Standard Operating Procedure

Task: Stoichiometric Gas Additions
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Date: 05/19/2021
Revision Date (Author): <<Date (Author)>>

Training Requirements:

- ✓ Department of Chemistry Safety Training
- ✓ Saouma Group Safety Training
- ✓ Fully read and understand this SOP
- ✓ Checked out to use gas cylinders (see SOP)
- ✓ Checked out on Schlenk line (see SOP)
- ✓ Checked out on using cryogenics (see SOP)
- ✓ If pertinent, checked out to use CO (see SOP)

Potential Hazards:

- High pressure gases
- Stripping (tank or regulator)
- Backfilling liquid nitrogen-cooled glassware will condense CO_2 which can result in an explosion.

Special PPE Requirements:

- Labcoat
- safety glasses
- nitrile gloves
- ventilation hood

Materials Needed:

- Hoses, adapters, etc.
- H grease
- Rubber bands
- Torch or heat gun
- Copper wire and pliers
- IN2
- Dewars
- Water baths
- Calibrated bulb (Placed under the UV spectrophotometer in a Cabinet Drawer with label Gas addition tubes)
    - 2 x 4 mL (approximate)
    - 3 x 250 mL (approximate)

Background:

This SOP is for adding known amounts of a gas to a reaction vessel and makes use of the ideal gas law (equation 1).

(1) $PV = nRT$

Knowledge of the temperature (T), pressure (P), and volume (V) allows for the number of moles (n) to be determined. If pressure is measured in mmHg (or Torr), and volume in mL, then:

$$R = 8.31446 \frac{m^3 \cdot Pa}{K \cdot mol} \times \frac{1cm^3}{10^{-6}m^3} \times \frac{1mmHg}{133.32Pa} = 6.24 \times 10^4 \frac{cm^3 \cdot mmHg}{K \cdot mol}$$

Note, T is in Kelvin, so 20 ºC = 293 K.

Thus, by adding a known pressure of gas (measured by noting the change in Hg levels in the monometer) to a calibrated bulb of known volume at room temperature, you are adding a known amount of gas (in terms of moles). Opening the bulb to your evacuated reaction flask allows you to hence add a known amount of gas. Note, if you do not condense the gas, then the bulb becomes part of your reaction head-space (see table below).

Gas	Boiling Point (ºC)	Condensable with lN_2 (-195 ºC)?
CO_2	-78	yes
CO	-191.5	no
N_2	-195.8	no
H_2	-252.9	no

SOP

1. Leak test your line. To do this, place the entire system under static vacuum, and close the gas/vacuum cross-over valve (the valve that connects the two). Note overnight if any of the monometers dropped mercury. Note, the best way to do this is to re-open the system to dynamic vacuum and look for changes in the Hg level, as atmopspheric pressure may have changed. If there are any changes, DO NOT PROCEED. Repeat the leak test, starting by putting the system to static vacuum and closing the valves closest to the monometers to see if the leak is around the monometers (where it usually is). Once you find the leak, adjust the line carefully, this will require many leak test iterations.

2. Make sure your calibrated bulb is calibrated; if you are unsure, weight the bulb (with two Teflon stopcocks, carefully add water to the bulb so there is no air bubbles when the stopcocks are closed (and no extra water on the outside), and re-weigh. Place in oven to dry when done.

3. Place your entire Schlenk line under dynamic vacuum, including the gas line (traps up and filled with lN_2). Connect the gas/vacuum lines either through the cross-over valve, or by opening the two valves going to one port (Figure 1). Make sure **A** and **D** are open.

Figure 1

4. Connect the calibrated bulb and your reaction to the Schlenk line and evacuate up to the Teflon stopcock that is connecting the calibrated bulb to your reaction by opening valve **F**. At this point, the calibrate bulb and the space above your reaction is open to the vacuum manifold (valves **B** and **C** are also open).
    a. DO NOT clamp anything in place- the vacuum should hold it in place so add things stepwise.
    b. Use H-grease to connect all ground-glass joints (two thin strips then rotate under heat) then rubber-band the joints together (do not use Keck clips).

5. At this point everything is under dynamic vacuum except for your reaction which is under atmosphere. Using the torch (or heat gun), heat the entire line under dynamic vacuum, down to the Teflon stopcock of your reaction. Be very careful if using a heat gun as to not knock anything over. You should see water condense at the glass; once you see this move on to another part of the line.

6. Close the cross-over valve (Figure 1, valve **D**), and bubble your gas through the gas-line. For this you will open the gas manifold to the hose that is connected to your tank, then you will open the regulator valve and the tank – slowly (Figure 1). This will flush it out, keep it bubbling throughout the rest of the steps. ***NEVER have a regulator exposed to dynamic vacuum.***

a. If using $^{13}CO_2$: You will condense the CO_2 directly from the storage bulb; once you attach the bulb, evacuate everything above/flame dry as described below. If you want to "flush" the line, do so by bubbling N_2 and evacuating 3 times. Be sure to condense all of the CO_2, either to your vessel or the storage bulb; ***talk to Caroline before performing.***

b. If using another labelled gas from a lecture bottle: ***Talk to Caroline first, as there is limited volume and you need to devise a game-plan to not waste any of the gas.***

7. Freeze-pump-thaw your reaction vessel 3 times. ***The lN_2 should be only to the solvent level and well-below the Teflon stopcock to avoid condensation of oxygen.***

8. After the third FPT cycle, your vessel is now under vacuum. Close your reaction vessel to the line, then close the bottom of the calibrated bulb (**C**), so that only the bulb and above is exposed to the dynamic vacuum (**B** is open). If you are condensing the gas it may be convenient to keep your vessel in lN_2.

9. Close the valve between the vacuum manifold and the traps, so that now the system is under static vacuum (Figure 1 valve **E**).

10. At this point, you can add the gas to the calibrated bulb.

a. Note your starting pressure on the vacuum manifold monometer, and using a sticky-note, indicate the pressure drop that is desired.

b. Slowly open the cross-over valve (Figure 1, valve **D**). This should be done slow enough such that the gas-line bubbler continues to bubble or just stops to bubble. Once you reach the desired level, close the cross-over valve **D**.

c. If you over-shot, with the cross-over valve closed, slowly open the vacuum manifold to the vacuum pump (valve **E**) until you get the desired level. If you overshoot here, repeat b.

During this time, you should hear no hissing of the lN2 as you are not adding any gas to the reaction.

11. Close the top of the calibrated bulb (**B**), such that the bulb is now fully closed, and contains the desired pressure of gas (Figure 1).

12. Now open the bottom of the calibrated bulb (**C**), then your reaction. Follow steps 13 (condensing) or 14 (not condensing).

13. If you are condensing the gas:

a. You should hear hissing; one the hissing stops, wait ~ 1 minute then close your reaction flask then the bottom of the calibrated bulb (**C**).

b. At this point, evacuate the vacuum line (by opening **E**), then place it under static vacuum (close **E**).

c. Open the top of the calibrated bulb (**B**) to the static vacuum. If all of the gas condensed, then there should be no change in the Hg level.

d. Now open the bottom of the calibrated bulb (**C**) to the static vacuum. If there is no change in the pressure, then you know all the gas has condensed and your reaction vessel is closed.

e. Close the top and bottom of the calibrated bulb (**B** and **C**) and place the vacuum line under dynamic vacuum by opening **E**. This restores the Schlenk line to "normal" working conditions.

f. Remove your reaction flask; this can be done by carefully detaching (if a jyoung adapter), or by opening the calibrated bulb to the gas manifold (**A**) and opening each valve of the calibrated bulb one at a time, starting from the top (**B** then **C**). This will relieve the vacuum from the calibrated bulb and the space between the bulb and your reaction flask.

g. Close the gas tank, regulator, and port that was used to add the gas to the line.

h. Disconnect the hose.

i. Evacuate the gas manifold by opening the crossover valve **D**, then close the cross-over valve **D**. This is so that the gas manifold stays under static vacuum (and hence can be leak tested until the next time this is done).

j. When done, close the vacuum line from the traps and drop the traps, keeping the vacuum manifold also under static vacuum (**E** is closed).

14. If you are not condensing the gas:

a. The calibrated bulb has become part of your headspace; do not disconnect it until you are done with your reaction. This likely will entail pumping down the reaction, then closing your reaction and backfilling with N_2 to disconnect it from the calibrated bulb.

b. With the top of the calibrated bulb closed to the manifold, place the vacuum line under dynamic vacuum and follow steps **g-j** of step **13**.

References and Related SOPs:

- CO SOP
- Gas cylinders
- Schlenk line
- Cryogenics SOP