FURNACE ASSEMBLY FOR REACTIONS
IN CONTROLLED LIGAND ATMOSPHERES

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By impressing a known pressure on a liquid in a properly-designed furnace, a sample can be decomposed or reacted in an atmosphere of that material. If the liquid is a de-composition product of the sample, the variation of decomposition temperature with pressure can be studied for thermodynamic reversibility (van't Hoff plot). Reactions between solid and vapor can be carried out. The system is particularly useful for study of complexes. It can be used with many solvents. Its present use is for differential thermal analysis but it can be used readily for preparative work or corrosion studies.

Need for temperature data on decomposition of complexes at temperatures near the boiling point of the ligand led to the design and construction of a furnace assembly which provides an internally-generated atmosphere at a controlled pressure. The assembly afford direct visual observation of the ligand level to avoid inadvertent dissolving of the sample during the establishment of the steady state operation.

This work was initiated because of three classes of problems with which this principal author had been concerned. Certain hydrates, for example, copper(II) sulfate pentahydrate and barium chloride dihydrate have transitions of the $solid_1 \rightarrow solid_2 + water$ type not far below the boiling point of water at one atmosphere and other decomposition steps not far above. These first transition temperatures have a structural dependence which can be illustrated by the shift of temperature upon substitution of heavy water for ordinary water [1]. For barium chloride, the product is a lower hydrate whose stoichiometry is in dispute. Some authors assume the monohydrate. The evidence from this laboratory indicated a slightly higher state of hydration, ca. 1.08 H_2O [2].

Another kind of problem is that of the transition metal Werner complexes, some of which contain water either in the inner complex ion or as a salt hydrate. There have been many studies of their thermal decomposition but very few of these have used experimental conditions which provided even the most basic test for reversibility. Generally, air or nitrogen or a vacuum constituted the vapor environment; as a result, the mode of decomposition is highly dependent upon the geometry of the sample.

Still other work at this laboratory concerns the so-called "sandwich" complexes, wherein a metal atom, particularly chromium, is coordinated with an aromatic

in three adjacent bonding orbitals and with another in the opposite three. A "half-sandwich" complex may be prepared by crystallization from an aromatic solvent — a substituted benzene — starting with chromium hexacarbonyl. This compound retains three carbonyls and substitutes a benzene ring (with its substituent) for the other three. These are three questions here: In what order do the ligands depart? Does the order depend upon the atmosphere or pressure? Is each decomposition step reversible? This latter problem initiated the present project after some preliminary studies had been performed in another type of DTA furnace asembly [2]. The materials had been decomposed in a neutral atmosphere (nitrogen), in a self-generated atmosphere, and in carbon monoxide. The results will be reported elsewhere.

Principles leading to design

Even though differential thermal analysis is obviously a very useful tool for the study of complexes, there is considerable variation in the results on some of these materials because some decomposition processes are rapidly reversible. This implies a dependence on the atmosphere; that is, if there is an appreciable amount of the departing species in the atmosphere surrounding the sample, the decomposition process is repressed.

A concentration of this reaction product gas may be built up either by supply of that gas or by confinement of the products of the reaction. This confinement may be by inadvertent design — as in a deep crucible, well or capillary — or by intentional design — as in the self-generated atmosphere sample holder [3, 4].

The self-generated atmosphere sample holder delineates the (a) irreversible reactions from the (b) reversible and also from (c) those which have a reversible step but which are not reversible overall, but it does not distinguish between the latter two. For example, the mineral kaolinite dehydroxylates at a temperature which is dependent on water vapor pressure, whether supplied externally or by self-generation, but the overall reverse process is not achievable in any convenient time frame.

On the other hand, many hydrates lose their water reversibly and rapidly. In a self-generated atmosphere, however, the reverse reaction is not observed because only the small amount of water vapor still in the sample holder is available for the rehydration. The establishment of reversibility requires the use of a water vapor atmosphere or substantial partial pressure. Providing a water vapor atmosphere at a known and controlled pressure is not difficult, so long as the water is above its boiling point at that pressure [5, 6].

The same principle, vaporization at a variable rate to maintain the imposed pressure, can be used with other materials. It may be used (a) in an otherwise closed system or (b) with a leak to provide a dynamic atmosphere of the material or (c) to provide a static constant pressure with a bleeding-off of any other gases produced by the sample. The pressure may be sub-ambient as well as supra-ambient.

Furnace design

The principle of the internally generated vapor furnace at variable pressures is perfectly straightforward although not immediately obvious. The essential features of this furnace assembly are:

1. A heated zone above an unheated zone with an intermediate region of varying temperature;

2. Closure or limited flow of the vapor; and
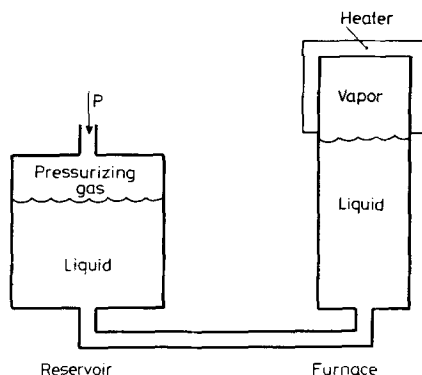
3. An externally applied pressure on the liquid.

Fig. 1. The furnace assembly and liquid ligand supply for controlled atmosphere DTA. Pressure on the liquid in the reservoir drives the liquid only high enough into the furnace that the liquid surface is at the boiling point corresponding to the imposed pressure

First noting that in a closed system the pressure is everywhere constant, it is clear that if a liquid is forced into a region which is at a temperature above its boiling point it will vaporize. Hence an assembly as shown schematically in Fig. 1 can be used to provide a constant known pressure of, for example, benzene within the upper part of the furnace chamber. If the initially-present air is pumped out or driven out by vapor, the atmosphere is benzene at a pressure equal to that applied to the reservoir by gas pressure as shown or by piston.

The effects of changing the pressure and temperature are illustrated in Fig. 2. Assuming that the temperature of the furnace chamber is higher than the 4-atm boiling point of benzene, an increase in the pressure in the reservoir from the initial 2 atm. (A) to 4 atm (B) will push the liquid upward until the surface is at the new boiling point. The vaporization will proceed rapidly enough to maintain a back pressure of four atmospheres.

Going back to the initial conditions, 2 atm (A), assume that a heating program is begun. The higher temperature of the furnace chamber does not change the pressure but the higher temperature of the external heater (and furnace wall) would tend to alter the temperature gradient and heat the surface of the liquid above its

boiling point. The transient increased pressure pushes the surface down to the cooler level, namely the 2-atm boiling point. This adjustment is totally automatic.

The description applies to any set of materials or temperature range. The immediate problem involved materials that decomposed only slightly above the boiling point of the ligand. For this reason a "see-through" furnace was built. This enabled intervention by stopping the flow if there was danger of immersing the sample in the liquid ligand. The furnace is shown in Fig. 3 and the furnace block and sample support are shown in Fig. 4.
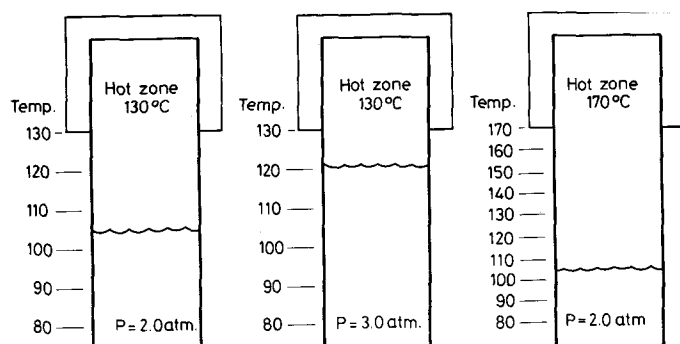

Fig. 2. Illustration of internally-generated atmospheres using an arbitrary temperature gradient and benzene as the single component. If benzene is pushed into furnace A at a pressure of 2.0 atm., the liquid cannot be hotter than 104 °C. Some will vaporize to fill the chamber with vapor at 2.0 atm. If the pressure is increased to 3.0 atm., the liquid level must rise to its new boiling point (in B) ca 121 °C. If furnace A is being heated, so that the temperature gradient changes (in C), the liquid level will change in position but not in temperature.

The thermocouples are Chromel-Alumel shielded with stainless steel having an outside dimension of 1.0 mm. The recorded temperature is that of the sample. Various types of sample holders can be set on the thermocouples to provide different degrees of exposure to the atmosphere within the furnace.

The furnace is sealed against leakage by O-rings in two kinds of location. The furnace tube is sealed to the end pieces by compression of an O-ring between the end flange and a second ring. The depth of the cut provides the correct squeeze for good sealing. This kind of seal places no strain on the end of the tube, so differences in thermal expansion need not be taken into consideration.

This flange is sealed against the base or the aluminum block by a second O-ring which is compressed properly when the nuts are tightened on the screws. The screws pass through spacer tubes which keep the end flanges at a fixed distance apart. The initial adjustment leaves about 3 mm clearance between the end of the quartz tube and the base of the aluminum block. When a liquid is not being used, we substitute an aluminum tube to avoid the possibility of the quartz shattering. A safety shield is used whenever the quartz tube is used above 2 atmospheres.
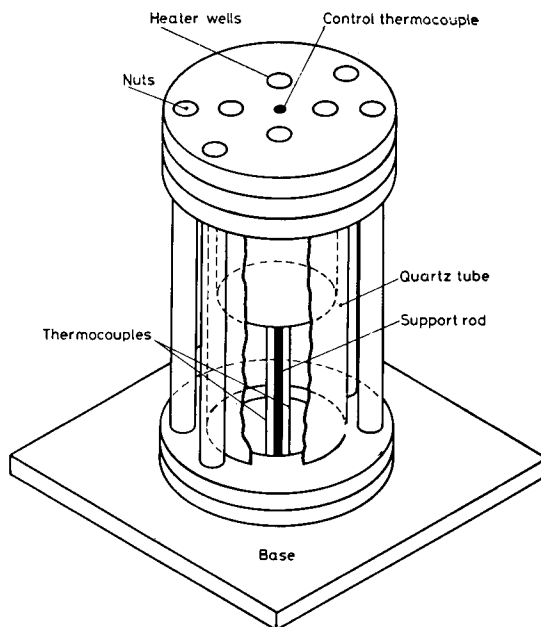
Fig. 3. Visible level furnace. To work with vapors only slightly above the boiling point of the liquid, a quartz tube was used to enable operator monitoring. Metal tubes were substituted when visual observation was not needed
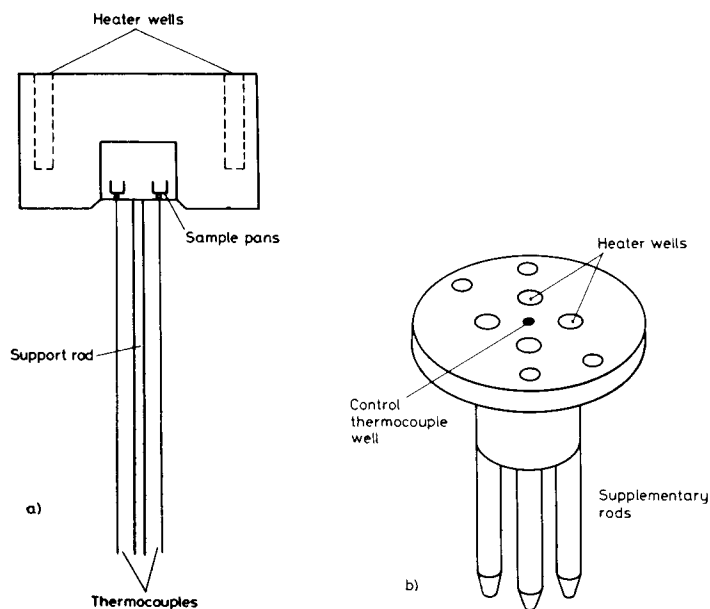

Fig. 4. Furnace block and sample holder assemblies. The sample holder assembly is centered in the block by a disk at the top of the support rod. The supplementary rods extend the temperature gradient downward, keeping the liquid away from the furnace block except when working very near the boiling point

Operation

Several operating options are available. In typical operation, after loading in the sample and sealing the furnace, the furnace tube is filled to near the bottom of the sample chamber, with, for example, benzene, from a reservoir as previously described. The inlet is closed and the outlet closed down to a $3-5$ ml min^{-1} flow. The block temperature is brought to slightly above the boiling point of benzene at the selected pressure. The vaporizing benzene sweeps out the air; completion is detected by the lack of bubbles from an exit tube immersed in benzene. In the meantime, the liquid level has retreated downward but the vaporization continues because heat is conducted to the liquid by the heat flow rods. The inlet is opened and the selected pressure is set. A steady state is set up in which the pressure in the system corresponds to the vapor pressure of benzene at the temperature of the liquid surface. The exit valve may then be closed for static operation or left slightly open for a flowing atmosphere.

If the temperature of the thermal event is very close to the ligand boiling point, it is advantageous to evacuate the furnace, then admit the ligand up to quite near the bottom of the furnace block and close off the supply line. As the heating proceeds, the pressure of ligand increases as the interface temperature rises. When the furnace pressure reaches the selected pressure, the supply line valve can be opened slowly. The level of the interface may change but if the valve is opened before the thermal event begins there should be no problem.

For studies in which there is a substantial temperature interval between the boiling point and the thermal event, we have simply begun the program — having adjusted the exit orifice to a suitable flow — and opened the inlet slightly. By the time the interface reaches the furnace block, the block temperature is high enough to vaporize the liquid.

The programming and recording apparatus have been described [7]. The heat requirements for this furnace assembly are small enough that a similar assembly should be useable with virtually any commercial apparatus.

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References

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Résumé — En exerçant une pression connue sur un liquide dans un four conçu à cet effet, on peut décomposer ou faire réagir un échantillon dans l'atmosphère de ce matériau. Si le liquide est un produit de décomposition de l'échantillon, la variation de la température de décomposition avec la pression peut être étudiée afin d'établir sa réversibilité thermodynamique (fonction de Van't Hoff). On peut effectuer des réactions entre des corps solides et des vapeurs. Le système se prête en particulier à l'étude des complexes. Il peut être utilisé avec de nombreux solvants. Actuellement, il est destiné à l'analyse thermique différentielle, mais il peut aussi bien servir à un travail préparatif ou aux études de corrosion.

ZUSAMMENFASSUNG — Durch Anlegen eines bekannten Druckes an eine Flüssigkeit in einem entsprechenden Ofen kann eine Probe in einer Atmosphäre jenes Stoffes zersetzt oder einer Reaktion unterworfen werden. Ist die Flüssigkeit ein Zersetzungsprodukt der Probe, so kann die Änderung der Zersetzungstemperatur mit dem Druck auf ihre thermodynamische Reversibilität geprüft werden (van't Hoffsche Funktion). Reaktionen zwischen Festkörpern und Gasen können durchgeführt werden. Das System ist besonders geeignet zur Untersuchung von Komplexverbindungen. Es kann mit vielen Lösungsmitteln eingesetzt werden. Sein gegenwärtiges Anwendungsgebiet ist die Differentialthermoanalyse, doch kann es sehr gut für präparative Arbeiten oder zu Korrosionsstudien eingesetzt werden.

Резюме — Используя известное давление над жидкостью в строго предназначенной для этой цели печи, образец может быть разложен или может вступить в реакцию в атмосфере того же материала. Если жидкость является продуктом разложения вещества, изменение температуры разложения с давлением может быть изучено с точки зрения термодинамической обратимости (график Вант—Гоффа). Этим методом могут быть проведены реакции между твердым телом и парами. Такая система особенно полезна при изучении комплексов и ее можно использовать со многими растворителями. Метод может быть применен в дифференциальном термическом анализе, а также в препаративной работе или при исследовании коррозии.