Chemistry Resource NAME: _____

Formal Charge and Resonance Block: _____

Formal Charge

Formal charge is a means of identifying the "best" Lewis dot structure when more than one valid dot structure can be drawn for a molecule or molecular ion. The *formal charge* can be assigned to every atom in a electron dot structure. The formal charge assigned for a particular atom is calculated from the number of valence electrons the atom would have and the number of electrons around the atom when it is bonded in the molecule. The calculate the *formal charge* of an atom, start with the number of **valence electrons**, $N_{v.e,}$ then subtract the number of **unshared electrons**, $N_{us.e}$, and half of the **bonding electrons**, ½ $N_{b.e}$.

Formal charge = $N_{v.e.} - N_{us.e.} - ½\ N_{b.e.}$

The **formal charge** is a *hypothetical* charge assigned from the dot structure. The formal charges in a structure tell us the "quality" of the dot structure. Some practice of assigning formal charge is necessary before you master this technique.

If you can draw multiple *valid* Lewis dot structures for a particular molecule or ion dot structures, then together they form a set of possible resonance structures. So, how does one choose which structure is the most reasonable choice – that is to say, which is the most stable? Another tool for your toolkit is called *formal charge*. Formal charge is a useful way to compare the stability for a set of valid Lewis dot structures. After calculating the formal charge on each atom for each of the structures in the set, the most stable structure(s) are determined by application of the **formal charge rules**

- Structures with the lowest magnitude of formal charges are more stable.
- More *electronegative* atoms should have *negative* formal charges.
- *Adjacent* atoms should have *opposite* formal charges (or zero formal charge).

Example: Draw Lewis dot structure for SO_2

- Write out the atoms with the correct number of valence electrons:

```
  ..        ..        ..
: O :     : S :     : O :
```

- Arrange the atoms to make a skeletal structure, then complete the Lewis dot structure – verify that the structure satisfies the octet rule:

```
 ..    ..    ..
: O : : S : : O : ← octet rule not satisfied
 0     0     0   formal charge
```

- Adjust bonding electrons so that octet rules apply to all the atoms:

```
 ..  ..    ..
: O : S : : O : ← octet rule satisfied
 ' '
–1  +1    0     formal charge
```

- Since the left O has 6 unshared plus 2 shared electrons, it effectively has 7 electrons for a 6–valence–electron O, and thus its formal charge is –1.
- Formal charge for O = 6 – 6 – (2/2) = –1.
- Formal charge for S = 6 – 2 –(6/2) = +1.

➢ Here is yet another structure that does not satisfy the octet rule, but is a reasonable structure:

```
 ..  ..  ..
: O : S : O : ←  octet rule satisfied
 ''      ''

–1  +2   –1  formal charge
```

Resonance Structures

When several structures with different electron distributions among the bonds are possible, all structures contribute to the electronic structure of the molecule. These structures are called resonance structures. A combination of all these resonance structures represents the real or observed structure. The Lewis structures of some molecules do not agree with the observed structures. For such a molecule, several dot structures may be drawn. All the dot structures contribute to the *real structure*. The more stable structures contribute more than less stable ones.

For resonance structures, the skeleton of the molecule (or ion) stays in the same relative position, and only distributions of electrons in the resonance structures are different.

Let us return to the SO_2 molecule. The molecule has a bent structure due to the lone pair of electrons on S. In the last structure that has a formal charge, there is a single S–O bond and a double S=O bond. These two bonds can switch over giving two resonance structures as shown below.

```
    ..              ..              ..              ..
    S               S               S               S
  /   \    ↔    //   \    ↔    /   \\    ↔    //   \\
:O:   :O:      :O:   :O:      :O:   :O:      :O:   :O:
''    ''               ''      ''

    1               2               3               4
```

In structure **1**, the formal charges are +2 for S, and –1 for both O atoms. In structures **2** and **3**, the formal charges are +1 for S, and –1 for the oxygen atom with a single bond to S. The low formal charges of S make structures **2** and **3** more stable or more important contributors. The formal charges for all atoms are zero for structure 4, given earlier. This is also a possible resonance structure, although the octet rule is not satisfied. Combining resonance structures **2** and **3** results in the best overall description of the bonding for the molecule.

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Example: Draw the resonance structures of nitrate (NO_3^-).

```
      –1            . .  –1          . .  –1
   :O:              :O:              :O:
    ||               |                |
    N       ↔        N       ↔        N
   /  \            //  \            /  \\
:O:    :O:      :O:    :O:      :O:    :O:
' '     ' '              ' '      ' '
```

The three resonance structures are shown in the figure. Note that only the locations of double and single bonds change here. What are the formal charges for the N atoms? What are the formal charges for the oxygen atoms that are single bonded and double bonded to N respectively? Please *work* these numbers out.

- Formal charges: N, +1; =O, 0; –O, –1
- The most stable structure has the lowest formal charge values (minimum separation of charge).
- In a stable structure, adjacent atoms should have formal charges of opposite signs.

The more stable the structure, the more it contributes to the resonance structure of the molecule or ion. All three structures above are the same, only the double bond rotates.

Exceptions to the octet rule

We can write Lewis dot structures that satisfy the octet rule for many molecules consisting of main–group elements, but the octet rule may not be satisfied for a number of compounds. For example, the dot structures for NO, NO_2, BF_3 ($AlCl_3$), and $BeCl_2$ do not satisfy the octet rule.

```
·N:::O:                    ..
                     .    :F:
                    N      |        . .      . .
compare            //  \   B      :Cl : Be : Cl:
with             :O:   :O:  /  \    ' '      ' '
                        ' '  :F:  :F:
:C:::O:                      ' '  ' '
```

The above are structures for the gas molecules. The solids of $AlCl_3$ and $BeCL_2$ are polymeric with bridged chlorides.

```
 . .        . .
:Cl:  :Cl:  :Cl:            :Cl:  :Cl:  :Cl:
    \  /  \  /     Polymeric /   \  /  \  /   \
    Al    Al         solid      Be    Be
    /  \  /  \     structures \   /  \  /  \   /
:Cl:  :Cl:  :Cl:            :Cl:  :Cl:  :Cl:
 . .        . .
```

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Aluminum chloride, $AlCl_3$, is a white, crystalline solid, and an ionic compound. However, it has a low melting point of 465 K (192°C), and the liquid consists of *dimers*, Al_2Cl_6, whose structure is shown above. It vaporizes as *dimers*, but further heating gives a monomer that has the same structure as the BF_3.

In compounds PF_5, PCl_5, :SF_4, ::ClF_3, :::XeF_2 and :::I_3^-, the center atoms have 10 electrons instead of 8. In compounds SF_6, IOF_5, IF_5, BrF_5, XeF_4, PF_6^- etc, the center atoms have 12 electrons.

Practice Problems

1. Draw the Lewis dot structures and resonance structures for the following. Some hints are given. As you draw them, keep in mind that some of the resonance structures may not satisfy the octet rule. For example, the NO_2 molecule has an odd number of electrons, thus the octet rule cannot be satisfied for the nitrogen atom.

   a. **CO_2** :O::C::O: (plus two more dots for each of O)
   b. **NO_2** $^{\cdot}NO_2$ (bent molecule due to the odd electron)
   c. **NO_2^-** :NO_2^- (same number of electron as SO_2)
   d. **HCO_2^-** H–CO_2
   e. **O_3** (ozone, OO_2 same number of electron as SO_2)
   f. **SO_3** (consider O–SO_2, and the resonance structures)
   g. **NO_3^-** (see the example above)
   h. **CO_3^{2-}** (similar to nitrate)

2. Draw the Lewis dot structures and resonance structures for

   a. HNO_3
   b. H_2SO_4
   c. H_2CO_3
   d. $HClO_4$
   e. C_5H_5N
   f. NO_3^-
   g. SO_4^{2-}
   h. CO_3^{2-}
   i. ClO_4^-
   j. Benzene – C_6H_6
   k. Cl_2CO
   l.

   Draw these examples on paper – putting dots around the symbols is very difficult using a word processor. The octet rule should be applied to HNO_3, NO_3^-, H_2CO_3, CO_3^{2-}, C_5H_5N, C_6H_6, and Cl_2CO.