SOP: PARR HYDROGENATION APPARATUS

HYDROGENATION – is a chemical **reaction** between molecular hydrogen (H_2) and another compound, usually in the presence of a catalyst such as Nickel, Palladium, Platinum or Rhodium. The process is commonly employed to reduce or saturate organic compounds.

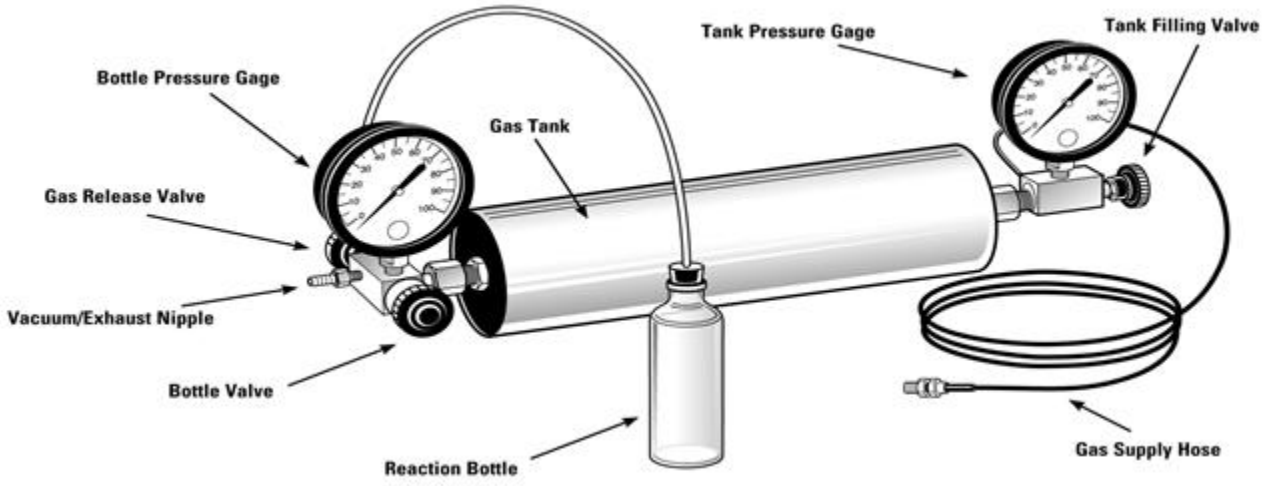
This process usually requires the addition of a solid [or soluble] catalyst to the reaction flask containing a dissolved reactant. The reaction flask has to be evacuated of oxygen by using nitrogen or argon gas & evacuation and sealing the mixture off from air contact. Hydrogen gas is then supplied from a H_2-filled cylinder or via a hydrogen generator. The resulting three phase mixture is agitated to promote mixing. Hydrogen uptake can be monitored, to follow the progress of a hydrogenation. This is achieved by readout of a pressure gauge.

Samples to be reduced in a Parr hydrogenator are placed in a reaction bottle with a catalyst and clamped securely in the shaking mechanism. A connection is made from the reaction bottle to a multiple valve and all air is removed by evacuation, then the reaction bottle is flushed with hydrogen. The bottle is then shaken vigorously to initiate the reaction. Heating or cooling can be applied, if necessary. After the reaction reaches the desired point the shaker is stopped, the bottle vented and the product and catalyst are recovered.

Users must be constantly aware of the serious consequences that can result from mistakes as: breaks or leaks releasing hydrogen, opening the wrong valve, mixing combustible vapours with air or oxidizing gases, adding reactants too fast or failing to observe and prevent sudden increases in temperature or pressure.

Only persons that have been trained, supervised by a competent person for their first 2 times using the Parr hydrogenation apparatus and signed off on it may use the hydrogenator!

The individual steps in this operating procedure are listed below. These can be varied to suit each individual application.



1. **Check/ make sure that the hydrogen cylinder is connected properly** and all connections from hydrogen cylinder & to vacuum pump are properly clamped and closed and sealed.

2. **Set up the reaction in the reaction bottle in the fume hood**:
   a. Dissolve your starting material in an appropriate solvent [ideally non-flammable], add to the reaction bottle, and flush the reaction bottle with nitrogen or argon gas, stop gas flow and close the bottle with a stopper [keep O_2 out].
   b. Weigh out the catalyst in a glass flask, add a small amount of solvent carefully with a pipette to avoid possible vapour ignition by the dry catalyst.
      If you use a solvent that can ignite – this is to be done carefully!
   c. Use the pipette to mix catalyst with the solvent used to form a slurry.
   d. Use the pipette to transfer the slurry into the reaction bottle.
   e. Wash down any catalyst stuck to the flask walls. All of the catalyst should be submerged at this point.
   f. The total volume of solution should not exceed ½ of the capacity of the bottle.
   g. Close bottle with rubber stopper.

3. **Bring reaction bottle to Parr hydrogenator**:
   a. Attach the Parr stopper/screw cap with connecting tube to top of bottle
   b. Slide the bottle into the guard screen
   c. Set the assembly in the bottle holder
   d. Tighten the knurled clamping nuts [only by hand, no tools!] until airtight

4. **Set up of the reaction**
   a. Attach a vacuum hose to the vacuum nipple on the valve, open the connection
   b. Evacuate until the solvent "starts to boil" – indicating residual air which is dissolved in the solvent is removed
   c. Evacuate to a negative pressure sufficient to remove most of the air.
   d. Close the valve connecting the pump to the hydrogenation bottle
   e. Open the connection between the hydrogen cylinder and the hydrogenator reservoir and fill to the desired pressure of hydrogen.
   f. Open the hydrogen gas release valve and fill reaction bottle with hydrogen
   g. Close the connection to the hydrogen reservoir
   h. Repeat the evacuation and fill again with hydrogen [see above].
   i. Switch off vacuum pump
   j. Close the valve connecting the hydrogen reservoir of the hydrogenator and the hydrogen cylinder & leave it closed throughout the run.
   k. Read the bottle pressure gauge after equilibrium has been established – leave for another 2 minutes without shaking [rapid loss of pressure indicates a leak!]
   l. Re-adjust the hydrogen pressure to the desired level if needed
   m. Start the shaker and follow the progress of the reaction by observing the bottle pressure gauge

5. If the reaction proceeds too rapidly it can usually be interrupted by stopping the shaker.
6. If complete hydrogenation is desired, continue shaking until there is no further pressure drop.
7. For partial or quantitative hydrogenation, continue shaking until the pressure drops to a calculated value as determined by prior standardization runs.

8. **At the end of the run**
   a. Stop the shaker.
   b. Close the bottle valve to the hydrogen reservoir and allow the catalyst to settle.
   c. Any residual pressure in the bottle and connecting tube has to be discharged ***[careful!]*** by opening the gas release valve before opening/disconnecting the hydrogenation bottle.
   d. Open the bottle clamp and remove the bottle.
   e. Make sure the hydrogen cylinder is closed off.
   f. CLEAN UP THE PARR SHAKER FOR THE NEXT USER!!!.

MAINTENANCE

Periodic cleaning may be performed on the exterior surfaces of the instrument with a lightly dampened cloth containing mild soap solution. All power and the hydrogen cylinder should be disconnected when cleaning the instrument. There are no user serviceable parts inside the product other than what is specifically called out and discussed in the manual for the Parr shaker.

* To check for leaks, use soapy water and squirt it on valves
* It should not be necessary to use extreme force to close any of the valves on this apparatus. If a tight seal cannot be secured without a hard turn on the valve handle, dismantle the valve and replace the 20VB valve seat and any other worn or damaged parts.
* If the valve leaks through the packing, back the needle away from its seat and tighten the 8VB2 packing nut. If this does not stop the leak replace the 4VB3 packing rings.
* The connecting rod has oil-impregnated bronze bearings which do not require heavy lubrication. Place a drop or **two of light oil on each bearing** **about once a month**.
* Lubricate the **flywheel shaft** by placing a few drops of light oil in the oil cup at **regular intervals**.
* A light application of a **lithium grease** such as “Lubricate” on the **shaker pivots** is also advisable. The spacing of these pivots should be adjusted so that the bottle clamp swings freely without excessive friction.
* To inspect and replace the valves, unscrew the 8VB2 packing nut and remove the needle and knob. The internal parts can then be removed with a small wire hook.
* These will come out in the following sequence:
    - 6VB packing cover, two 4VB3 packing rings, 21VB lantern ring, and 20VB valve seat.
    - If the plastic valve seat will not slide out of its socket, use a 1 1/2” wood screw as a removal tool.
    - Replace these parts in the same order; insert the valve needle and tighten the 8VB2 packing nut firmly with a wrench.

Caution: Always back the valve needle away from its seat before tightening the packing nut.

HEALTH & SAFETY ISSUES

Pressure reactions with hydrogen are not unduly hazardous if the user maintains his hydrogenator in good condition and operates it with the realization that hydrogen is highly flammable and that pressures and reaction rates must be carefully controlled at all times.

1. Be careful of moving parts – especially scarfs, hair
2. Use additional protection such as an extra barricade:
   a. for a reaction that may run out of control
   b. An unexpected bottle breakage can produce a hazardous spill of toxic or flammable materials
3. **Fire & explosion hazard:**
   Hydrogenation reactions pose a significant fire hazard due to the use of flammable solvents. The presence of hydrogen gas increases the risk of explosion. Therefore:
   a. No gas burners or open flames near apparatus.
   b. Area must be well ventilated.
   c. Gas released from the apparatus to be discharged into fume hood or ventilating duct.
   d. Care must also be taken to prevent ignition by a static charge from an uninsulated object.
   e. Use **ONLY** the Parr Reaction Bottles which is made from Borosilicate Glass.
   f. Always place reaction bottle in the steel shielding jacket.
   g. Ensure the rubber stopper is properly clamped before starting.
   h. Bottle can break – take precautions to protect yourself & others from the explosion and the possible fire from catalyst & hydrogen exposure to oxygen.
4. **Spillage & Fire:**
   a. In case of small fires: use fire blanket, CO_2 or DCP/powder fire extinguisher. DO NOT use water if the reaction was run in a non-alcoholic solvent.
   b. In case of an explosion, close the sash of the fume hood. An explosion during a hydrogenation usually expels the contents of the reaction vessel, which can lead to a fire. Be prepared to extinguish a fire.
   c. If the contents do not immediately ignite, use a large volume of water or sand to quench the catalyst.
   d. All catalysts must be handled cautiously – they are highly reactive, and cause a fire when brought into contact with organic liquids or combustible vapours in the presence of oxygen because of their ability to promote rapid oxidation.
   e. Any catalyst that has been exposed to hydrogen is also potentially hazardous and may ignite spontaneously as it dries – keep used catalysts always wetted and out of contact from combustible vapours or solids. **DO NOT** add dry catalyst to a bottle containing a flammable solution or vapour.
   f. Add the catalyst first and cover it immediately with the sample in solution OR pipette solvent to catalyst.
   g. Precautions must also be taken to wash the catalyst from the thermocouple, the inlet tube and the stopper when opening the bottle.
5. Working pressures should never exceed 60 psi when using either 250 or 500 mL bottles.
6. When working in a fume hood always keep sash lowered whilst reaction is busy.
7. Place blast shield between hydrogenator and fume hood sash.
8. Personal Protection: Gloves, laboratory coat, and safety glasses (or goggles)
9. Reactions under pressure should be placed behind a blast shield.
10. Catalyst waste to be stored and discarded separately.