

1 EMR energy calculation

Classic plug and chug

$$E = h\nu \quad v = c/\lambda \quad \text{you are given } h, c \text{ with equations}$$

Stay in mks units
meter \rightarrow kg seconds

Know your metric conversions

$$\begin{array}{ccccccc} n & 10^{-9} & 10^{-6} & 10^{-3} & 10^{-2} & 10^3 & 10^6 \\ m & & & & & K & m \\ \text{meter} & \text{kg} & \text{seconds} & & & & \end{array}$$

LDE Planck relation 001

001 10.0 points

What is the energy, in Joules, of a photon of wavelength 200 nm? What bond energy would this correspond to, in $\text{kJ} \cdot \text{mol}^{-1}$?

1. $9.94 \times 10^{-21} \text{ J}$; $5.99 \text{ kJ} \cdot \text{mol}^{-1}$
 2. $1.32 \times 10^{-40} \text{ J}$; $7.95 \times 10^{-20} \text{ kJ} \cdot \text{mol}^{-1}$
 3. $9.94 \times 10^{-17} \text{ J}$; $1.65 \times 10^{-43} \text{ kJ} \cdot \text{mol}^{-1}$
 4. $1.32 \times 10^{-31} \text{ J}$; $7.95 \times 10^{-11} \text{ kJ} \cdot \text{mol}^{-1}$
 5. $1.32 \times 10^{-21} \text{ J}$; $795 \text{ kJ} \cdot \text{mol}^{-1}$
 6. $9.94 \times 10^{-19} \text{ J}$; $599 \text{ kJ} \cdot \text{mol}^{-1}$ correct
-

Explanation:

$$\lambda = 200 \text{ nm}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$$

For a photon $c = \lambda\nu$, so

$$E = h\nu = \frac{hc}{\lambda}$$

where c is the speed of light and h is Planck's constant.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= (6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (3 \times 10^8 \text{ m/s}) \\ &\quad \cdot \frac{1}{200 \text{ nm}} \cdot \frac{10^9 \text{ nm}}{1 \text{ m}} \\ &= 9.94 \times 10^{-19} \text{ J} \end{aligned}$$

$$\begin{aligned} (9.94 \times 10^{-19} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1}) \\ = 599 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

2 Ryberg equation application

$$v = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad R = 3.3 \times 10^{15} \text{ Hz}$$

Need to understand the Bohr atom context for $n_f < n_i$
and be able to understand boundaries and values for
various n values

Which of the following electronic transitions
for a hydrogen atom would correspond to the
highest energy emission found in the Balmer
series?

1. $n=4$ to $n=2$ correct

2. $n=3$ to $n=2$

3. $n=2$ to $n=4$

4. $n=1$ to $n=2$

5. $n=2$ to $n=1$

6. $n=3$ to $n=1$

Explanation:

The Balmer series is electronic transitions
that involve $n=2$ and some higher principle en-
ergy level (n greater than 2) for the hydrogen
atom. An emission occurs when an electron
moves from some energy level to a lower en-
ergy level. Combining these constraints, $n=4$
to $n=2$ will be the highest energy emission
in the Balmer series, of the available answer
choices.

3 Failures of classical mechanics theory

explain in your own words. Explain what the photoelectric effect is, give simple examples in real life, explain what classical mechanics says happens, and then what actually happens.

Hint. Draw a picture of P.E. effect and then use the P.E equation to explain it $E_k = \frac{1}{2}mv^2 = h\nu - \phi$

Which of the following statement(s) is/are true?

- I) The failure of classical mechanics to predict the absorptions/emission spectra of gases is called the ultraviolet catastrophe.
- II) Quantum mechanics accurately predicted the behavior of blackbody radiators.
- III) The emission spectra of gases are discrete rather than continuous.
- IV) Any frequency of light will eject an electron from a metal surface as long as the intensity is sufficient.

- 1. II and III correct
- 2. III and IV
- 3. I, II and IV
- 4. II, III, and IV
- 5. I and III

Explanation:

Classical mechanics predicted that the power radiated by a blackbody radiator would be proportional to the square of the frequency at which it emitted radiation, and thus approach infinity as the frequency increased. This was false, since at higher frequencies blackbody radiators emit less, not more power. This was termed the ultraviolet catastrophe. Classical mechanics also predicted that the energy (velocity) of electrons emitted from a metal surface is proportional to the intensity of light. In reality, the energy (velocity) is only dependent upon the frequency of light. Once the threshold frequency is reached, however, the number of emitted electrons is proportional to the intensity of light. Classical mechanics also fails in explaining the discrete lines in absorption/emission spectrum, which are due to discrete energy levels of electrons in atoms.

provided that Δx is greater than unity (and vice versa).

II is false because an electron can only be observed in one place at one time, although there may be an equal probability of observing it at two different places.

III is true because quantum mechanics can only give probabilities of a particle having a certain position or momentum and not an exact value.

4 Uncertainty principle theory

$$m \Delta v \Delta x \geq \frac{\hbar}{2}$$

Δv and Δx are finite and inverse
does not apply to large objects because
 m is so big. Explains that we can't know
exactly where e^- is
so need

LDE Uncertainty Principle Theory 001 004 10.0 points

Which of the following are true consequences
of the uncertainty principle?

- I) The uncertainty in an electron's momentum can never be less than $\frac{\hbar}{2}$;
- II) An electron can be measured in two places at once;
- III) Electrons and other particles do not have a well-defined position or momentum like particles in classical mechanics do.

1. II and III

2. I and II

3. I only

4. III only **correct**

5. I and III

6. II only

Explanation:

I is false because Δp may be less than $\frac{\hbar}{2}$

Q. M.
to
find
probab. l. ty
of
location
from
 Ψ^2

5 de Broglie equation calculation

plug and chug

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

Hint: How do you convert 12 g C/mole C into kg in 1 atom C

- keep your values in mks units
- remember to separate decimal and exponent terms and work separately
- Example $\lambda = \frac{6 \times 10^{-34}}{(2 \times 10^{-3})(3 \times 10^16)} = \left(\frac{6}{2 \times 3}\right) \times 10^{-34+3-16} = 1 \times 10^{-19} \text{ m}$

must be
mks
units

Consider a flea of mass 4.5×10^{-4} g moving at 1.0 m/s midway through its jump. What is its de Broglie wavelength?

1. $2.9818 \times 10^{-40} \text{ m}$
2. $1.4725 \times 10^{-30} \text{ m}$
3. $2.9818 \times 10^{-37} \text{ m}$
4. $1.47244 \times 10^{-27} \text{ m}$ correct

Explanation:

$$m = 0.00045 \text{ g} \times \frac{0.001 \text{ kg}}{1 \text{ g}} = 4.5 \times 10^{-7} \text{ kg}$$

$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{h}{m \cdot v} \\ &= \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{(4.5 \times 10^{-7} \text{ kg})(1 \text{ m/s})} \\ &= 1.47244 \times 10^{-27} \text{ m} \end{aligned}$$

6 Schrodinger equation & P in a B theory

Quantum mechanics– Schrodinger equation theory

So what do you know about this equation that delivers the quantum numbers for the H atom atom that permit values of Ψ^2 to tell us where the electrons are. How does Schrodinger work for the particle in a box model and the multielectron system? Pay careful attention to V, KE, Ψ , E.

Quantum mechanics application - Particle in a box

The simplest solution for Schrodinger assumes $V(x)=0$ and is a fine model for a standing wave. Be able to draw Ψ^2 for various values of n.

LDE schrodinger equation 01 006 10.0 points

Which of the following statements about the Schrödinger equation is incorrect?

1. There are both kinetic and potential energy terms in the equation

2. The hydrogen atom solution is simplified by changing to spherical coordinates.

3. The classical standing wave equation solution for a guitar string yields the same solution as the particle in a box case.

4. Setting the potential energy term to zero allows the accurate calculation of wave equation solutions for the hydrogen atom. correct

5. The principle, angular momentum and magnetic quantum numbers yield information about energy (size), shape and orientation of the electron orbits.

Explanation:

Setting the potential energy term to zero is from the particle in a box model. The particle in a box model is useful for practice because it is so simple to analyze - it does not give accurate solutions to real atoms, which are far more complicated.

7 Quantum number rules

Understand and apply the boundary conditions for n, l, m_l

$n = 1, 2, \dots \infty$ energy and size

$l = 0, 1, 2, \dots n-1$ shape
s p d

$m_l = -l, \dots, 0, \dots +l$ orientation



Given specific boundary conditions describe what shells, subshells, orientations, electrons are allowed

Which of the following sets of quantum numbers are **invalid**, i.e. violate one or more boundary conditions?

I) $n = 3, l = 2, m_l = -2, m_s = +\frac{1}{2}$

II) $n = 9, l = 5, m_l = 6, m_s = +\frac{1}{2}$

III) $n = 2, l = 1, m_l = 0, m_s = +1$

IV) $n = 2, l = 0, m_l = 0, m_s = +\frac{1}{2}$

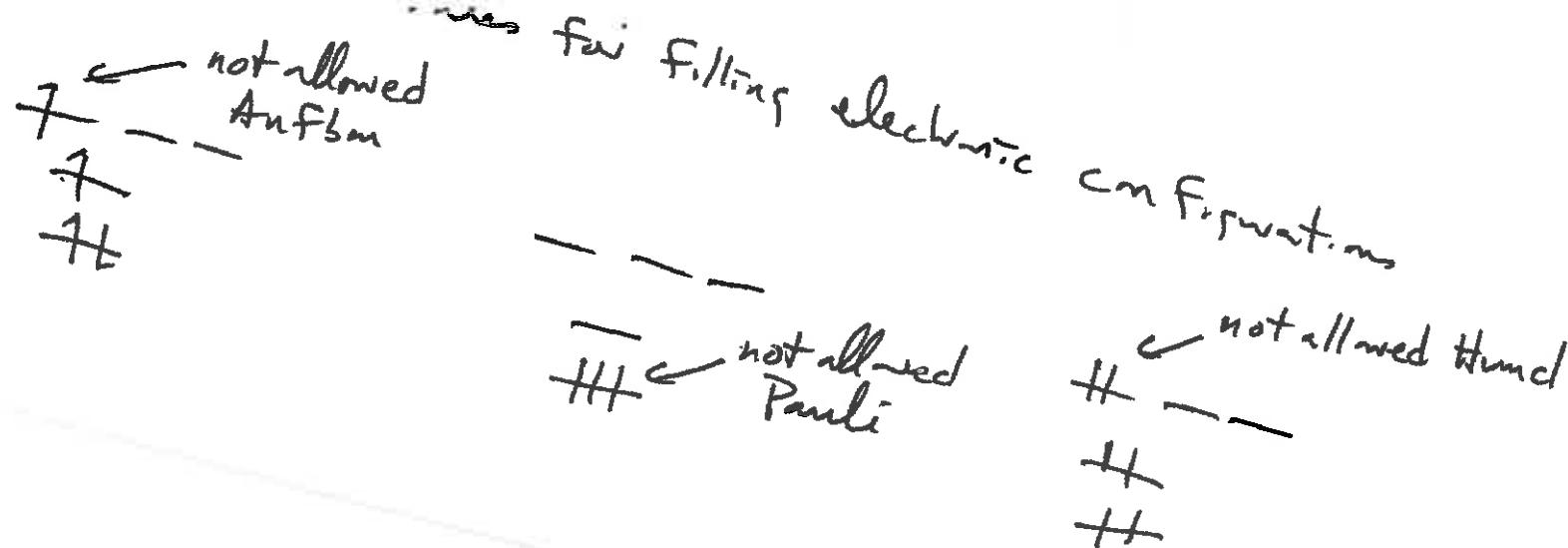
V) $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$

Explanation:

Set II and III are invalid. For II, $m_l = 6$ is disallowed because $l = 5$. For III, $m_s = +1$ is disallowed because m_s may only be $+\frac{1}{2}$ or $-\frac{1}{2}$.

1. I, II, IV
2. III only
3. I, IV
4. II, III correct
5. I, III, IV
6. I only
7. II only

8A



Msci 05 1648
008 10.0 points

Hund's rule states that

1. it is impossible to determine accurately both the momentum and position of an electron simultaneously.
2. no two electrons in an atom may have identical sets of four quantum numbers.
3. electrons occupy all the orbitals of a given sublevel singly before pairing begins. correct

9 Electronic configurations

You will be given an atom with a specific number of electrons. You will need to assign its electronic configuration first by finding the closest noble gas [He], [Ne], [Ar], [Kr], [Xe] followed in sequence by the number of electrons in subshells till the number of e^- is exhausted.

Write the electron configuration for P.

1. $1s^2 2s^2 2p^6 3d^5$

2. $1s^2 2s^2 2p^6 3s^2 3p^6$

3. $1s^2 2s^2 2p^6 3s^2 3p^3$ correct

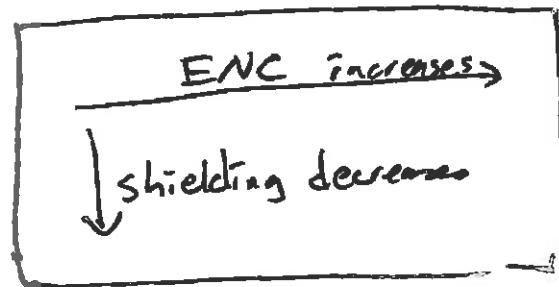
4. $1s^2 2s^2 2p^6 3p^5$

Explanation:

P has atomic number 15. Follow the pyramid

10 ENC, shielding and periodicity theory

Trends in periodicity follow simple arguments



A simple estimate of ENC is



$$ENC = \# \text{ of protons} - \# \text{ shielding } e^-$$

so Al 1s e^- has $ENC = 13$

Al 2s, p e^- have $ENC = 11$

Al 3s e^- have $ENC = 3$

LDE periodic trend theory 001

010 10.0 points

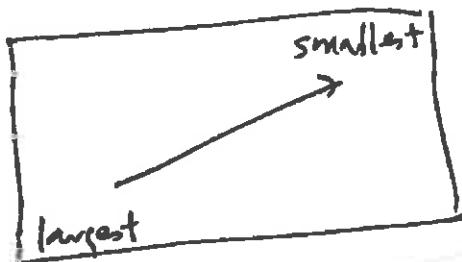
Which of the following BEST describes the purpose of effective nuclear charge?

1. It is used to rationalize chemical bonding in covalently bonded molecules.
2. It is a measure of how many protons a given atom has which is useful because of variations from isotope to isotope.
3. It is a method to evaluate how much attraction a given electron "feels" from the nucleus so that periodic trends can be predicted and rationalized. **correct**
4. It is used to determine the number of valence electrons of a given species.
5. It exists only to torture foolish CH 301 students who did not study.
6. It is a measure of the effect of filled and half-filled subshells on the stability of atoms and ions.

11 Ranking periodic trends

Ranking periodic trends without exceptions, atomic radius

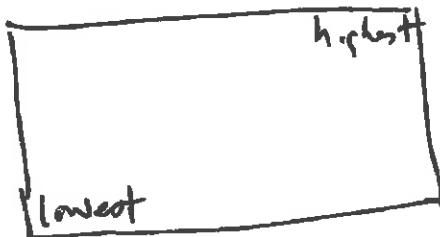
Atomic radius is easiest to rank because of the smooth trends



the reason is that ENC increases left to right
and shielding increases going down the table

Ranking periodic trends with exceptions, 1st ionization energy

Ionization energy increases generally from lower left to upper right



but does so unevenly

why?

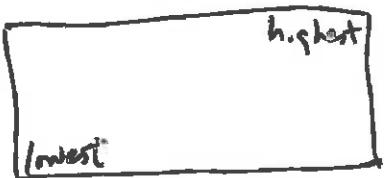
$\begin{array}{c} \text{+} \text{+} - \text{p}^2 \\ \text{+} \text{+} + \text{p}^3 \\ \text{+} \text{+} + \text{+} \text{p}^4 \end{array}$

wants to stay p^3
wants to lose e^- to be p^3

so IE ranking is $\text{p}^2 < \text{p}^4 < \text{p}^3$

Ranking periodic trends with exceptions, electron affinity

Electron affinity increases generally from lower left to upper right



but does so unevenly

why?

$\begin{array}{c} \text{+} \text{+} - \text{p}^2 \\ \text{+} \text{+} + \text{p}^3 \\ \text{+} \text{+} + \text{+} \text{p}^4 \end{array}$

loves e^-
happy at $\frac{1}{2}$ filled
wants 2 more e^- to be filled

so EA ranking is $\text{p}^3 < \text{p}^2 < \text{p}^4$

12 Lattice energy ranking

Lattice energy scales with charge density. So rank charge density and you have ranked lattice energy.

Example Rank CaO MgO and KCl

first step, assign charge $\text{Ca}^{\text{+2}}$ $\text{Mg}^{\text{+2}}$ $\text{K}^{\text{+1}}$ $\text{Cl}^{\text{-1}}$

second step, sort by amount of charge $\text{KCl} < \text{CaO}, \text{MgO}$

third step, sort by size. Mg is small so MgO charge density is larger $\text{KCl} < \text{CaO} < \text{MgO}$

ChemPrin3e T02 07
012 10.0 points

Which of the following has the highest lattice energy?

1. CaO
2. MgO correct
3. NaCl
4. BaO
5. KI

LDE Ranking trends 002

011 10.0 points

Rank the following species in terms of increasing electron affinity: Sulfur (S), Rubidium (Rb), Germanium (Ge), Krypton (Kr), Fluorine (F)

1. Not enough information
2. Ge < Rb < S < F < Kr
3. Rb < Ge < S < F < Kr
4. Kr < Rb < Ge < S < F correct
5. Kr < Ge < Rb < S < F
6. F < Ge < S < Rb < Kr

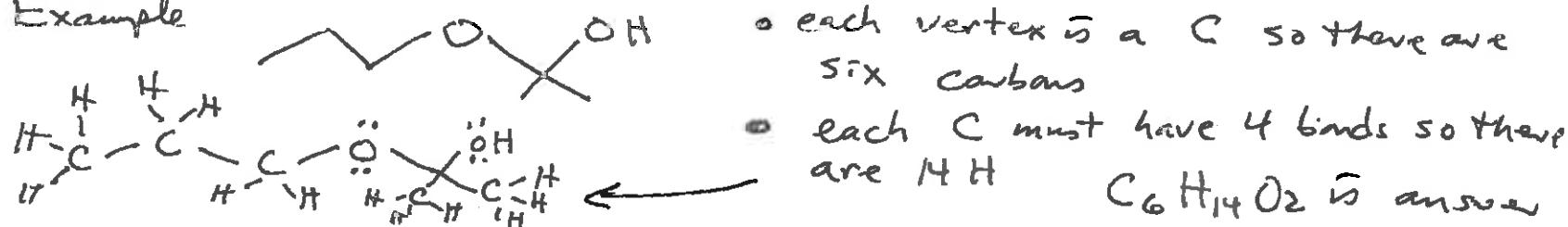
Explanation:

Elements' electron affinities increase across a given period and up and down a given group. Noble gases (i.e. Kr) have an electron affinity of essentially zero. Rb is greater than zero, Ge is greater than Rb, S is greater than Ge, and

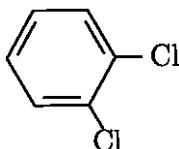
13 Determining formulas from line drawings

You need to be able to interpret an organic molecule drawing and assign molecular formula. Hint: You assign C and H

Example



Determine the molecular formula for the molecule:



1. C_6H_4Cl
2. $C_4H_{12}Cl_2$
3. $C_6H_4Cl_2$ correct
4. $C_6H_6Cl_2$
5. C_6H_6
6. $C_4H_4Cl_2$

14 Lewis structures – multiple bonds

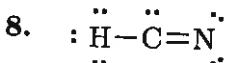
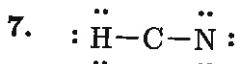
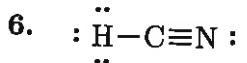
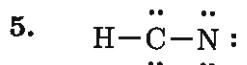
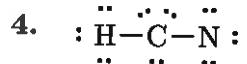
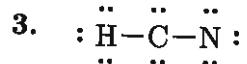
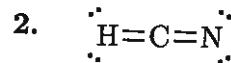
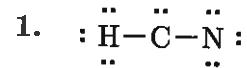
Look at a bunch of molecules. Draw them. Which has multiple bonds.

Hint: In the 5 step process, "is everyone happy" is answered for multiple bonds by showing to make = or ≡ bonds

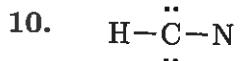
Hint: Know the famous multiple bonds so you don't have to draw them

= bonds: O₂, C₂H₂, CO₂ ≡ N₂, C₂H₂

Which of the following is the correct Lewis formula for hydrogen cyanide (HCN)?



9. H—C≡N : correct



Explanation:

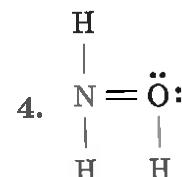
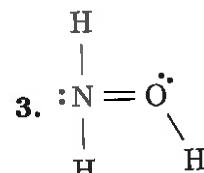
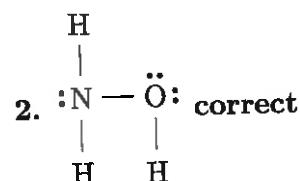
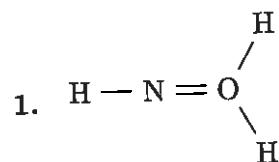
The Lewis formula for hydrogen cyanide

15 Lewis structures - multiple central atoms

Be able to draw a structure w/ more than one central atom.
 The key is to spread out atoms with perimeter atoms on outside (always H, usually halogen, often oxygen =O)
 Then assign 2 or 8 to perimeter, make bonds w/ rest and fill in extra e⁻s on central atoms. Then make sure octet is satisfied by sharing.

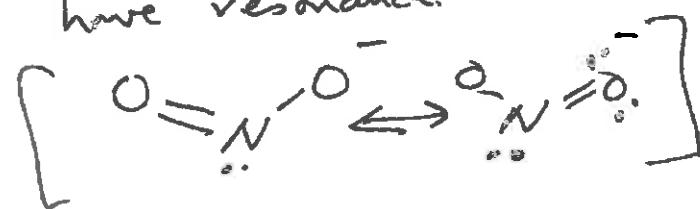
Hint: Often we find out if you drew structure correctly by asking
 the number of bonding e⁻s, unbonded e⁻s, bonds, unbonded pairs

 Which of the following is the correct Lewis structure of hydroxylamine (NH_2OH)?



16 Lewis structures – resonance

Lewis structures – resonance
When you draw the structure of a compound, if there are multiple bonds that are equivalent and can share a bond, you have resonance.



Hint. Here are the famous resonance structures benzene
 O_3^- , NO_2^- , NO_3^- , $CO_3^{=}$, 

How many resonance structures are there for the NO_3^- polyatomic ion?

1. This molecule does not exhibit resonance.

2.2

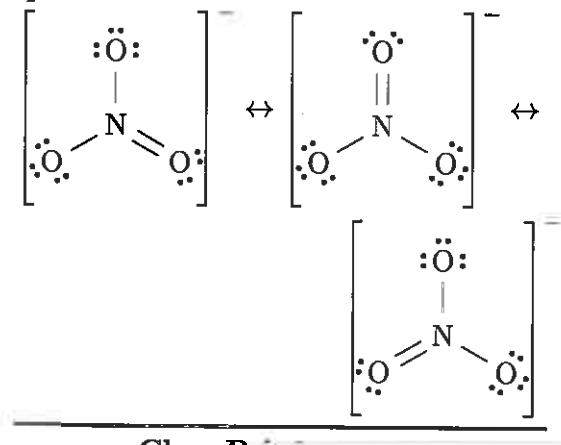
3. 1

4. 4

5. 5

6. 3 correct

Explanation:

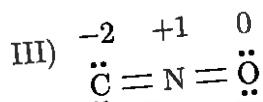
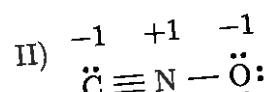
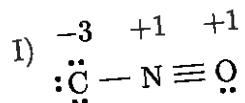


17 Lewis structures – formal charge application

You will be given structures to compare and asked which has the best structure based on formal charge.
You will need to draw the molecule, assign F.C., and whichever has the smallest values on atoms is best.

Example $\overbrace{\text{O}, \text{O}, \text{O}, \text{O}}^{\text{FC values}}$ is better than $\overbrace{\text{O}, \text{O}, -1, +1}^{\text{FC values}}$

UnemPrin3e 02 76
017 10.0 points
Which of the three Lewis structures is the most important for the fulminate ion (CNO^-)?



- 1. II and III only 6
- 2. None of these is important.
- 3. All of these are important.
- 4. III only
- 5. I and III only
- 6. I and II only
- 7. II only **correct**
- 8. I only

Explanation:



is probably the most important as it is the structure with the formal charges of the individual atoms closest to zero.

18 VSEPR - electronic & molecular geometries

Draw a structure. Count e^- rich regions. Assign electronic geometry.

2 linear

3 trig planar

4 tetrahedral

5 trig bipyramidal

6 octahedral

Draw a structure. Count e^- rich regions. Divide into $:B + :U$

apply

| | |
|----------------------------------|----------------|
| <u>AB_2</u> | linear |
| <u>AB_3</u> | trig. planar |
| <u>AB_2U</u> | bent |
| <u>AB_4</u> | tetrahedral |
| <u>4 RHED AB_3U</u> | trig pyramidal |
| <u>AB_2U_2</u> | bent |

| | | | | | |
|--------|-----------|-------------|--------|-----------|------------------|
| 5 RHED | AB_5 | trig bipyrr | 6 RHED | AB_6 | octahedral |
| | AB_4U | seesaw | | AB_5U | square pyramidal |
| | AB_3U_2 | T-shap | | AB_4U_2 | square planar |
| | AB_2U_3 | linear | | | |

Brodbelt 08 04

018 10.0 points

ICl_3 is sp^3d hybridized. What is the electronic and molecular geometry?

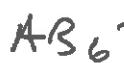
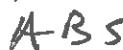
1. trigonal bipyramidal, seesaw
2. octahedral; T-shaped
3. tetrahedral; pyramidal
4. trigonal planar; trigonal planar
5. trigonal bipyramidal; T-shaped correct

Explanation:

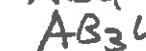
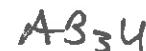
The hybridization tells us that there are 5 regions of high electron density. Three of those regions are the bonded Cl atoms. The other two regions must be lone pairs of electrons on the central I atom. This corresponds to trigonal bipyramidal electronic geometry and T-shaped molecular geometry.

19 VSEPR - molecular polarity

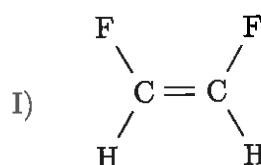
Draw molecules. Look for 3 planes of symmetry.



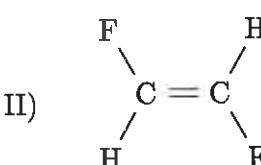
all are
non-polar
+ symmetrical
if B is same char



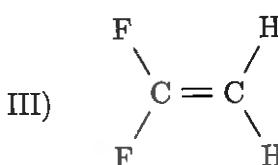
all are polar +
asymmetrical



1. II, III



2. I, II



3. III only

4. II only

5. I, III correct

6. I only

7. I, II, III

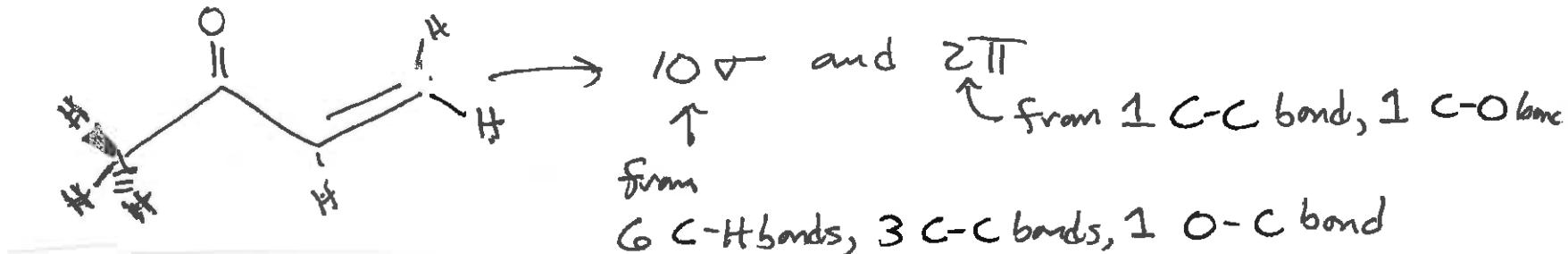
Which of the following molecules is/are polar?

Explanation:

Molecule II is symmetrical and therefore its individual dipole moments cancel, making it non-polar. Molecules I and III are asymmetrical and therefore polar.

20 VB theory - sigma and pi bonds

Draw a structure. Count all the first bonds. These are σ bonds. The rest are $=$ or \equiv and are π bonds.



LDE VB Sigma Pi Bonds 004

020 10.0 points

How many sigma (σ) and pi (π) bonds are in the Lewis structure for $C(COOH)_4$?

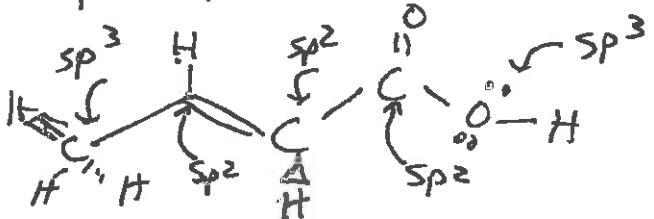
1. 8 σ , 4 π
 2. 12 σ , 4 π
 3. 12 σ , 0 π
 4. 16 σ , 0 π
-

21 VB theory - identifying hybrid orbits

Table

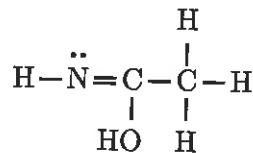
- 2 sp
- 3 sp^2
- 4 sp^3
- 5 dsp^3
- 6 d_2sp^3

Draw a structure. Count electron rich regions. Use table to assign hybridization



021 10.0 points

Give the hybridization of each central atom:
nitrogen, middle carbon, right carbon.



1. sp^3, sp^2, sp^3
2. sp^2, sp, sp^2
3. sp^2, sp^2, sp^3 correct
4. sp^2, sp^2, sp^2
5. sp, sp, sp
6. sp^3, sp^3, sp^3
7. sp^2, sp^3, sp^3
8. sp, sp^3, sp^3

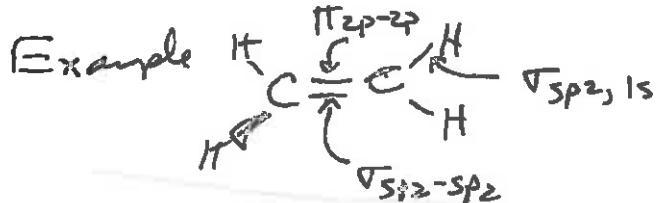
Explanation:

Hybridization is chosen based on the electronic geometry around the central atom, which is based on the number of RHED around the central atom. The RHED are three, three, and four.

22 MO theory - AOs that comprise MOs

Draw a structure. Pick a bond. If it is first (single) Then it is σ . The second and third are π .

Then assign AOs.

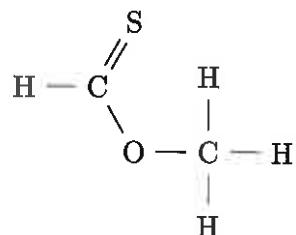


- the central σ are hybridized AOs.
- the periphery are $H \equiv 1s \quad O \equiv$ hybridized
- The π bonds are always P-P AOs.

LDE VB Hybridization 002

022 10.0 points

Consider the thionoester molecule

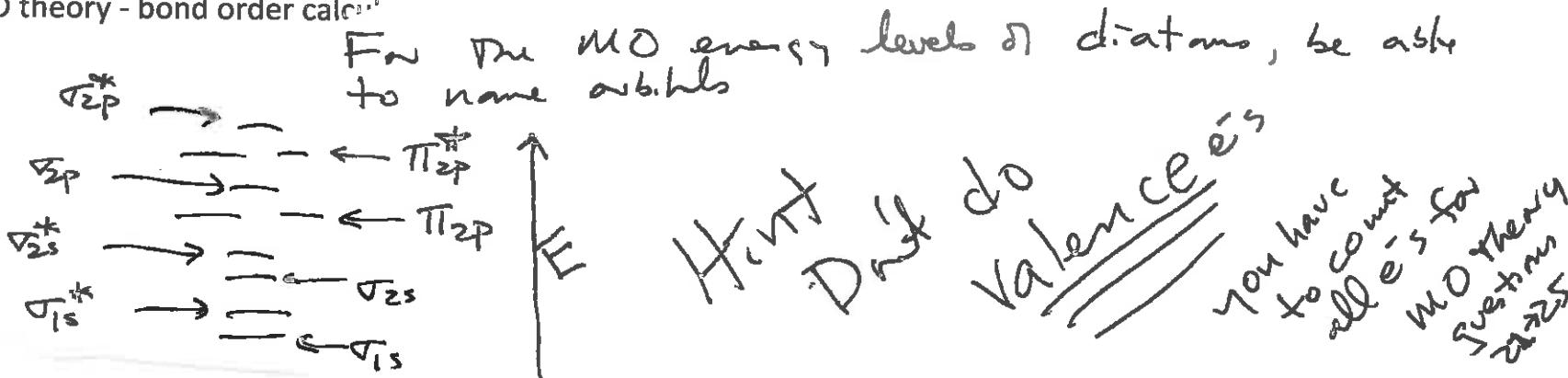


What orbitals were used to form the π (pi) bond?

V

1. $2s, 3p$
2. $2p, 3p$ correct
3. $sp^2, 3s$
4. $sp^3, 3p$
5. $sp^3, 3s$

23 MO theory - bond order calc:



Add up all the bonding e⁻ (num *) - the antibonding (#) = bond order

$$\begin{array}{c} \text{---} \\ | \\ + - + \\ | \\ \# * \\ | \\ \# * \end{array} \rightarrow \frac{7 \text{ bonding}}{\text{ant.}} = \frac{3}{2} = 1.5 \text{ bo}$$

LDE Bond Order 009

023 10.0 points

All of the species below have the same bond order except for one of them. Which is it?

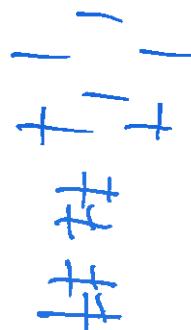


Explanation:

All of the species have a bond order of 0.5 except for B₂⁻, which has a bond order of 1.5.

24 MO theory – magnetism

Draw the orbitals



+ + ← and look for unpaired e's



LDE Paramagnetism 004

024 10.0 points

Which of the following species is/are paramagnetic?

- I) Li_2^-
- II) O_2
- III) H_2^+

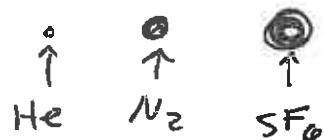
- 1. II and III
- 2. II only
- 3. I and II
- 4. I only
- 5. I and III
- 6. III only
- 7. I, II and III correct

Explanation:

Li_2^- and H_2^+ both have an odd number of electrons and therefore must be paramagnetic. O_2 has 16 total electrons, the last two of which must go into separate degenerate π^* anti-bonding orbitals.

25 Dalton's law of partial pressures calculation

Isn't the Ideal gas law great? It says that



are all the same. Simple countable hard spheres. So

$5\text{He} + 6\text{N}_2 + 3\text{SF}_6 = 14$ gas molecules. And by extension

$$P_A + P_B + P_C = P_{\text{TOT}}$$

Msci 12 0911

025 10.0 points

2.0 g of H₂ and 8.0 g of He are put in a 22.4 liter container at 0°C. The total pressure is

1. 10.0 atm.
2. 5.0 atm.
3. 3.0 atm. correct
4. 1.0 atm.

Explanation:

$$n_{\text{H}_2} = \frac{2 \text{ g} \cdot \text{mol}}{2 \text{ g}} = 1 \text{ mol} \quad V = 22.4 \text{ L}$$

$$n_{\text{He}} = \frac{8 \text{ g} \cdot \text{mol}}{4 \text{ g}} = 2 \text{ mol} \quad n_{\text{total}} = 3 \text{ mol}$$

$$T = 0^\circ\text{C} + 273 = 273 \text{ K}$$

Applying the ideal gas law equation,

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{(3 \text{ mol}) (0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (273 \text{ K})}{22.4 \text{ L}} \\ = 3.00032 \text{ atm}$$

26 Combined gas law calculation

$$\frac{P_1 V_1}{T_1} = nR = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$$

a true sentence

This is classic Plug + Chug. You will be given 5 or 6 variables and will solve for unknown.

Steps

- Rewrite to solve for unknown first
- Plop in known values (change °C → K) ~~→~~
- Perform simple math estimates to get answer w/out any actual calculations

Explanation:

$$P_1 = 1201 \text{ torr}$$

$$V_1 = 40 \text{ L}$$

$$T_1 = 50^\circ + 273.15 = 323.15 \text{ K}$$

$$P_2 = 760 \text{ torr}$$

$$T_2 = 273.15 \text{ K}$$

Using the Combined Gas Law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

and recalling that STP implies standard temperature (273.15 K) and pressure (1 atm or 760 torr), we have

$$\begin{aligned} V_2 &= \frac{P_1 V_1 T_2}{T_1 P_2} \\ &= \frac{(1201 \text{ torr})(40.0 \text{ L})(273.15 \text{ K})}{(323.15 \text{ K})(760 \text{ torr})} \\ &= 53.4302 \text{ L} \end{aligned}$$

27 Relating number density to pressure

$$PV = nRT$$

$$\hookrightarrow PV = \frac{g}{MW} RT$$

$$\hookrightarrow P = \frac{g}{V} \frac{RT}{MW}$$

$$\hookrightarrow P = \rho \frac{RT}{MW}$$

↑ pressure ↗ density

The derivation on left isn't needed because equation is on cover sheet, but it is instructive.

Note

- As mass density goes up, P goes up.
- As MW goes up, P goes down
- As T goes up, P goes up
- There is no V in equation (it is in P already)

Be able
to understand
these
functional
relationships

Mass Density and Pressure

027 10.0 points

A sample of nitrous oxide gas (NO) has a density of 12 g L^{-1} . What pressure does the sample exert at 27°C ?

1. 61.6 atm
2. not enough information
3. 997.9 atm
4. 1.0 atm
5. 9.9 atm correct

Explanation:

By thoughtful substitutions and rearrangement, the ideal gas law can be used to relate the mass density of a gas to its pressure.

$$PV = nRT$$

Recalling that a number of moles (n) is equal to a mass (m) divided by a molecular weight (M.W.), we can substitute into the ideal gas law.

$$n = \frac{m}{M.W.}$$

$$PV = \frac{m}{M.W.} RT$$

28 Gas reaction stoichiometry and $PV = nRT$

Hint: ① STP means
1 mole = 22.4 L

g $\xrightarrow{\text{mole react}}$ moles product $\xrightarrow{\text{Volume of gas}}$

$n \#$ $\xrightarrow{\text{Guy Lussac}}$ lets us avoid a lot of $PV=nRT$ calculation

So once the Δn (difference in moles gas)

$\xrightarrow{\substack{\text{found} \\ \text{in reaction}}}$, the volume of gases is easy to find $\Rightarrow 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2(\text{g})$

Example. At STP

$$\Delta n = 3 \text{ moles gas}$$

$$= \sim 67.2 \text{ L}$$

hardest

g
 $n \#$
 \uparrow
convert
to moles

$\xrightarrow{\text{mole react}}$ $\xrightarrow{\text{mole prod}}$ $\xrightarrow{\text{P of gases}}$

figure out
total Δn_{gas}

$$P = \frac{nRT}{V}$$

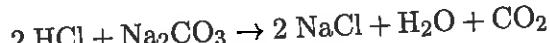
all moles gas
make same P

Lots of math
but answers
are way far
apart so
ROUND!!

limiting
reagent
problem!!

distinguish
what is a gas,
liquid, solid

For the reaction



179.2 liters of CO_2 is collected at STP. How
many moles of NaCl are also formed?

1. 16.0 moles correct

2. 4.0 moles

3. 32.0 moles

4. 8.0 moles

5. 6.0 moles

6. 12.5 moles

Explanation:

$$V_{\text{CO}_2} = 179.2 \text{ L}$$

At STP we can use the standard molar
volume, 22.4 L/mol.

$$\frac{179.2 \text{ L}}{22.4 \text{ L/mol}} = 8.00 \text{ mol CO}_2$$

$$8.00 \text{ mol CO}_2 \times \frac{2 \text{ mol NaCl}}{1 \text{ mol CO}_2} = 16.0 \text{ mol NaCl}$$

29 Graham's law calculation

diffusion, effusion, speed all follow equation of cover sheet

$$\frac{V_1}{V_2} = \sqrt{\frac{MW_2}{MW_1}}$$

note inverse square root relationship

Example, $\overset{2}{H_2}$ is 4 times faster than $O_2 \leftarrow 32$

$$\sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

ideality - theory

This is effectively a plus and chug, but have to be cautious about ratio

- bigger gas is slower
- Hint: a ratio has 1 in the denominator sometimes.

rms velocity of He 01

029 10.0 points

Helium has a rms velocity (v_{rms}) that is 4.21 times faster than which of the following gases?

1. argon, Ar
2. neon, Ne
3. xenon, Xe
4. oxygen, O₂
5. chlorine, Cl₂ correct

Explanation:

The relationship of rms velocities between different molecules is:

$$\frac{\text{rateA}}{\text{rateB}} = \sqrt{\frac{\text{massB}}{\text{massA}}}$$

Let massA be helium's mass of 4.0 and 4.21 be helium's rate so that:

$$\frac{4.21}{1} = \sqrt{\frac{\text{massB}}{4.0}}$$

$$(4.21)^2 = \frac{\text{massB}}{4.0}$$

$$70.9 = \text{massB}$$

This only matches the chlorine gas, Cl₂.

30 Gas non-ideality theory

The Van der Waals equation (on cover sheet) corrects non-ideality with $a + b$ coefficients

Be able to assign a and b to gases

$a \equiv$ corrects IMF
in P term

Example: If $\frac{a}{R}$ is 0.2 it is He while 4 is NH_3

$b \equiv$ corrects size
in V term

If $\frac{b}{R}$ is 0.01 it is H_2 while 0.06 is SF_6

Be able to do relative rankings

Non-ideality happens

- gases have volume
- gases have IMF

This non-ideality occurs,

- when P increases
- T decreases

{ why? }

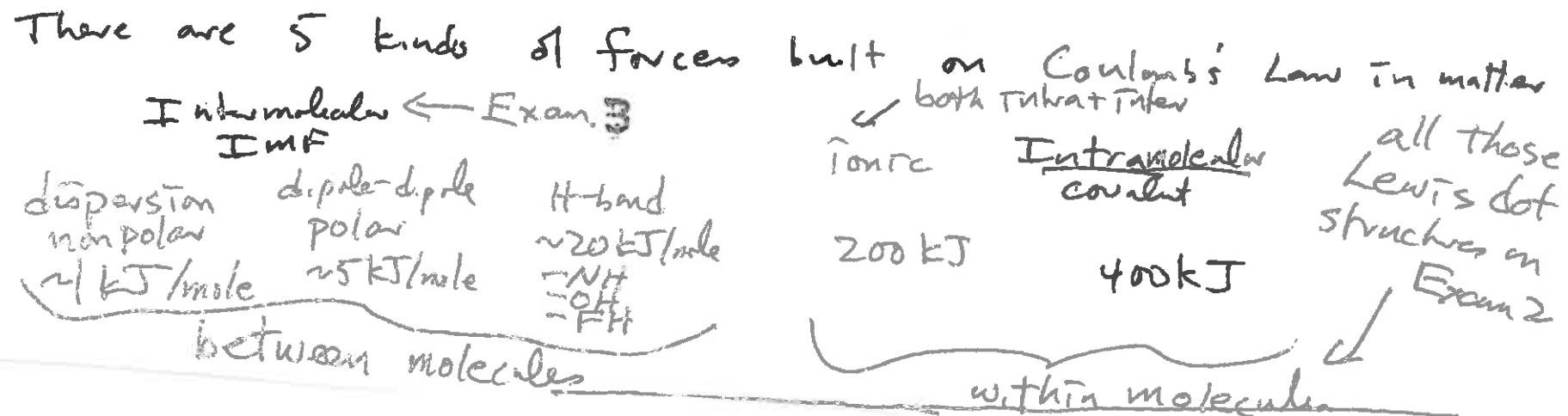
You will be given a collection of T/F statements and must find the correct answer

Which of the following does not affect the ideality of gases?

- I) the temperature of the gas
- II) the density of the gas
- III) the size of the gas molecules

1. none of the above correct
2. I, II, and III
3. I and III
4. II and III
5. I only
6. I and II
7. II only

31 IMF theory



LDE Intermolecular Forces 001 031 10.0 points

Which of the following statements regarding intermolecular forces (IMF) is/are true?

- I) Intermolecular forces result from attractive forces between regions of positive and negative charge density in neighboring molecules.
- II) The stronger the bonds within a molecule are, the stronger the intermolecular forces will be.
- III) Only non-polar molecules have instantaneous dipoles.

1. II and III
2. I and II
3. I only correct
4. II only
5. III only
6. I, II, and III
7. I and III

Explanation:

Statement I is true - all IMF result from Coulombic attraction. Statements II and III are both false; the strength of the bonds within a molecule have no bearing on the strength of the bonds between molecules; all molecules have London forces.

32 Assigning IMF to molecules

You will be given a bunch of compounds and asked the dominant IMF in each

| | | | |
|---------|------------------------|---|----------------------------|
| Example | CaH_6 | = | dominant dispers... |
| | CH_3OH | = | H bond... d.pole-d.pole |
| | O_3 | = | d.pole-d.pole |
| | NaCl | = | Ion-Ic |

make sure
you remember
how to draw
3D Lewis structures
to assign polarity/nonpolar

LDE Intermolecular Forces 002

032 10.0 points

Which of the following is not correctly paired with its dominant type of intermolecular forces?

1. NH_3 , hydrogen bonding
2. C_6H_6 (benzene), instantaneous dipoles
3. CaO , ionic forces
4. SiH_4 , instantaneous dipoles
5. HBr , hydrogen bonding **correct**

Explanation:

London forces, dispersion forces, van der Waals' forces, instantaneous or induced dipoles all describe the same intermolecular force. London forces are induced, short-lived, and very weak. Molecules and atoms can experience London forces because they have electron clouds. London forces result from the distortion of the electron cloud of an atom or molecule by the presence of nearby atoms or molecules.

Permanent dipole-dipole interactions are stronger than London forces and occur between polar covalent molecules due to charge separation.

H-bonds are a special case of very strong dipole-dipole interactions. They only occur when H is bonded to small, highly electronegative atoms - F, O or N only.

Ion-ion interactions are the strongest due to extreme charge separation and occur between ions (including polyatomic ions). They can be thought of as both inter- and intramolecular bonding.

HBr is a polar molecule that does not contain H bonds; therefore, dipole-dipole forces will be the most significant type of intermolecular forces present.

33 Theory behind liquid property ranking

Ranking properties of liquids (direct relationship with IMF)

Most liquid properties increase with increasing IMF b.p., s.t., c.a., visc, ΔH_{vap} , etc

So to rank them, first need to rank IMF: The bucket method

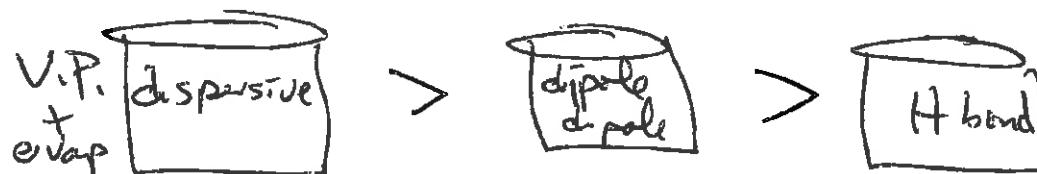


Of course size matters and dispersive wins as molecules get bigger, but not something to know in ranking

this is a rough first start and works often in ranking problems

Ranking properties of liquids (inverse relationship with IMF) tricky

Evaporation and vapor pressure are inversely related to IMF so do what you did for 22 above in reverse



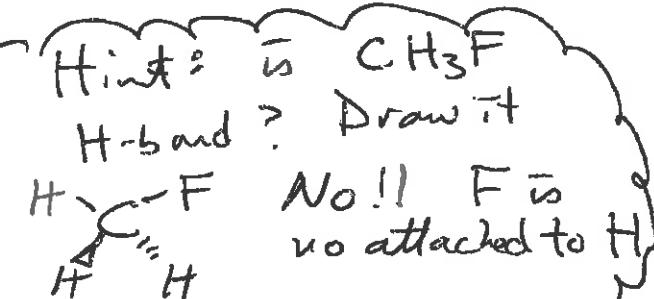
036 10.0 points

Which of the following substances would you predict might evaporate the fastest?

1. C₈H₁₈
2. C₁₀H₂₂
3. C₁₂H₂₄
4. C₆H₁₄ correct

Explanation:

All the listed molecules are nonpolar hydrocarbons; therefore the dominant intermolecular force that exists in the condensed phase of all listed molecules is dispersion forces. Therefore, the molecule with the least number of atoms and the lowest molecular weight would have the lowest dispersion forces, and therefore would evaporate the easiest.



34 Physical property definitions

Just like the Gas laws, be able to write a sentence explaining
boiling point }
surface tension }
viscosity }
evaporation }
vapor pressure }
capillary action }

be able to sort through a collection of
T/F statements on the question

LDE Physical Properties 001

034 10.0 points

Which of the following statements about boiling is false?

1. The boiling point of a liquid is independent of atmospheric pressure. **correct**
2. For a given pressure, the boiling point is always at a higher temperature than melting point.
3. Boiling occurs when vapor pressure exceeds atmospheric pressure.
4. As intermolecular forces increase, boiling point increases as well.

Explanation:

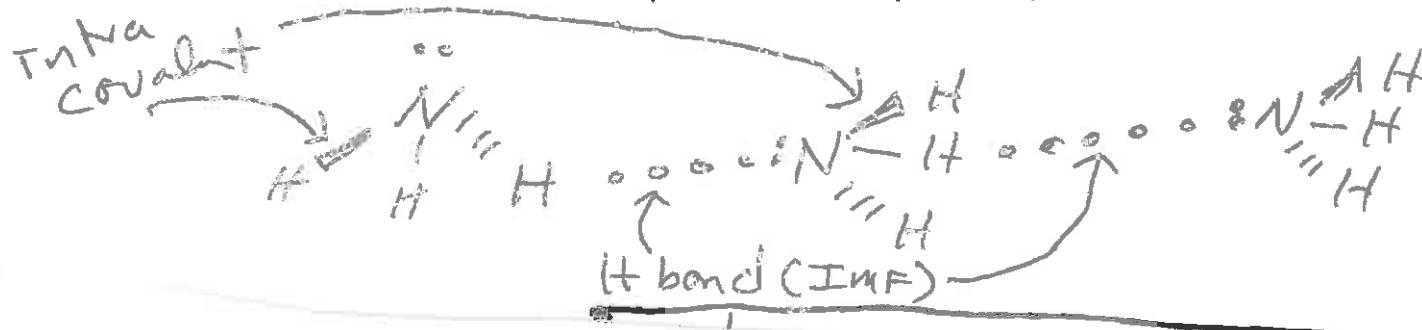
Boiling point is directly proportional to atmospheric pressure.

35 Ranking physical properties by IMF

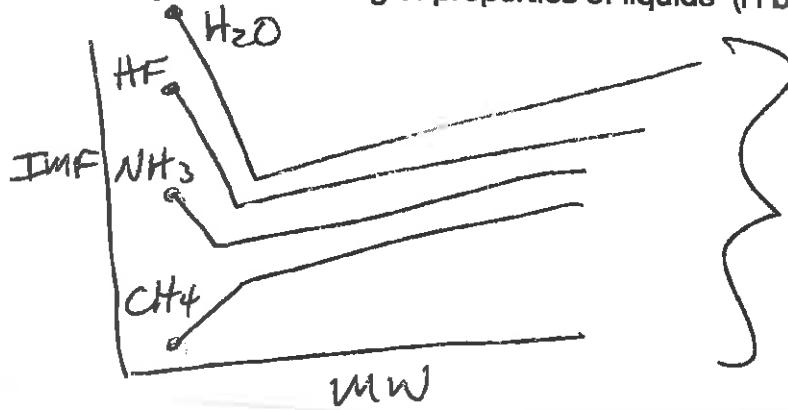
describe dispersive (instantaneous d.pole = London = dispersion) forces.

Be able to explain the origin and application of this most ubiquitous (everything has dispersion force) IMF

Be able to draw simple compounds w/ H-bonding and distinguish different types of bonds (covalent vs H-bond)



Theory behind ranking of properties of liquids (H bonding) medium

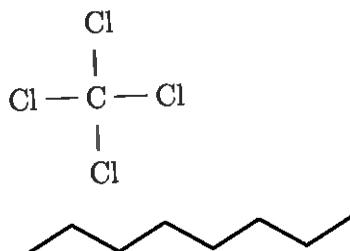


this is a very famous plot of H bonding that shows how special the OH, FH, NH is period 2 are.
Be able to explain the trends

36 Ranking physical properties by IMF

Explaining Dispersion Forces 033 10.0 points

Carbon tetrachloride (CCl_4) and *n*-octane (C_8H_{18}) are both non-polar molecules. At standard pressure, they boil at 345 K and 399 K, respectively. Which answer choice below correctly explains their boiling points?



1. CCl_4 has a lower boiling point because its greater molecular weight enables it to form stronger instantaneous dipoles.

2. C_8H_{18} has a higher boiling point because its greater molecular weight enables it to form stronger instantaneous dipoles.

3. C_8H_{18} has a higher boiling point because its electron cloud is larger and allows it to form more instantaneous dipoles. **correct**

4. C_8H_{18} has a higher boiling point because its smaller surface area allows it to form stronger instantaneous dipoles.

5. CCl_4 has a lower boiling point because its smaller surface area allows it to form stronger instantaneous dipoles.

VP IMF Ranking

035 10.0 points

Rank the compounds

$\text{CH}_3\text{CH}_2\text{OH}$ CH_3NH_2 CH_3OH NaOH

in terms of increasing vapor pressure.

1. $\text{NaOH} < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_3\text{OH}$
 $< \text{CH}_3\text{NH}_2$ **correct**

2. $\text{CH}_3\text{NH}_2 < \text{CH}_3\text{OH} < \text{CH}_3\text{CH}_2\text{OH}$
 $< \text{NaOH}$

3. $\text{NaOH} < \text{CH}_3\text{NH}_2 < \text{CH}_3\text{OH}$
 $< \text{CH}_3\text{CH}_2\text{OH}$

4. $\text{CH}_3\text{CH}_2\text{OH} < \text{CH}_3\text{OH} < \text{CH}_3\text{NH}_2$
 $< \text{NaOH}$

5. $\text{NaOH} < \text{CH}_3\text{OH} < \text{CH}_3\text{NH}_2$
 $< \text{CH}_3\text{CH}_2\text{OH}$

Explanation:

Carbon tetrachloride (CCl_4) and *n*-octane (C_8H_{18}) both have only instantaneous dipoles. Despite the fact that (CCl_4) has a greater molecular weight ($153.81 \text{ g mol}^{-1}$) compared to C_8H_{18} ($114.23 \text{ g mol}^{-1}$), the latter boils at a substantially higher temperature. In general, dispersion forces are greater in molecules with greater molecular weight, more total electrons and a larger surface area (i.e. the shape of the molecule). Since *n*-octane is a long skinny molecule, more of its electrons are accessible and ready to form instantaneous dipoles.

37 Thermodynamic laws theory

- 1st Law $\Delta U_{univ} = \Delta U_{sys} + \Delta U_{surv} = 0$ energy of universe conserved
- $\Delta U_{sys} = -\Delta U_{surv}$ from first law is basis of calorimetry
- $\Delta H = \Delta U + P\Delta V$ to permit measure of q in open systems
- $\Delta H = q_p$ $\Delta U = q_v$
 - q_p q_v
 - atm closed volume
- ΔH and ΔU are usually similar magnitudes because $P\Delta V$ is often small or 0 if ΔV is small or 0

Here are some nutts

- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surv} > 0$ happens
- $\Delta S = \frac{q}{T}$ which means ΔS is larger for high q + low T
so exploding H₂ balloon at North pole is big ΔS
- $\Delta G_{sys} = -T\Delta S_{univ}$ is how we get to use ΔG_{sys} rather than ΔS_{univ}
- $\Delta S_{surv} = -\frac{\Delta H_{sys}}{T}$ is how heat from exothermic reaction makes chaos in surroundings

Which of the following statements concerning the laws of thermodynamics is not true?

1. Entropy always increases in an isolated system.

2. $\Delta U_{univ} = 0$

3. $\Delta S_{univ} > 0$

4. $S = 0$ for a perfect crystal at absolute zero.

5. Free energy is conserved in a closed sys-

Explanation:

Free energy is conserved in an isolated system, but not in a closed system.

38 PV work calculation

$$W = -\underset{\text{ext}}{P}\Delta V = -\Delta nRT$$

This is a plug and chug. Only difficulty

is units. Work is typically kJ but $P\Delta V$ is

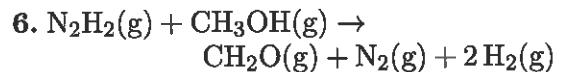
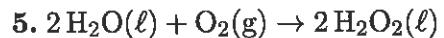
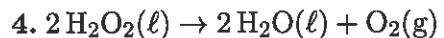
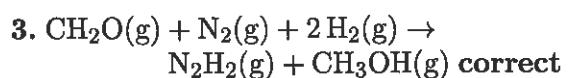
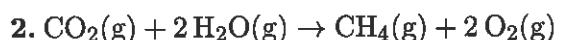
l atm so need to use conversion 1 atm = 101.3 kJ

~~*** signs!!~~ if V decreases, work on system is \oplus
if V increases, work on surroundings is \ominus

LDE Thermodynamic Work 0034

038 10.0 points

For which of the following reactions at room temperature (25°C) would there be 5.0 kJ of work done on the system?



Explanation:

At room temperature (298 K), the product of the gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is very close to $2.5 \text{ kJ} \cdot \text{mol}^{-1}$. Based on $5.0 \text{ kJ} = -\Delta n_{\text{gas}} (2.5 \text{ kJ} \cdot \text{mol}^{-1})$, the reaction for which $\Delta n_{\text{gas}} = -2$ will be the correct an-

If asking for W given
a chemical rxn, find change
in Δn_{gas} and multiply
by RT which is $\approx 2.5 \text{ kJ}$
at room T. Remember signs,

39 Bomb calorimetry calculation

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surv}} = -(m c \Delta T + C_{\text{H}_2\text{O}} \Delta T)_{\text{calorim}}$$

- easy plug and chug using ΔT twice
- two $C_{\text{H}_2\text{O}}$, Calorimeter values
- convert $\text{L} \rightarrow \text{ml}$ to grams
- usual answer is per amount like $\text{J}/\text{cheetos}$ or kJ/gram

Correct
for per
like explos
4 cheetos but
per cheetos

LDE Bomb Calorimeter 002

039 10.0 points

If we set up a bomb calorimetry experiment to determine the molar internal energy of combustion of ethene (C_2H_4) using 1 L of water as our heat sink, 2.805 g of ethene, and measure an initial and final temperature of 25.20°C and 58.92°C , respectively, what will be the experimentally determined molar internal energy of combustion of ethene? Assume the density of water is $1.00 \text{ g} \cdot \text{mL}^{-1}$ and the calorimeter itself absorbs no heat. The specific heat capacity of water is $4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$.

1. $-14,110 \text{ kJ} \cdot \text{mol}^{-1}$

2. $-14.11 \text{ kJ} \cdot \text{mol}^{-1}$

3. $-141,100 \text{ kJ} \cdot \text{mol}^{-1}$

4. $-1,411 \text{ kJ} \cdot \text{mol}^{-1}$ correct

5. $-141.1 \text{ kJ} \cdot \text{mol}^{-1}$

Explanation:

$$\begin{aligned}\Delta T &= T_f - T_i = 58.92^\circ\text{C} - 25.20^\circ\text{C} \\ &= 33.72^\circ\text{C} = 33.72 \text{ K}\end{aligned}$$

$$m = (1 \text{ L}) \cdot \frac{1000 \text{ mL}}{\text{L}} \cdot \frac{1.00 \text{ g}}{\text{mL}} = 1000 \text{ g}$$

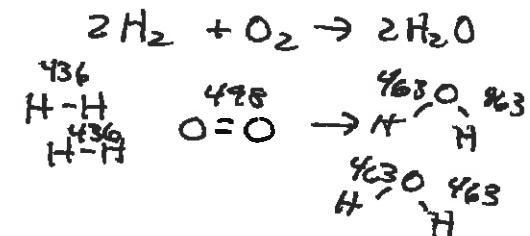
$$n = 2.805 \text{ g ethene} \cdot \frac{28.05 \text{ g}}{\text{mol}} = 0.1 \text{ mol}$$

$$\begin{aligned}\frac{\Delta U_{\text{rxn}}}{n} &= \frac{-\Delta U_{\text{cal}}}{n} = \frac{-mc\Delta T}{n} \\ &= -\frac{1000 \text{ g} \cdot \frac{4.184 \text{ J}}{\text{g}\cdot\text{K}} \cdot 33.72 \text{ K}}{0.1 \text{ mol}} \\ &= -1,411 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

40 Hess' law - bond energy calculation

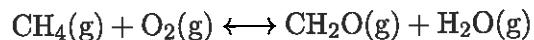
Give table of BE on front page

- write the Lewis structures bond by bond
- label each bond with B.E.
- add up reactants $4 \times 436 + 498$ and products 4×463
- $\sum \text{reactants} - \sum \text{products} = \text{BE} \approx -500$ (actual is -482)
- Don't over round off. Take your time w/ the math



040 10.0 points

Using the provided bond enthalpy data, calculate the change in enthalpy for the following reaction:



1. $-349 \text{ kJ} \cdot \text{mol}^{-1}$ correct
2. $-710 \text{ kJ} \cdot \text{mol}^{-1}$
3. $-577 \text{ kJ} \cdot \text{mol}^{-1}$
4. $710 \text{ kJ} \cdot \text{mol}^{-1}$
5. $349 \text{ kJ} \cdot \text{mol}^{-1}$
6. $577 \text{ kJ} \cdot \text{mol}^{-1}$

Explanation:

$$\begin{aligned}
 \Delta H_{rxn} &= \sum \text{BE}_{\text{reactants}} - \sum \text{BE}_{\text{products}} \\
 &= [4(412 \text{ kJ} \cdot \text{mol}^{-1}) + 496 \text{ kJ} \cdot \text{mol}^{-1}] \\
 &\quad - [2(412 \text{ kJ} \cdot \text{mol}^{-1}) + 743 \text{ kJ} \cdot \text{mol}^{-1} \\
 &\quad \quad + 2(463 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= \underline{\underline{-349 \text{ kJ} \cdot \text{mol}^{-1}}}
 \end{aligned}$$

41 Hess' law - ΔH_f calculation

Simple plug and chug using the table
of ΔH_f° values to solve

$$\Delta H_{rxn}^\circ = \sum \Delta H_{prod}^\circ - \sum \Delta H_{react}^\circ$$

ChemPrin3e T06 48

041 10.0 points

Calculate the standard enthalpy of combustion of butane ($C_4H_{10}(g)$) at 298 K from standard enthalpy of formation data.

1. $-2877.04 \text{ kJ} \cdot \text{mol}^{-1}$ correct

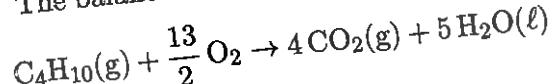
2. $-2342.32 \text{ kJ} \cdot \text{mol}^{-1}$

3. $-2056.49 \text{ kJ} \cdot \text{mol}^{-1}$

4. $-895.49 \text{ kJ} \cdot \text{mol}^{-1}$

5. $-2843.5 \text{ kJ} \cdot \text{mol}^{-1}$

The balanced equation is



$$\begin{aligned}\Delta H_{comb} &= \sum \Delta H_f^\circ_{prod} - \sum \Delta H_f^\circ_{react} \\ &= [5 \Delta H_f^\circ_{H_2O(l)} + 4 \Delta H_f^\circ_{CO_2(g)}] \\ &\quad - \Delta H_f^\circ_{C_4H_{10}(g)} \\ &= [5(-285.83 \text{ kJ/mol}) \\ &\quad + 4(-393.51 \text{ kJ/mol})] \\ &\quad - (-126.15 \text{ kJ/mol}) \\ &= -2877.04 \text{ kJ/mol}\end{aligned}$$

Explanation:

42 Thermodynamic conventions - signs/descriptions

For a given set of conditions be able to assign *be the system*

| | | | | | | |
|--------------------------|-------------------------|-------------------------|-------------------------|---|-------------------------|-----|
| ΔS_{univ} | ΔG_{sys} | ΔH_{sys} | ΔS_{sys} | ΔS_{sum} | q | w |
| + ↑ happens | - ↑ happens | + | + | - ↑ opposite sign of ΔH_{sys} | endo gas is messy | + |

w ← For example if given a phase change producing gas at high T, then the signs are as shown starting with $\Delta H_{\text{sys}} +$, $\Delta S_{\text{sys}} +$ because that is clue given. And $w \ominus$ because gas formed in clue

LDE Thermodynamic Signs 001

042 10.0 points

When wood is burning (i.e. a combustion process is occurring), which of the following quantities is positive?

1. Change in entropy. correct
2. Change in Gibbs' free energy.
3. Work.
4. Change in enthalpy.

Explanation:

A burning piece of wood produces a lot of gas and thus does expansion work on the surroundings so work is negative, not positive. It is an exothermic reaction (producing heat) so enthalpy change is negative, not positive. It happens spontaneously so change in free energy is negative, not positive. Finally, all the gas produced yields an increase in entropy so the change is indeed positive.

43 Ranking molar entropy

Given a collection of compounds, rank S_m° using logic:

$s \rightarrow l \rightarrow g$ is large S_m°

Small \rightarrow large is large S_m°

Simple \rightarrow complicated is large S_m°

Example
are in the
cover page
tables

this is
not ΔS
this is
for cmpds

Example $H_2O(l) < H_2O_2(l) < H_2O(g) < H_2O_2(g)$

ChemPrin3e 07 25 26
043 10.0 points

Which one shows the substances in the increasing order of their molar entropy?

1. $H_2O(l), Ar(g), Ne(g), CO_2(g)$
2. $H_2O(l), Ne(g), Ar(g), CO_2(g)$ correct
3. None of these
4. $CO_2(g), Ar(g), Ne(g), H_2O(l)$
5. $H_2O(l), CO_2(g), Ne(g), Ar(g)$
6. $CO_2(g), H_2O(l), Ne(g), Ar(g)$

Explanation:

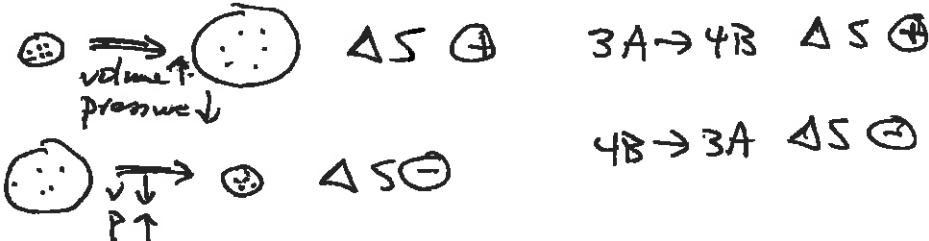
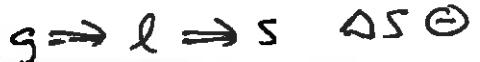
For H_2O entropy increases going from a solid to a liquid to a gas. We would automatically expect $C(s, \text{diamond})$ to have less entropy than any liquid. Water is a molecular substance held together in the solid phase by weak hydrogen bonds, and the carbons in $C(s, \text{diamond})$ are more rigidly held in place and will have less entropy.

The correct order is

$C(s, \text{diamond}) < H_2O(s) < H_2O(l)$
 $< H_2O(g)$

44 Predicting changes in entropy

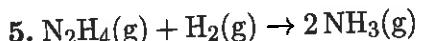
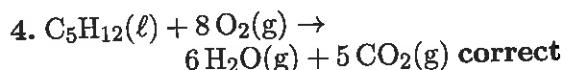
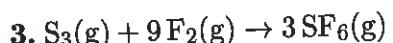
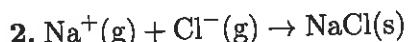
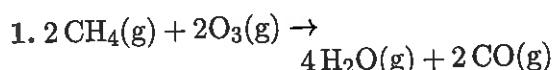
Given a series of chemical and physical processes, predict sign of ΔS_{sys}



LDE Entropy 002

044 10.0 points

Which of the reactions below will likely have the largest increase in entropy (ΔS_{rxn})?



Explanation:

The reaction with the greatest positive value for Δn_{gas} will have the greatest value of ΔS_{rxn} .

45 Boltzmann equation calculation

$$S = k \ln W = k \ln \#^N \quad \# \rightarrow \text{orientation} \quad N \Rightarrow \#\text{of molecules}$$

$\# = 2$ for CO
 $\# = 3$ for BH_2Cl
 $\# = 4$ for CH_3Cl
 $\# = 6$ for $\text{C}_6\text{H}_5\text{Cl}$

- remember $k \times \frac{\text{molecules}}{\text{mole}} = R = 8.3$
- remember $\ln 2 = 0.7 \quad \ln 3 = 1.1$
- remember $\ln xy = \ln x + \ln y$

Example
What is S for 5 moles CH_3Cl

$$S = k \ln 4^{5N} = k \ln 2^{25N}$$

$$= 10Nk \ln 2 = 10(8.3) \ln 2$$

$$\hookrightarrow 83(1.7) \approx 60 \frac{\text{J}}{\text{K}}$$

LDE Stat Thermo Entropy 004

045 10.0 points

What is the residual entropy of 0.5 moles of CH_3Cl ?

1. $11.52 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
2. $0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
3. $5.76 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ correct
4. $9.13 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

Explanation:

$$\begin{aligned}
 S &= k \cdot \ln W = k \cdot \ln (4^{0.5 N_A}) \\
 &= N_A k \cdot \ln(2) = R \ln(2) \\
 &= 5.76 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
 \end{aligned}$$

46 Second law calculation - ΔS_{surr}

In calculating ΔS_{univ} , ΔS_{sys} comes from table of molar entropies.

But ΔS_{surr} comes from table of ΔH_{rxn}

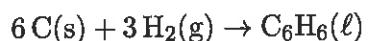
$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T}$$

- make sure signs are right, ΔS_{surr} opposite ΔH_{sys}
- get units right. Use J for everything, not kJ

Example What is ΔS_{surr} if $\Delta S_{\text{sys}}^{\circ} = 22 \text{ J/K}$ and $\Delta H_{\text{rxn}}^{\circ} = 6 \text{ kJ}$ at 298K

$$\Delta S_{\text{surr}} = -\frac{(-6000 \text{ J})}{298} = +30 \frac{\text{J}}{\text{K}}$$

Calculate $\Delta S_{\text{surr}}^{\circ}$ at 298 K for the reaction



$$\Delta H_r^{\circ} = +49.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ and } \Delta S_r^{\circ} = -253 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

1. $-417 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

2. $+253 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

3. $-164 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ correct

4. $+164 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

5. $-253 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

↑
2 negatives, one
from equation
and one from
sign of water
 ΔH freezing



- Note you don't use ΔS_{sys}
- Note l \rightarrow s is exo so use -6000 not $+6000$
- Note ΔS_{surr} \oplus became exothermic

Explanation:

$$\Delta H_r^{\circ} = 49000 \text{ J} \cdot \text{mol}^{-1} \quad T = 298 \text{ K}$$

$$\begin{aligned} \Delta S_{\text{surr}}^{\circ} &= \frac{q_{\text{surr}}}{T} = \frac{-q}{T} = \frac{-\Delta H_r^{\circ}}{298 \text{ K}} \\ &= \frac{-(+49000 \text{ J} \cdot \text{mol}^{-1})}{298 \text{ K}} \\ &= -164.43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

47 Spontaneity and temperature - phase changes

$\Delta G = \Delta H - T\Delta S = 0$ at phase change so

$$\Delta H = T\Delta S$$

$$T_{\text{phase}} = \frac{\Delta H}{\Delta S}$$

- be careful with units of T
K vs °C

- Notice how similar question 21 is.

Example What is T for H₂O boiling if

$$\Delta H_{\text{vap}} = 40 \text{ kJ} \text{ and } \Delta S_{\text{vap}} = 107 \text{ J/K}$$

$$T = \frac{40000}{107} \approx 373 \Rightarrow 100^\circ\text{C}$$

Based on the enthalpy of sublimation ($\Delta H_{\text{sub}} = 393.5 \text{ kJ/mol}^{-1}$) and entropy of sublimation ($\Delta S_{\text{sub}} = 2.023 \text{ kJ/mol}^{-1}\cdot\text{K}^{-1}$) of carbon dioxide, at what temperature does this phase transition occur?

1. -78.5 K
2. -78.5 °C correct
3. 0.2 °C
4. 78.5 °C
5. 0.2 K

Explanation:

$$T_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{\Delta S_{\text{sub}}} = \frac{393.5 \text{ kJ/mol}^{-1}}{2.023 \text{ kJ/mol}^{-1}\cdot\text{K}^{-1}} =$$

$$194.5 \text{ K} = -78.5^\circ\text{C}$$

48 Spontaneity and temperature - chemical reactions

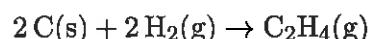
$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

| | | |
|---|---|----------------|
| + | + | happens high T |
| + | - | rarely happens |
| + | + | always happens |
| - | - | happens low T |

ChemPrin3e T07 59

048 10.0 points

For the reaction



$\Delta H_r^\circ = +52.3 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S_r^\circ = -53.07 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at 298 K. The reverse reaction will be spontaneous at

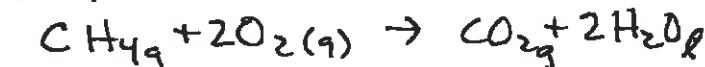
1. all temperatures. **correct**
2. temperatures below 1015 K.
3. temperatures below 985 K.
4. temperatures above 985 K.
5. no temperatures.

Explanation:

$\Delta G = \Delta H - T\Delta S$ is used to predict spontaneity. (ΔG is negative for a spontaneous reaction.) T is always positive; for the reverse reaction, we reverse the sign of ΔH and ΔS . We thus have $\Delta G = (-) - T(+)$ for the reverse reaction, so ΔG will be negative for any physically possible value of T .

In a process, be able to assign
 ΔS_{univ} , ΔS_{sys} , ΔS_{sur} , ΔG_{sys} , ΔH_{sys}

Examples



$\Delta H_{sys} \ominus$ combustion, $\Delta S_{sys} \ominus$ $g \rightarrow l$

so $\Delta S_{sur} \oplus$, ΔS_{univ} and $\Delta G_{sys} \ominus$ at low T

Example $\text{H}_2\text{O(g)} \xrightarrow{90^\circ} \text{H}_2\text{O(l)}$ happens

$\Delta G \ominus$, $\Delta S_{univ} \oplus$, $\Delta S_{sys} \ominus$, $\Delta H_{sys} \ominus$, $\Delta S_{sur} \oplus$
 note happens low T ($< 100^\circ\text{C}$)

49 ΔG_{rxn} from table values

Given a chemical reaction



What is ΔG_{rxn} at 300K

- use $\Delta G = \Delta H - T\Delta S$
- use cover sheet data
- Hint: Combustion reaction ΔG°
- Hint: $T\Delta S$ is usually small
so $\Delta H \approx \Delta G$

ChemPrin3e T07 52

049 10.0 points

Calculate ΔG_r° for the decomposition of mercury(II) oxide

| | | |
|---|----------|------------------------------|
| ΔH_f° (kJ · mol ⁻¹) | 2 HgO(s) | 2 Hg(l) + O ₂ (g) |
| -90.83 | - | - |
| 70.29 (J · K ⁻¹ · mol ⁻¹) | 76.02 | 205.14 |

at 298 K.

1. +246.2 kJ · mol⁻¹

2. -64.5 kJ · mol⁻¹

3. +117.1 kJ · mol⁻¹ **correct**

4. -117.1 kJ · mol⁻¹

5. -246.2 kJ · mol⁻¹

$$\Delta H = \sum \Delta H_{prod}^\circ - \sum \Delta H_{react}^\circ$$

$$-2(286) \xrightarrow{\substack{\text{become} \\ \Delta H_f = 0}} -572 \text{ kJ}$$

$$\Delta S = \sum S_m^\circ_{prod} - \sum S_m^\circ_{react}$$

$$= 2(70) - [2(130) + 205] \\ 140 - 465 = -325$$

$$T\Delta S = 300(-325) = -975$$

$$\Delta G_{rxn} = -572 - (-97) = -475$$

Explanation:

In order to find ΔG_r° at 298 K, we must first calculate ΔH_r° and ΔS_r° .

$$\begin{aligned} \Delta S_r^\circ &= 2 \cdot S_{\text{Hg}(l)}^\circ + S_{\text{O}_2(g)}^\circ - 2 \cdot S_{\text{HgO}(s)}^\circ \\ &= 2 \left(76.02 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) + 205.14 \frac{\text{J}}{\text{K} \cdot \text{mol}} \\ &\quad - 2 \left(70.20 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\ &= 216.6 \frac{\text{J}}{\text{K} \cdot \text{mol}} \end{aligned}$$

$$\begin{aligned} \Delta H_r^\circ &= 2 \cdot H_{\text{Hg}(l)}^\circ + H_{\text{O}_2(g)}^\circ - 2 \cdot H_{\text{HgO}(s)}^\circ \\ &= 0 - 2(-90.83 \text{ kJ/mol}) \\ &= 181.64 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta G_r^\circ &= \Delta H_r^\circ - T \Delta S_r^\circ \\ &= 181.64 \text{ kJ/mol} - (298 \text{ K}) \\ &\quad \times \left(216.6 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \end{aligned}$$

50 Predicting compound stability

If $\Delta G_f^\circ \leftarrow$ then compound is stable
 If $\Delta G_f^\circ \rightarrow$ Then compound not stable

Use the table data

| | ΔG_{rxn}° [kg/(mol · K)] |
|--|--|
| $\text{AgCl(s)} \rightarrow \text{Ag(s)} + \frac{1}{2} \text{Cl}_2(\text{g})$ | 109.7 |
| $2 \text{Ag(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{Ag}_2\text{O(s)}$ | -10.8 |
| $\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$ | 51.8 |
| $\text{HI(g)} \rightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{I}_2(\text{g})$ | -1.3 |

to pick the thermodynamically most stable species.

1. $\text{NO}_2(\text{g})$
2. $\text{Ag}_2\text{O(s)}$
3. AgCl(s) correct
4. HI(g)

Explanation:

Because the decomposition of solid silver chloride is highly non-spontaneous, its formation is highly spontaneous and it is quite stable.

Diamond as $\Delta G_f^\circ = +3 \text{ kJ/mole}$
 so not stable
 Benzene $\Delta G_f^\circ = +49 \text{ kJ}$
 so not stable
 Ethanol $\Delta G_f^\circ = -278 \text{ kJ}$
 so stable