3)

**3)** **Definitions, Concepts and Scope:**

Before continuing it is important to define some terms and provide the scope of the paper. Some of the definitions are identical to other definitions, for example to SIO/IUPAC. However, there are some important differences. The following are conventional but need to be placed into a clear understanding what the thermodynamic system is.

* **Adsorbent** This is the solid material that one is investigating. A gas is placed in contact with the adsorbent and is measured as attach strongly enough to cause a weight gain for the sample or an amount of gas lost from a gas aliquot exposed to the solid material.
* **Adsorbate** The material originally a gas that is removed from the gas phase and attached to the solid material.
* **Adsorptive**, The gas phase over the combination of the adsorbent and adsorbate.

Notice that the thermodynamic system is the adsorbent plus the adsorbate and the surroundings of theoretical interest is the adsorptive. The wording allows for both the gravimetric, mass loss measurement, and the volumetric, or gas pipette, techniques. In both cases there are things happening in the surroundings that effect the measurement (this includes things outside the vacuum system.)

A firm definition of chemisorption versus physical adsorption or physisorption[[1]](#footnote-1) needs to be clear. There seems to be some confusion in the literature. The traditional definition is that chemisorption involves chemical bonds and physisorption involves intermolecular attractions. So, what are the implications and the confusion? It is best to make it clear based on electron structure. The following is used here:

* In physical adsorption or physisorption the configuration of the electrons in the adsorbing molecule retains their topology
* In chemisorption the formation of the chemical bond changes the topology of the electrons, for example, by forming a chemical bond or by ionization.

Often chemisorption and physisorption are characterized by the energy of the bond. This is an error, since physisorption has been observed with an energy between 28 kJ mol-1 and nearly 0; whereas, chemical bonds have a wide range of energies of formation from 100s kJ mol-1 to negative energies. Thus, physisorption energies lie in the middle of the possible chemical bonding energies, so this definition is ambiguous.

This definition makes it clear by definition that there is no change in the number or identity of components upon detectable physisorption. Thus, the Gibbs’ phase rule, which applies to both the adsorbate and the adsorbent, includes the surface of the adsorbent-adsorbate, *A*γ (or θ**E**,) in addition to the normally specified, *PV* and *ST.* Thus, one degree of freedom must be added to the rule for surfaces. Without this additional term, physisorption would be impossible. This also implies that there is a phase change that must occur on the surface for the liquid phase to be the possible.

The scope of this paper is restricted to the following conditions, and features:

* The temperature of adsorption is between the critical point of the adsorptive and its melting point.
* The adsorbent condition will first be assumed to be homogeneous and non-porous to obtain the basic equations.
* The adsorptive is a single component.

Later the following are addressed with the advantages of the Modern Hypotheses.

* The addition of heterogeneity, microporosity, mesoporosity and other features will be defined according to their isotherm properties and not according to SIO/IUPAC.
* An example of how to calculate the binary isotherm from the unitary isotherms[[2]](#footnote-2).

The terms microporosity and mesoporosity needs clear definition. For the quantum mechanical (QM) definition, there are intermediate porosities. This is not really a problem since the QM looks at individual features rather than a “Type” of isotherm.

* Physisorption is a three-degree of freedom system, *P*, *T* and *n*ads (moles of adsorbate)
* An isotherm is an experiment at constant temperature and the amount of adsorbate and the pressure of the adsorptive are measure in a two-degree of freedom experiment.

The next section provides enough evidence that there is a need for reexamining the hypotheses about physisorption, especially the BET which is one of the “Henry’s law’ isotherms. This is followed a discussion of the most important experimental errors that are very common and can destroy the accuracy and meaning of an isotherm.

1. The word “physisorption” and “physical adsorption” mean the same thing. “physisorption” is a more modern word, just as is “chemisorption.” [↑](#footnote-ref-1)
2. This latter item could save a lot of engineering experimentation. It also opens the possibility of more accuracy in calculating flowing systems, for which the Langmuir isotherm is used today. [↑](#footnote-ref-2)