth is the lone pair). The molecular shape is, therefore, trigonal pyramid. (answer d)

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11. In a certain sample of air, the argon concentration is found to be 9340 ppm. What is the partial pressure of Ar, if the total pressure is 737 torr?

a. 6.88 torr
b. 68.8 torr
c. 7.89 torr
d. 12.7 torr
e. 127 torr

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Partial pressure of gas is $P_i = X_i P_{tot,}$ where Xi is the molar fraction. In this case for argon:
$X(Ar) = 9340 \cdot 10^{-6}$ and $P(Ar) = 9340 \cdot 10^{-6} \cdot 737$ torr = 6.88 torr (answer a)

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12. What is the molecular shape and polarity of $SF_4$?

a. trigonal bipyramidal, nonpolar
b. trigonal pyramidal, polar
c. seesaw, polar
d. T-shaped, polar
e. tetrahedral, nonpolar

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Total valence electrons in the molecule: 34. Four S-F bonds (8 e), lone pairs on fluorines (4 x 6). The remaining electrons (34 - 8 - 24) are the lone pair on S. Total electron domains is 5, the electronic structure is trigonal bipyramidal, with one lone pair. The molecular shape is seesaw (the lone pair is equatorial). The bond and lone-pair dipoles do not cancel so the molecule is polar. (answer c)

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13. Based on average bond energies, what is $\Delta H_{rxn}$ for the following reaction?

| | | | | | |
|---|---|---|---|---|---|
| C-C | 348 kJ/mol | C=C | 614 kJ/mol | C≡C | 839 kJ/mol |
| C-H | 413 kJ/mol | C-O | 358 kJ/mol | Cl-Cl | 242 kJ/mol |
| C-Cl | 328 kJ/mol | O-H | 463 kJ/mol | O-Cl | 222 kJ/mol |

$$H_3C-C\equiv C-CH_2-CH_2OH \quad + \quad 2Cl_2 \longrightarrow H_3C-CCl_2-CCl_2-CH_2-CH_2OH$$

a. –562 kJ/mol
b. +562 kJ/mol
c. –685 kJ/mol
d. +11 kJ/mol
e. –337 kJ/mol

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| Bonds broken: | | | Bonds made: | |
|---|---|---|---|---|
| | C≡C | 839 kJ/mol | C-C | 348 kJ/mol |
| | 2 Cl-Cl | 242 kJ/mol | 4 x C-Cl | 328 kJ/mol |
| | | 1323 kJ/mol | | 1660 kJ/mol |

$\Delta H_{rxn}$ = 1323 - 1660 = –337 kJ/mol (answer e)

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14. What is the hybridization of the six carbons in benzene?

a. all are $sp^6$ hybridized
b. all are $sp^3$ hybridized
c. all are $sp^2$ hybridized
d. all are sp hybridized
e. they have alternating $sp^2$ and $sp^3$ hybridization

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Each C atom in benzene forms three σ-bonds (to H and two other C's) and participates in formation of the π-system, providing one *p* orbital. They are all $sp^2$ hybridized. (answer c)

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15. What is the rms speed (in m/s) of carbon tetrachloride ($CCl_4$) molecules at 22 ˚C?

a. 6.96
b. 219
c. $4.83 \times 10^4$
d. 156
e. 478

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$u = \sqrt{\dfrac{3RT}{M}}$  For $CCl_4$ $M$ = 153.8 g/mol = 0.1538 kg/mol

$u = [3 \cdot 8.314 \cdot (273+22)/0.1538]^{0.5} = 219$ m/s  (answer b)

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16. In which of the following species, does the central atom **not** obey the octet rule?

a. $SCl_2$
b. $CO_3^{2-}$
c. $CN^-$
d. $NO_3^-$
e. $ClO_2$

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One may systematically draw all Lewis structures, or just count valence electrons.

a) $SCl_2$ valence electrons: 6 + 14 = 20. Two pairs are shared (4e, single bonds), the remaining are lone pairs on Cl (three each, total 12e) and S (two lone pairs, 4 e). Each atom has an octet.
b) $CO_3^{2-}$ valence electrons: 4 + 18 + 2 = 24. Three pairs are shared (6e, single bond), one pair is shared (2 e $\pi$ bond), and the rest are lone pairs on oxygens (2 x 6 + 1 x 4). Each atom has an octet.
c) $CN^-$ valence electrons: 4 + 5 + 1 =10. Three pairs are shared (6 e, one single, two $\pi$ bonds), the rest are lone pairs, one on N, one on C. Each atom has an octet.
d) $NO_3^-$ valence electrons: 5 + 18 + 1 = 24. Three pairs are shared (6e, single bond), one pair is shared (2 e $\pi$ bond), and the rest are lone pairs on oxygens (2 x 6 + 1 x 4). Each atom has an octet.
e) $ClO_2$ valence electrons 7 + 12 = 19; odd number of electrons, one atom cannot have octet. Two pairs are shared (4e, single bonds), the remaining are lone pairs on Os (12 e), and Cl (2 e), and the odd electron is on Cl. Chlorine does not have an octet (at least in one of the resonance forms).  (answer e)

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17. Which of the following compounds is the most polar?

a. $XeF_4$
b. $CF_4$
c. $SF_4$
d. $SiF_4$
e. $GeF_4$

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The polarity of the molecule is decided by its bond and lone-pair dipoles, and its overall shape (do the bond dipole cancel?).

a) $XeF_4$: there are 6 electron domains on Xe (octahedral electron-pair structure); the two lone pairs on Xe are in axial position, the molecular geometry is square planar, all bond dipoles and lone-pair dipoles cancel
b) $CF_4$: there are 4 electron domains on C (tetrahedral electron-pair structure); all are single bonds, the molecular geometry is tetrahedral, all bond dipoles and lone-pair dipoles cancel.
c) $SF_4$: there are 5 electron domains on S (trigonal bipyramidal electron-pair structure); four are single bonds, one is lone pair on S in equatorial position, the molecular geometry is seesaw. The dipoles and lone-pair dipoles do not cancel, the molecule is polar.
d) $SiF_4$ there are 4 electron domains on Si (tetrahedral electron-pair structure); all are single bonds, the molecular geometry is tetrahedral, all bond dipoles and lone-pair dipoles cancel.
e) $GeF_4$ there are 4 electron domains on Ge (tetrahedral electron-pair structure); all are single bonds, the molecular geometry is tetrahedral, all bond dipoles and lone-pair dipoles cancel.  (answer c)

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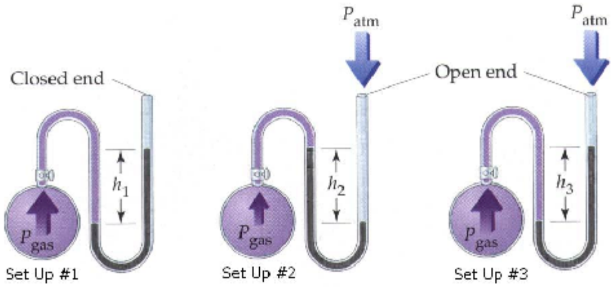
18. Referring to the mercury manometers below, which of the following statements about the pressure of the gas inside the container (expressed in mm Hg) **does not have to be true**?




a. In set up # 1, the pressure of the gas is greater than the atmospheric pressure.
b. In set up # 2 the pressure of the gas is less than atmospheric pressure.
c. In set up # 3, the pressure of the gas is greater than the atmospheric pressure by $h_3$.
d. In set up # 1, the pressure of gas is equal to the difference in the heights of the mercury levels in the two arms ($h_1$).
e. In set up # 2, the pressure of the gas is equal to $P_{atm} – h_2$, where $h_2$ is in mm Hg

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a) The statement is true only if $h_1$ is greater than the atmospheric pressure at given time. Since no information is given on the magnitude of $h_1$, or on the atmospheric pressure at the time of measurement, the statement may be false.
b) Extra weight of mercury ($h_2$) is needed to balance $P_{atm}$. The statement must be true.
c) Extra weight of mercury ($h_2$) is needed to balance gas pressure. The statement must be true.
d) Extra weight of mercury is needed to balance gas pressure. The statement must be true.
e) Extra weight of mercury ($h_2$) is needed to balance $P_{atm}$. The statement must be true.
(answer a)

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19. How many **additional** moles of argon must be added to a flask containing 2.00 moles of argon at 25 °C and 1.00 atm pressure in order to increase the pressure to 1.60 atm under conditions of constant temperature and volume?
a. 0.80
b. 1.00
c. 1.20
d. 2.20
e. 2.80

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Initial: $n_1 = P_1V_1/RT_1$ Final: $(n_1 + n_2) = P_2V_2/RT_2$, but $V_1 = V_2$, and $T_1 = T_2$: therefore $(n_1 + n_2) = P_2V_1/RT_1$. Dividing the final by initial: $(n_1 + n_2)/n_1 = P_2/P_1$ or $n_2 = n_1 \cdot P_2/P_1 - n_1$
Substituting: $n_2 = n_1 \cdot P_2/P_1 - n_1 = 2 \cdot (1.60/1.0) - 2 = 1.20$ mole (answer c)

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20. Acetylene gas, $C_2H_2(g)$, was produced (according to the reaction below) from 0.158 g of $CaC_2$, and it was collected over water at 23 °C. The vapor pressure of water at this temperature is 21 torr. The total pressure of the collected gas was 726 torr. What volume does **acetylene** occupy under these conditions?

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$

a. 32.3 mL
b. 64.6 mL
c. 50.4 mL
d. 121 mL
e. 12.1 mL

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The gas collected is a mixture of $C_2H_2(g)$ and $H_2O(g)$:
$P_{tot} = 726$ torr $= P_{acet} + P_{wat}$ and $P_{wat} = 21$ torr therefore $P_{acet} = (726 - 21)/760 = 0.928$ atm

From the equation: the number of moles of acetylene produced is equal the number of moles of carbide, $CaC_2$, used: $n_{acet} = n_{carb} = (0.158\ g)/(64\ g/mol) = 2.465 \cdot 10^{-3}$ mol

$V_{acet} = n_{acet} \cdot R \cdot T/P_{acet} = 2.465 \cdot 10^{-3} \cdot 0.0821 \cdot (273+23)/0.928 = 0.0646\ L = 64.6\ mL$ (answer b)

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21. Of the following species, which one has the $sp^2$-hybridized central atom?

a. $PH_3$
b. $CO_3^{2-}$
c. $ICl_3$
d. $I_3^-$
e. $SF_6$

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a) P in $PH_3$ has tetrahedral electron pair geometry and is $sp^3$ hybridized.
b) Only $CO_3^{2-}$ has trigonal planar electron-pair geometry with a double bond (a π bond), and therefore, an $sp^2$ hybridized carbon.
c) I in $ICl_3$ has trigonal bipyramidal electron-pair geometry (two lone pairs), and therefore, is $sp^3d$ hybridized.
d) I in $I_3^-$ has tetrahedral electron pair geometry and is $sp^3$ hybridized.
e) S in $SF_6$ has octahedral electron-pair geometry and its $sp^3d^2$ hybridized. (answer b)

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22. How many σ and π bonds does carbon atom form in H-C≡N molecule?
a. 4 π, no σ
b. 1 σ and 3 π
c. 2 σ and 2 π
d. 3 σ and 1 π
e. 4 σ, no π

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Carbon forms 2 σ bonds: one to H, one to N, and two π bonds (to N). Of multiple bonds, only one can be σ-type. The rest must be other type (π). (answer c)

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23. The van der Waals equation, $[P + n^2a/V^2][V - nb] = nRT$, accounts for deviations from the ideal gas behavior. Which term in the equations corrects for molecular volume?

a. n
b. T
c. V
d. nb
e. $n^2a/V^2$

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In the equation *nb* term corrects for volume of molecules, *n* is the number of moles, and *b* is the volume (vol/mol) of gas molecules. Parameter *a* corrects for intermolecular interactions.

(answer d)

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24. What kind of orbitals overlap to form the σ C-C bond in ethane ($H_3C$-$CH_3$)?

a. a *p* orbital and an $sp^3$ orbital
b. an *s* orbital and a *p* orbital
c. two *p* orbitals
d. two $sp^3$ orbitals
e. two $sp^2$ orbitals

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Both carbons are $sp^3$ hybridized: the bond forms by overlap of $sp^3$ hybrids. (answer d)

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25. In its initial state a sample of argon occupies a 5 L flask at 0 °C. This sample is completely transferred to a 10 L flask, and then the gas is heated to 273 °C. What is the final pressure, when the final temperature is reached?

a. the final pressure is half of the initial pressure
b. the final pressure is twice the initial pressure
c. the final pressure is R (gas constant) times the initial pressure
d. the final pressure is 4 times the initial pressure
e. the final pressure is equal to the initial pressure

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Since the number of moles of gas is constant $P_1V_1/T_1 = P_2V_2/T_2$ or
$P_1/P_2 = T_1V_2/T_2V_1 = (273)(10)/(273+273)(5) = 2\cdot(273)(5)/2\cdot(273)(5) = 1$ (answer e)

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26. Which of the following gases would be most likely to exhibit ideal-gas behavior?

a. He at 1 atm and 10 K
b. Ne at STP
c. Ar at 10 torr and 400 K
d. Ne at 100 atm and 273 K
e. Ar at 50 atm and 100 K

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The real gas resembles ideal gas the most at high temperatures and low pressures. Argon at 10 torr and 400 K would do it best. (answer c)

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**END OF EXAM**



# Constants & Equations

$1 \text{ J} = 1 \text{ kg}\cdot \text{m}^2\cdot\text{s}^{-2}$ $R_H = 2.18 \times 10^{-18}$ J

$c = 3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1}$ $e = -1.60 \times 10^{-19}$ C

$h = 6.63 \times 10^{-34}$ J·s $1 \text{ D} = 3.33 \times 10^{-30}$ C·m

$N = 6.02 \times 10^{23} \text{ mol}^{-1}$

R = 8.314 J/(mol·K)
R = 0.08206 L·atm/(mol·K)
R = 1.987 cal/(mol·K)

1 atm = 760 mmHg = 760 torr
$1 \text{ atm} = 1.01325 \times 10^5$ Pa
1 atm = 1.01.325 kPa

1 mol of gas at STP occupies
V = 22.41 L

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

$d = PM/(RT)$

$c = \lambda\nu$ $E = h\nu$

$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ $\lambda = h/mv$

$\mu = Q\,r$ $E = k_LQ_1Q_2/d$

$q = m \cdot c \cdot \Delta T$ $P_i = X_i\,P_{tot}$

$u = \sqrt{\frac{3RT}{M}}$ $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

$\Delta H°_{rxn} = \Sigma\, n\, \Delta H°_f(\text{products}) - \Sigma\, m\, \Delta H°_f(\text{reactants})$

$\Delta H°_{rxn} = \Sigma\, (\Delta H \text{ of bonds broken}) - \Sigma\, (\Delta H \text{ of bonds formed})$