

### GAS FLOW IN THERMOGRAVIMETRIC EXPERIMENTS

The control of gas flow in thermogravimetric experiments is essential to the success and repeatability of the experiments. The gas flows in Thermo Cahn Thermogravimetric Experimental Stations (TherMax 200, 300, 400 and 700) are in three directions. These gas flows in the Thermo Cahn TG instruction manual are called purge gas, reaction gas, and vent gas. The instruction manual refers to one other gas, which is furnace air. Since this gas is used only to cool the furnace, it will not be discussed along with the gases that are in contact with the sample or its by-products. Furnace gas however, does influence the thermal behavior of the sample. The gas flow diagram for these gases is detailed in Figure 1. The computer Controlled solenoid valves for controlling the gas flow are shown also in this figure.

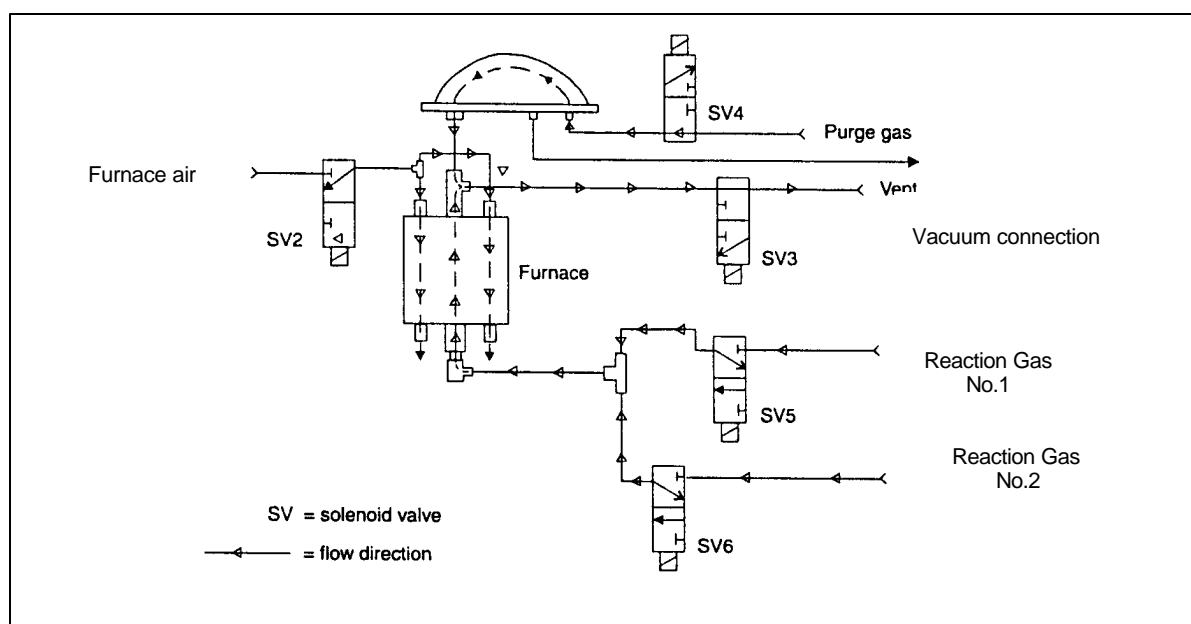


Figure 1: Gas Flow Diagram

The purge gas enters the system below the balance platform and flows through the balance and downward into the reactor tube. The purge gas exits the system through the side vent tube of the reactor tube after passing through the baffles. All Thermo Cahn TG baffles are designed to reduce thermal noise. Ports are located in the baffles to reduce upper reactor tube dead space and to provide purge gas venting at side vent level.

Vent gas is sometimes called exit gas, exhaust gas, or effluent gas.

The reaction gas after entering the system at the bottom flows upward through the reactor tube and out the side vent tube. The reaction gas and purge gas flow counter to each other and the merged gases leave the system through the side vent tube.

Up to this point, gas flow has been assumed necessary without a discussion of the merits of gas flow versus static

condition. Thermogravimetry is in most cases dynamic in that weight changes are recorded against precisely controlled heating rates that produce a continuously changing temperature. Since the sample evolves a gaseous product as the temperature increases, the concentration of the ambient static atmosphere around the sample will change. As the rate of decomposition increases, the concentration of the evolved products will increase. If the reaction is reversible, the reaction rate could decrease. Convection currents in the reactor tube, however, could cause the gas concentration around the sample to change continuously. Results would not be reproducible. Aside from concentration considerations, no gas flow produces uneven temperature gradients in the system and poor temperature repeatability. If the system is to remain inert, without gas flow back diffusion of air will occur. If the system is sealed, pressure build up will cause buoyancy changes to affect the weight readings.

Purge gas flowing downward and out the upper baffle ports reduces the furnace heat moving upward toward the balance, and reduces the chance of reaction gases reaching the balance chamber. Procedures for significantly reducing this contamination will be discussed later. Purge gas also sweeps the balance clean of air, which could possibly affect the sample. The recommended purge gas should be inert and lighter than the reaction gas. The gas of choice is helium. The flow rate should be approximately 50 to 100 ml/min. Flow rate extremes are no slower than 20 ml/min and no faster than 200 ml/min. It takes approximately one hour to purge the balance chamber.

Reaction gas can be an inert gas such as nitrogen or argon if no reaction with the sample is the objective. Explosive gases such as hydrogen and oxygen should be used with extreme caution (see Thermo Cahn Instruction Manual). Generally, a blend of low percentage of hydrogen in an inert gas is a relatively safe procedure. Air is a safe substitute for oxygen. All corrosive gases should be used with extreme care. Reaction gases should flow at 50 to 70 ml/min, but no slower than 20 ml/min and no faster than 100 ml/min. Reaction gas, as all gases, should be at low inlet pressure (approximately 5-10 psig) to prevent gas from rushing into the system. This rush will produce instability and could possibly blow the sample out of the pan. This is of particular concern when switching from vacuum to a flowing gas. Precise needle valve control is recommended in this case. If the experiment requires switching from one reaction gas to another during the experiment, there is a chance that the second gas could have increased in pressure. Pressure increase may be avoided by relief valves or relief flow.

The purge gas and reaction gases are at the proper flow rates when the two gases meet in a narrow zone above the sample without touching the sample. The helium purge gas flows from the balance chamber and leaves through the side vent tube simultaneously with the upward flowing reaction gas which flows past the sample entraining any gaseous product and leaves through the side vent tube. This condition is called Gas Flow Separation. The basis of gas flow separation is the difference in gas densities. The less dense or lighter gas is always the purge gas (or top gas). Since gas densities at the same temperature and pressure follow Avogadro's Law, lower molecular weight gases are lighter. Gas densities vary in direct proportion to the pressure and inversely in proportion to the temperature in degrees Kelvin. So, the flow rates will be influenced by furnace temperature.

The flow rates for separation can be optimized by the following procedure:

1. Place a non-absorbent specimen on the sample side (a quartz rod for example).
2. Fill the system with static air or nitrogen and tare electrically (the recorded weight should be 0.00000g).
3. Purge the system with helium by flowing through the balance chamber and out the bottom of the reactor tube through the reaction gas inlet line disconnected from the frame. The side vent tube should be momentarily capped. After all the air or nitrogen is purged, stop the flow and record the weight within 30 seconds. Reconnect the line.
4. Set the helium purge gas flow in the recommended range of 50 to 100 ml/min. Set the reaction gas flow (air or nitrogen) in the recommended range of 50 to 100 ml/min while flowing up the reactor tube through the gas inlet and out the side vent tube (now uncapped) so that we are now in the normal operational mode of purge and reactor gas flowing simultaneously. Momentarily stop the reaction gas flow and as soon as possible record the weight to 10µg. The air or nitrogen is now static. Immediately,

restart reaction gas flow. Adjust helium purge gas flow to bring the last recorded static air weight toward zero. Repeat stop and start operations for reaction gas with helium flow adjustments until readings match the original “static air zero reading”.

5. The sample is surrounded now by air and there is no helium in the vicinity of the sample.
6. The correct flow readings have been established;

<u>Typical Results</u>	<u>Condition</u>	<u>Weight</u>
	Static Air	0.000000g
	Helium	0.0034g
	Helium Purge (40ml/min) + Air Upward (50ml/min) Static State	0.0000g

In this case, the last weight reading with 40 ml/min helium and 50 ml/min air matched the static air reading. This means that the sample is entirely surrounded by air.

The above presentation is by no means a complete discussion of gas flow conditions in thermogravimetric experiments. Pressure fluctuations, downstream obstructions, and mechanical vibrations can cause variations in weight readings. Many of these factors are discussed in the following Thermo Cahn publications:

Paper 1192 “Conditions for Optimum Sensitivity in Thermogravimetric Analysis at Atmospheric Pressure

Paper 1189 “Aerodynamic Forces in Thermogravimetry”

Paper TN-2 “Planning a Flowing Gas Experiment”

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