

Thermal Cracker Application Note

Molecular gases can be thermally dissociated on hot filaments or, more efficiently, in heated refractory metal tubes to yield atomic species such as H, O, N, Cl, C, etc, but how can we measure the cracking efficiency? Some researchers have set up sophisticated modulated molecular beam experiments, whilst others have made estimates by measuring, for example, the rate of oxidation of a silver or copper film¹. We demonstrate here a simple, almost direct technique that we will call “the lost parent/precursor (LP) method” which can be readily applied to most gases.

When, for example, ammonia (the “parent” species) is thermally dissociated in a vacuum chamber, the resultant atomic and radical species, H, N, NH and NH₂ react with surface species such as O and C to form, respectively, water and hydrocarbons (“daughter” products) i.e. there is little or no recombination to form reconstituted NH₃. Thus the dissociated ammonia is “lost” permanently. Mass spectrometric measurements of the NH₃ partial pressures, before and after switching on the cracker, thus give a direct measurement of the dissociation efficiency (figure 1).

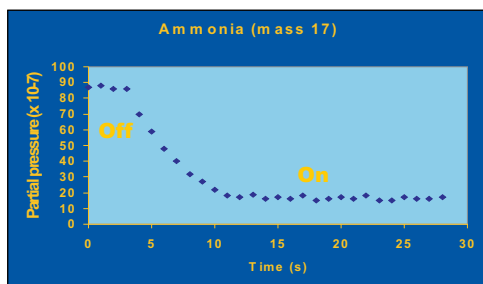


Figure 1

The same principle applies to molecular oxygen which is permanently lost to the formation of oxides (figure 2).

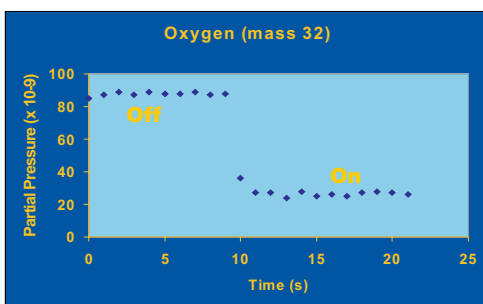


Figure 2

Methane, when cracked, gives rise to carbides, hydrogen and higher hydrocarbons *not* to reconstituted CH₄ (figure 3).

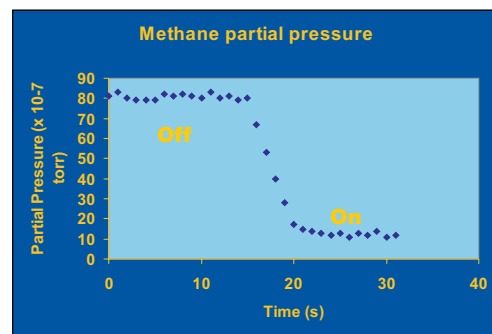


Figure 3

Atomic chlorine from thermally cracked Cl₂ is likewise lost permanently as HCl and metallic chlorides (figure 4).

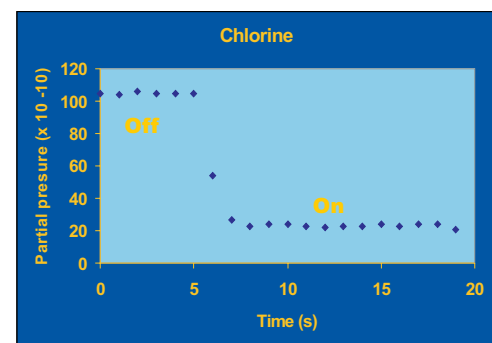


Figure 4

Molecular hydrogen is a singular exception: the surfaces of vacuum chambers are generally saturated with chemisorbed H atoms (from dissociatively chemisorbed H₂, H₂O etc). Consequently when H₂ is thermally dissociated, the resultant H atoms encounter an abundance of surface-bound H atoms with which to form reconstituted H₂ - potentially two molecules for each one dissociated. Thus when H₂ is thermally cracked the resultant H₂ partial pressure will indicate a dissociation efficiency lower than the true value.

In practice, in an unbaked vacuum system, some H atoms will be lost as H₂O and hydrocarbons in addition to reconstituted H₂.

This H₂ artefact can be circumvented, in the measurement of its dissociation efficiency, by using D₂ as the parent gas. In a vacuum system not previously exposed to D₂ the dissociate D atoms are lost permanently as HD, HDO, and deuterated hydrocarbons (figure 5).

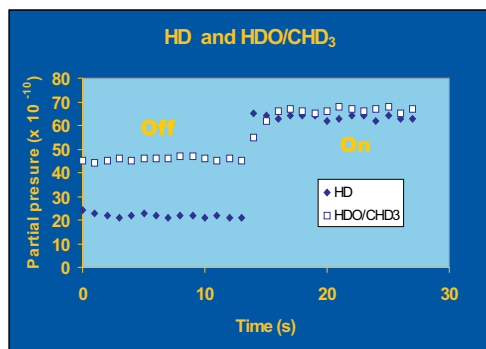


Figure 5

Thus the D₂ (and essentially H₂) dissociation efficiency can be measured by the LP method (figure 6).

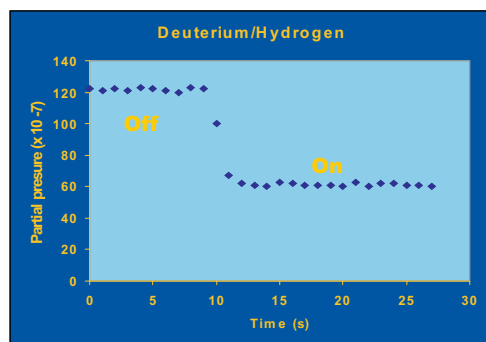


Figure 6

Interestingly, however, it is well known that D₂ undergoes isotope exchange with surface-adsorbed H atoms. Figure 7 shows an electron-stimulated ion spectrum² of a surface previously exposed to D₂. Note the presence of adsorbed D atoms.

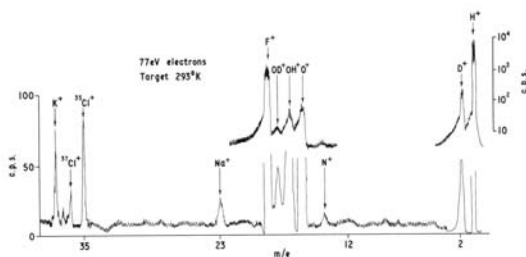


Figure 7

Consequently, we would expect to observe some reconstituted D₂ following prolonged exposure of the chamber to D₂ gas.

The initial loss of D₂ parent is followed a few seconds later by an increase in D₂ partial pressure as dissociated D atoms combine with surface-bound D atoms to desorb as reconstituted D₂ (figure 8). [NOTE, the power employed to collect the data shown in figure 8 was higher than that used to collect the data shown in figure 6. Hence the true (initial) dissociation fraction is higher.]

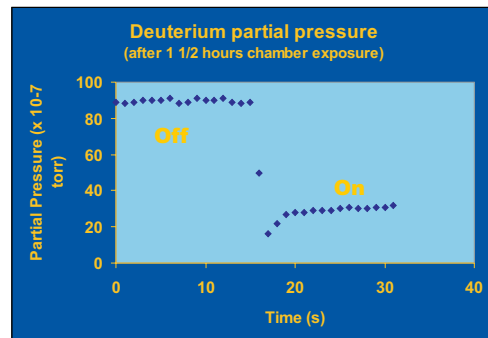
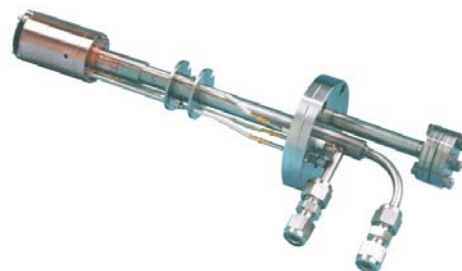


Figure 8

TC50 - Universal Thermal Cracker

All data were collected using the Oxford Applied Research Universal Thermal Cracker - model TC50.



The TC50 cracker uses a electron-beam heated, catalytic cracking zone, which allows operation and cracking at significantly lower power than that required in conventional thermal crackers. Coupled with the efficient, full water-cooling this leads to minimal outgassing and a lower chamber heat load. Furthermore, the TC50 can be used with reactive gases such as oxygen. For a full datasheet please contact us at the address below.

References

1. Locquet, J-P and Mächler, E., J. Vac. Sci. Tech. **A10** (5), 3100, 1992
2. Clampitt, R., Proc. 2nd Adsorption-Desorption Phenom., Florence, Acad. Press (1971).