Pressure calibrations for cell filling

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Purpose:

To describe procedures useful in filling various gas sample cells with pre-determined amounts (pressures) of gases.

Two cases: (1) cell is sealed off; (2) cell has a valve.

I. INTRODUCTION

For many of the NMR experiments performed in our lab group, a sample cell needs to be filled with a certain mixture of gases. Typically, the gases used are some combination of one or more spin-1/2 noble gases (i.e., ^{3}He and ^{129}Xe), nitrogen, and oxygen (in cells intended for thermally-polarized NMR experiments). Naturally, the proportions of each gas are determined by the goals and requirements of the experiment.

Generally speaking, there are two types of cells we are concerned with: "valved" cells and "sealed" cells. Valved cells include a valve which allows one to repeatedly fill and empty the cell; in contrast, a sealed (glass) cell is permanently sealed (with a torch) after being filled with gases. Practically speaking, valved cells are easier to calibrate and fill, but may not have the longevity of a sealed cell – though valved cells are not intrinsically inferior to sealed cells, human error (e.g., accidentally opening the valve) has led to occasion problems. Again, the choice between using a valved or sealed cell depends on the experimental requirements.

The basic idea in filling a cell involves loading a pre-determined amount of gas into a "reservoir" volume on the pump station (this is often referred to as the *pump station manifold*); a high pressure (0–1000 Torr or higher) Baratron$^\circledR$ gauge allows one to determine the load pressure. During this step, the cell is isolated from the reservoir, usually by a valve either on the cell itself or on the pump station manifold. When the desired load pressure is reached, the valve is opened and the gas is allowed to fill the cell.

The majority of "cell fillings" for the noble gas NMR work uses ^{129}Xe; this gas is particularly easy to work with because it has a melting temperature of $\sim$ 161 K and a boiling temperature of $\sim$ 166 K. Using liquid nitrogen, one can cool a sample cell to $\sim$ 77 K, and thus easily condense xenon into the cell. Practically, this means that all the gas initially loaded into the reservoir volume will end up in the cell. Other gases, such as nitrogen or oxygen, are added afterwards, assuming the sample cell is kept cold enough for the xenon to stay frozen. Care must be taken to account for residual vapor pressures of non-condensing gases which fill both the cell and the reservoir volume. Obviously, once the cell is either sealed or valved off, gas left in the reservoir does not contribute to the amount found in the cell.

Before one is ready to fill a cell with a desired amount of gas, one must first determine some relative volumes between the reservoir and cell. Depending on the type of cell used, different methods apply. Note that the procedures described in this paper for *loading* the gases in the cell are valid only for a binary gas mixture where one of the gases can be condensed (i.e., frozen) in a cell cooled to liquid nitrogen temperature; binary (or higher) gas mixtures, where the gases do not condense at a convenient temperature, are not considered here. Nonetheless, the pressure calibrations to determine relevant volume ratios discussed below may also be used in these latter cases.

II. CALIBRATIONS FOR A CELL TO BE SEALED

A. Loading xenon

Let P_{Xe} to be the final partial pressure of xenon we want in the cell, and let $P_{Xe\ load}$ be the xenon gas pressure we must first place into the manifold prior to the freeze-transfer process described above.

Let $V_{manifold}$ represent the volume of the pump station manifold up to some valve to the outside; let V_{tube} be the volume that exists between the valve and the limit of the cell to be sealed off; and finally, let V_{cell} be the volume of the cell to be sealed (see Fig. [1]). We assume that the valve (on the pump station) between the manifold and the cell is closed off while filling $V_{manifold}$ with $P_{Xe\ load}$; the volume $V_{cell} + V_{tube}$ will be under vacuum.

Since all the xenon loaded in $V_{manifold}$ will freeze into V_{cell}, we can use the ideal gas law, $PV = nRT$, and write:

$$P_{Xe}V_{cell} = P_{Xe\ load}V_{manifold} \qquad (1)$$

at STP. Therefore, we need to determine the value for $P_{Xe\ load}$ assuming we have a P_{Xe} in mind. What is left to determine is the ratio $V_{cell}/V_{manifold}$.
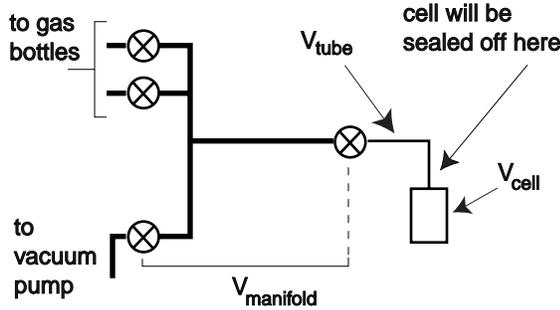
To do this, we perform the following steps:

FIG. 1. Schematic of *sealed* cell and pump station manifold with relevant volumes labeled

step 1   when the system is at vacuum, close off the valve from the manifold to the cell, and fill only $V_{manifold}$ with a test gas (e.g., nitrogen). Record the pressure as $\mathbf{P_1}$.

step 2   open the manifold valve to allow the test gas to expand into the cell (V_{cell}) and interstitial tubing (V_{tube}). Record the reduced pressure as $\mathbf{P_2}$.

step 3   now place the cell volume into a bath of liquid nitrogen, so that the cell volume V_{cell} is at 77K, while the remaining volumes ($V_{manifold} + V_{tube}$) are at room temperature ($\sim$297K). Record the overall pressure as $\mathbf{P_4}$.

note: *there will be a slight amount of error in this last measurement because (i) the temperature of the latter volumes will not be uniformly at room temperature, with parts of V_{tube} close to 77K, and (ii) depending on the test gas used, there may be some liquification of the test gas at 77K, resulting in an inaccurate reading for P_4. Calculations below assume that P_4 is measured with all the test gas in the gaseous phase.*

From these pressure measurements, the following are true:

$$P_1 \left(\frac{V_{manifold}}{T_{room}} \right) = P_2 \left(\frac{V_{manifold} + V_{tube} + V_{cell}}{T_{room}} \right) \quad (2)$$

$$= P_4 \left(\frac{V_{manifold} + V_{tube}}{T_{room}} + \frac{V_{cell}}{T_{liquid\ N_2}} \right) \quad (3)$$

We can simplify Eqs. [2, 3] by multiplying by T_{room}, and letting $\alpha = T_{room}/T_{liquid\ N_2}$.

$$P_1 V_{manifold} = P_2 \left(V_{manifold} + V_{tube} + V_{cell} \right) \quad (4)$$

$$= P_4 \left(V_{manifold} + V_{tube} + \alpha V_{cell} \right) \quad (5)$$

Solving for V_{tube} and eliminating it from Eqs. [4, 5], we have:

$$V_{manifold} \left(\frac{P_1}{P_2} - 1 \right) - V_{cell} = V_{manifold} \left(\frac{P_1}{P_4} - 1 \right) - \alpha V_{cell} \quad (6)$$

dividing both sides by $V_{manifold}$, we get

$$\left(\frac{P_1}{P_2} - 1 \right) - \frac{V_{cell}}{V_{manifold}} = \left(\frac{P_1}{P_4} - 1 \right) - \alpha \frac{V_{cell}}{V_{manifold}}$$

$$\frac{V_{cell}}{V_{manifold}} = \frac{\left[\left(\frac{P_1}{P_2} - 1 \right) - \left(\frac{P_1}{P_4} - 1 \right) \right]}{(1 - \alpha)} \quad (7)$$

This leaves us with the final result:

$$\frac{V_{cell}}{V_{manifold}} = \frac{P_1}{1 - \alpha} \left(\frac{1}{P_2} - \frac{1}{P_4} \right) \quad (8)$$

Going back to Eq. [1], we know that for a desired partial pressure of xenon inside a sealed cell, we need to fill the manifold (excluding V_{tube} and V_{cell}) to a pressure given by the following relationship:

$$P_{Xe\ load} = P_{Xe} \left(\frac{V_{cell}}{V_{manifold}} \right)$$

$$= P_{Xe} \left(\frac{P_1}{1 - \frac{T_{room}}{T_{liquid\ N_2}}} \right) \left(\frac{1}{P_2} - \frac{1}{P_4} \right)$$

$$= P_{Xe} \left[\frac{P_1}{P_2 P_4} \left(P_4 - P_2 \right) \right] \left(\frac{T_{liquid\ N_2}}{T_{liquid\ N_2} - T_{room}} \right) \quad (9)$$

B. Loading other gases (e.g., oxygen or nitrogen)

Loading the cell with oxygen or nitrogen presents a slightly different problem in that these gases do not all freeze into the cell (when the cell is at liquid nitrogen temperatures) as does xenon. Consequently, there will be some residual pressure of gas left in the cell and manifold, and one needs to factor this in when determining how much to initially load the manifold before filling the cell.

The problem is greatly simplified if the amount of gas to be placed into the cell is "relatively" small – by this, we mean that the gas pressure *at liquid nitrogen temperature* is less than the liquid vapor pressure (also at liquid nitrogen temperature). When this is the case, none of the gas will condense in the cell, and one can just treat the problem as a case where an isobaric ideal gas is at two different temperatures. For example, assume V_{cell} is at $T_{liquid\ N_2}$ (and will remain so until the cell is pulled off), while the rest of the manifold (which includes the pressure gauge) is at T_{room}. If P_{cell} is the final partial pressure of gas we want in the cell, then we will want to fill *both* the manifold and cell such that the pressure gauge reads P_{load}:

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$$P_{load} = P_{cell} \frac{T_{liquid\ N_2}}{T_{room}} \qquad (10)$$

Practically, one could just load $V_{manifold}$ with P_{load}, and then open the valve to the cell; the pressure will drop as one expects, and one reaches the desired P_{load} by slowly adding more gas into the manifold+cell volume from the gas bottle itself (or some other reservoir of gas).

If, however, we are loading so much gas into the cell that we do expect some amount of condensation to occur, the problem is slightly more complicated. One way to approach this this problem is by "counting" molecules or atoms, *i.e.*, looking at the values for n in the ideal gas law. Assume the fill procedure is as follows:

step 1 with the valve to the cell closed, fill the manifold with some pressure **P_{load}**. If appropriate, the cell will be in a liquid nitrogen bath (for instance, if xenon was first loaded into the cell).

step 2 open the valve, letting the gas in the manifold expand (with some condensation) into the cell. As one would expect, the pressure drops significantly; the pressure **P_{vapor}** should level off at the vapor pressure of the gas at liquid nitrogen temperature.

step 3 seal the cell and pull it off; the leftover pressure in the manifold and glass tube should be close to **P_{vapor}**.

In the end, the total number of gas molecules must be conserved; so the initial $n_{manifold}$ must be equal to the sum of the final n's of the leftover in the manifold and what was loaded into the cell, *i.e.* n_{cell} and $n_{left\ over}$. Thus we have the following relationships:

$$\frac{P_{load}V_{manifold}}{(RT_{room})} = n_{manifold}$$
$$= n_{left\ over} + n_{cell}$$
$$= \frac{P_{vapor}(V_{manifold} + V_{tube})}{RT_{room}} + \frac{P_{cell}V_{cell}}{RT_{room}} \qquad (11)$$

where P_{cell} is the (desired) final partial pressure of gas in the cell.

One can look up the vapor pressure of various gases as a function of temperature in various tables or graphs (for example, see Fig. [2], taken from reference [1]).

To determine how much gas should be loaded initially into the manifold, we have the following relationship after simplifying Eq. [11]:

$$P_{load} = P_{vapor}\left(1 + \frac{V_{tube}}{V_{manifold}}\right) + P_{cell}\left(\frac{V_{cell}}{V_{manifold}}\right) \qquad (12)$$

The pressure calibrations already described in Section II A provide enough information for us to determine
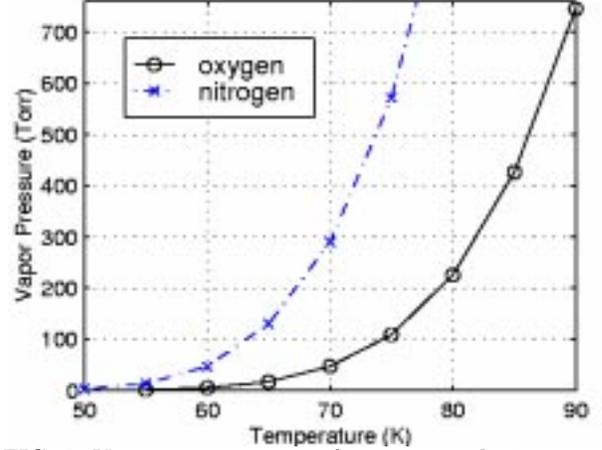

FIG. 2. Vapor pressure curves for oxygen and nitrogen as a function of temperature (near liquid nitrogen temperatures).

the needed volume ratios. From Eq. [7], we have an expression for $V_{cell}/V_{manifold}$; now we need to determine the ratio of $V_{tube}/V_{manifold}$. Using Eq. [4]. we can write:

$$\frac{V_{tube}}{V_{manifold}} = \frac{P_1}{P_2} - \frac{V_{cell}}{V_{manifold}} - 1 \qquad (13)$$

Together with Eq. [12], the final result is:

$$P_{load} = P_{vapor}\left(1 + \frac{V_{tube}}{V_{manifold}}\right) + P_{cell}\left(\frac{V_{cell}}{V_{manifold}}\right)$$
$$= P_{vapor}\left(1 + \frac{P_1}{P_2} - \frac{V_{cell}}{V_{manifold}} - 1\right) +$$
$$P_{cell}\left(\frac{V_{cell}}{V_{manifold}}\right)$$
$$= \frac{P_{vapor}P_1}{P_2} + \frac{V_{cell}}{V_{manifold}}(P_{cell} - P_{vapor})$$
$$= \frac{P_{vapor}P_1}{P_2} + \left[\frac{P_1}{P_2P_4}(P_4 - P_2)\right] \times$$
$$\left(\frac{T_{liquid\ N_2}}{T_{liquid\ N_2} - T_{room}}\right)(P_{cell} - P_{vapor}) \qquad (14)$$

Conversely, if the remaining pressure P_{left} in the manifold is not exactly P_{vapor}, one can determine the final gas partial pressure in the cell by solving for P_{cell} in Eq. [14] and replacing P_{vapor} with P_{left}:

$$P_{cell} = \left(P_{load} - \frac{P_{left}P_1}{P_2}\right)\left[\frac{P_2P_4}{P_1(P_4 - P_2)}\right] \times$$
$$\left(\frac{T_{liquid\ N_2} - T_{room}}{T_{liquid\ N_2}}\right) + P_{left} \qquad (15)$$
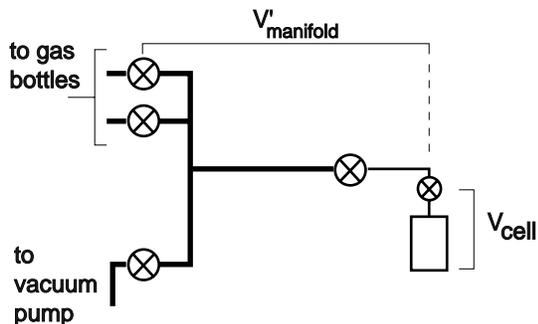
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FIG. 3. Schematic of a *valved* cell and pump station manifold with relevant volumes labeled

III. CALIBRATIONS FOR A VALVED CELL

In cases where the cell itself has a valve, we can simplify the pressure calibration procedure and consider only 2 relevant volumes: $V'_{manifold}$, which represents the volume of the pump station manifold plus any portion of the cell "outside" of the valved portion, and V_{cell}, the volume of the cell which is closed off by the cell valve (see Fig. [3]).

A. Loading xenon

As before, the key ratio that needs to be determined is $V_{cell}/V'_{manifold}$. This is accomplished with a procedure similar to the one described in Section II A:

step 1   when the system is at vacuum, close off the valve on the cell, *leaving the manifold valve to the cell open*, and fill only $V'_{manifold}$ with a test gas (e.g., nitrogen). Record the pressure as **P_1**.

step 2   open the *cell* valve to allow the test gas to expand into the volume V_{cell}. Record the reduced pressure as **P_2**.

The additional pressure measurement with the cell in a bath of liquid nitrogen is unnecessary since the cell valve allows us to disregard the volume V_{tube} (which one must factor out with a sealed cell).

It is a simple exercise to show that the required load pressure for a gas such as xenon (which can all be condensed into a cell at ~ 77 K) is given by

$$P_{Xe\ load} = P_{Xe}\left(\frac{P_1}{P_2} - 1\right) \qquad (16)$$

This is analogous to Eq. [9].

B. Loading other gases (e.g., oxygen or nitrogen) into a valved cell

The same cell filling steps as described in Section II B are applied to a valved cell, the obvious difference being that the cell does not need to be "sealed." Rather, one can simply close the cell valve when the required amount of gas has entered the cell. This flexibility allows one to leave a residual gas pressure P_{left} in the manifold that is *higher* than what is placed into the cell.

As before, let P_{cell} be the partial pressure of gas one wants to have in the cell. Following the same reasoning that led to Eq. [12], one obtains:

$$P_{load} = P_{left} + P_{cell}\left(\frac{V_{cell}}{V'_{manifold}}\right)$$
$$= P_{left} + P_{cell}\left(\frac{P_1}{P_2} - 1\right) \qquad (17)$$

In practice, one can first calculate the quantity $P_{cell}\left(\frac{P_1}{P_2} - 1\right)$, and arbitrarily set $P_{left} \geq P_{vapor}$ in order to find P_{load}; this pressure of gas is then placed into $V'_{manifold}$. Finally, the cell valve is opened, allowing the gas to fill the cell volume V_{cell}. When the pressure reaches P_{left} in the manifold, the cell valve is closed.

COMMON PRESSURE UNITS

Amagat	(not a pressure unit, but frequently used); the density of an ideal gas at STP (2.689×10^{19} cm^{-3}).
Pascal (Pa)	pressure unit equal to one newton per square meter.
Standard atmosphere (atm)	101,325 Pa.
Torr (T, or mm Hg, 0°C)	133.32 Pa, or 1/760 of an atmosphere.
Bar	100,000 Pa.
Pounds per sq. in. (psi)	6894.8 Pa; 14.7 psi = 1 atm.

SOME REFERENCE TEMPERATURES

gas	T_{melt} (K)	T_{boil} (K)
nitrogen	63.15	77.36
oxygen	54.36	90.20
xenon	161.25	165.05

[1] D.R. Linde, ed., *CRC Handbook of Chemistry and Physics, 75th ed.*, Chemical Rubber Publishing Company, Boca Raton (1994).