**4) Experimental precautions**

It is extremely important to have good equipment and good technique when measuring the isotherm. Do not overlook this section. Measurement of the isotherm is the primary measurement made for physical adsorption and the easiest. The problem is it may be too easy and the pitfalls are ignored. Furthermore, there are two primary methods to measure the isotherm, the gravimetric and the volumetric. A well-designed gravimetric system is less prone to error, but it is generally more expensive. The volumetric system on the other hand is usually less expensive but highly prone to error, some of which are built-in. The first two common errors essentially yields useless data, although there may be ways to recover from disaster. The other errors can have similar disastrous results.

**Error 1** is using a system that does not pump down to the high vacuum, HV. This has been thought of as unnecessary since the original statement of the BET discarded all data below a *P*/*P*vap = 0.01. This is perhaps because it started to deviate from the expected trend since they had the capability. At any rate, one seldom see isotherm data below this limit until recently.

Why is this important? The value of the quantity *E*a around which the entire calculation centers is usually found in the HV range, and sometimes in the ultrahigh vacuum (UHV) range. It is best to have a good vacuum system to reach this level. It is also needed to determine if there is microporosity (as defined later.)

**Error 2** is poor measurement and control of the adsorbent temperature and the adsorptive gas immediately over it. This is very common error with inexpensive volumetric systems. The solution that is commonly advertised is the dual hang-down tubes. This is better but not as good as it could be. This is because

* There is usually radiative heating problems, especially for cryogenic controls even though the sides of the cooling chamber are well above the sample, there is room temperature radiation from above. Shielding with metal foils will help, but usually, unless there are bends in the tubes, there is still some heat gain.
* If the adsorbent is a dark color or black this radiative heating problem should be worse.
* It is insufficient to assume that a cryogenic bath is at a constant temperature. The temperature of the bath is dependent upon the atmospheric pressure and not taking this into account, which the dual tubes should do, the answer can be wildly wrong.

This effect is not fully researched. However, it was recognized as a problem early in the work by deBoer and Zwikker[[1]](#endnote-1). Given little guidelines, it is best to play it safe and do everything possible to control and measure correctly the value of *P*/*P*vap. The control and measurement of the temperature to 0.01K is minimal for a liquid nitrogen temperature. If your are using a liquid cryostat, you might want to select a nice steady summer day to get data and keep an eye on the barometer. As a fact, recording the room pressure during the experiment is a good idea.

**Error 3** is a problem for the low end of the HV pressures. This is the point where liquid nitrogen temperature measurements have a problem with the Knudsen effect. This is very hard to handle with a volumetrics system where the tube size cannot be arbitrary. Langmuir solved this problem by calibrating each individual hang-down tube. Characteristic of this error is the occurrence of a “double dog leg[[2]](#footnote-1)” at the lowest pressures. With the dual hang-down tubes, this means calibrating both. For the best information on this problem see the Vacuum Technology book by Roth[[3]](#endnote-2)

**Error 4** is residual gas in the sample. This is especially bad with porous samples. It appears to be a common cause of hysteresis, but not the only one. An excellent paper on this subject is the one by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[[4]](#endnote-3) (AALR.) In this publication they emphasize the importance of 1) either a high temperature outgas of the dead space gas or 2) doing the dead space calibration last or 3) repeating the isotherm measurement two times. (For proper analytical analysis, a measurement should be repeated twice and if one of the three measurements disagrees to repeat more times or find out what has gone wrong.) This publication is very important for several reason and reading it is suggested.

**Error 5** is kinetic problems. This problem varies on the sample – porous versus nonporous, tightly packed versus loosely packed and other factors. Most instruments are automatic but the researcher should not go automatic. Set the wait time at different settings and see if it makes a difference. The length of time to settle “enough” depends upon where in the isotherm the measurement is being made, so keep track of this phenomenon throughout the measurement to get an indication of the wait time versus pressure.

**Error 6** needs some work by NASA to solve this problem, which is, bed porosity. This is the porosity between particles at high pressure that might be a problem. There has not been much work on this, but it seems like a good project to take to NASA to get involved in. Related to this is the question of surface exclusion. The question here is, “does the particles touching each other exclude some of the surface from adsorption?” It has been assumed that the energy toward adsorption exceeds the energy of gravitational force and interparticle forces. This is an unsettled question.

Fluidized beds are the norm in industry to overcome this last problem.

**Gravimetric versus volumetric**

Most of the above problems are much worse with volumetric systems than they are with gravimetric systems. For example, the temperature control and measurement, Knudsen problem, UHV use, are easily handled in a gravimetric system. The big problem the gravimetric system is cost.

For gravimetric, the biggest experimental problem is ground noise especially small earth quakes. Ground noise is a problem of location and to minimize this, a firm concrete slab foundation and sturdy well anchored table can handle it. Avoid close truck noise - that is, find a nice quite side street to avoid the annoyance. Earth quakes can happen almost anywhere on earth, but it is not usually a big problem. It may require redoing an isotherm because of an isolated quake. If there is a big one enough to damage the system, it would probably damage a volumetric system as well. Nearby blasting could also be a problem, but one may be able to arrange to know when this is scheduled to occur.

1. DeBoer and Zwikker, Z. Phys.. Chem. [↑](#endnote-ref-1)
2. A relatively sharp bend in an initially straight line to the right/left followed by a sharp turn to the left/right ending up in a parallel straight section. [↑](#footnote-ref-1)
3. A. Roth, “Vacuum Technology, 3rd updated and enlarged edition” Chapter 3 (1998) North Holland – Elsevier Publishing, Amsterdam, ISBN:0 444 88010 0 [↑](#endnote-ref-2)
4. J. Silvestre-Albero, A. M. Silvestre-Albero, Philip L. Llewellyn, and Francisco Rodríguez-Reinoso, J. Phys. Chem. C, **117** (2013), 16885−16889 [↑](#endnote-ref-3)