An update on the Non –Mass-Dependent Isotope Fractionation under Thermal Gradient

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Introduction: Mass flow and compositional gradient (elemental and isotope separation) occurs when fluid(s) or gas(es) in an enclosure is subjected to a thermal gradient, and the phenomenon is named thermal diffusion. Gas phase thermal diffusion has been theoretically and experimentally studied for more than a century, although there has not been a satisfactory theory to date. [1,2,3] Nevertheless, for isotopic system, the Chapman-Enskog theory predicts that the mass difference is the only term in the thermal diffusion separation factors that differs one isotope pair to another,with the assumptions that the molecules are spherical and systematic (monoatomic-like structure) and the particle collision is elastic. Thus a mass dependent relationship is expected, and for O-bearing (O^{16}-O^{17}-O^{18}) molecules the $\alpha^{17}O/\alpha^{18}O$ is expected at 0.5 to 0.515, for S-bearing (S^{32}-S^{33}-S^{34}-S^{36}) molecules the $\alpha^{33}S/\alpha^{34}S$ at 0.5 to 0.508 , where α is isotope fractionation factor between cold and warm reservoirs. We [4,5] recently reported that thermal diffusion may introduce Non-Mass Dependent (NMD) isotope fractionation for low-pressure O_2 and SF_6 gases. It was the first report on multiple isotopes of same element, in addition to previous reported “anomalous” isotopic behavior that Chapman-Enskog theory hardly explained, e.g.: 1) Reversal of the sign of thermal diffusion factor was found for ${}^{14}N^{14}N$-${}^{15}N^{15}N$, ${}^{13}C^{16}O$-${}^{12}C^{16}O$, ${}^{16}O^{16}O$-${}^{18}O^{18}O$ at the temperature close to the liquefaction temperature of the gas molecule [6,7,8]; 2) ${}^{16}O^{13}C^{16}O$ and ${}^{16}O^{12}C^{18}O$ behave differently at low temperature range with opposite signs of thermal diffusion factor [9]. It was suggested that some additional paramters need to be considered in the conventional thermal diffusion coefficient calculation to account for the observations, such as the symmetry or mass distribution or the internal degree of freedom of the molecule, dimer formation at low temperature or high pressure that affect the collision diameter, inelastic collision at low temperature [6,7,8,9,10,11]

Current Study: Our previous report indicates factors other than those above may be playing role because the NMD effect is found for both symmetric and asymmetric, linear and spherical polyatomic molecules over a wide range of temperature (-196ºC to +237ºC). The observed NMD phenomenon in the simple thermal-diffusion experiments demands quantitative validation and theoretical explanation. Besides the pressure and temperature dependency illustrated in our previous reports, efforts are made in this study to address issues such as the role of convection or molecular structure and whether it is a transient, non-equilibrium effect only.

Results and Discussion: Here we report new results on O_2 gas thermal diffusion:

1) in a purely diffusive vertical two-bulb setting with colder reservoir at lower position, time course experiments showed that the NMD effect persists after the system reach isotopic steady state between warmer and colder compartments, suggesting that the effect not an transient one;

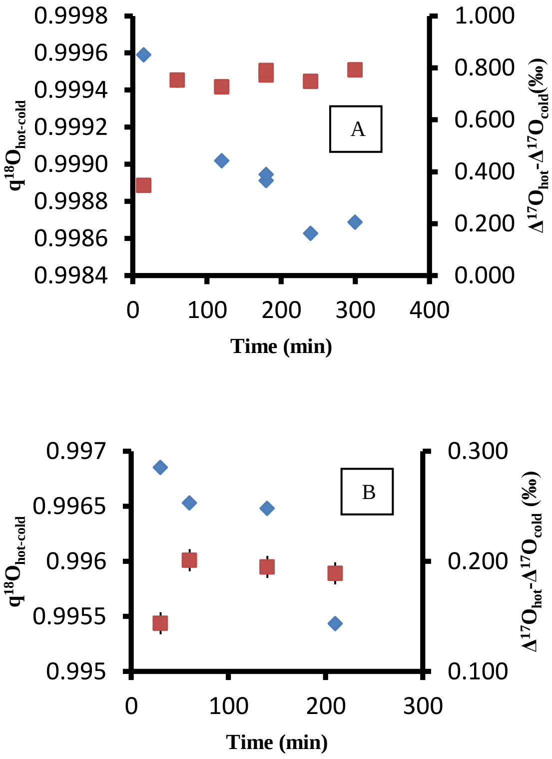

Figure 1, Time course for isotope fractionation factor ($q_{hot-cold}$, blue diamonds) and for $\Delta\Delta^{17}O$ ($\Delta^{17}O_{hot}$-$\Delta^{17}O_{cold}$, red square) difference between hot and cold reservoir. A) 5.3Torr pressure with upper +20ºC-lower -196ºC, B) 12 Torr pressure with upper +20ºC-lower +260ºC. Error bars (s. e. × t) are 0.00002 and 0.01‰ for $q_{hot-cold}$ and $\Delta\Delta^{17}O$, respectively. Error bar is smaller than symbol size if not shown.

2) the NMD effects are observed within a range of convection in a light bulb type system with a hot center (~700ºC, CeO_2 as isotope exchange media) and a cold wall (-20ºC). Such setting avoided “third party” collision along the temperature gradient and is also testing the rate of recording anomalous isotope composition into solid phase;

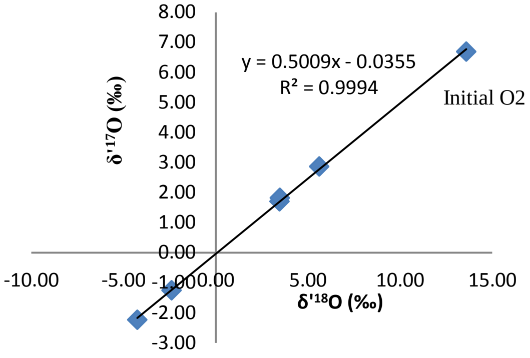

Figure 2, Relationships between the $\delta'^{17}O$ and the $\delta'^{18}O$ for final CeO_2 and initial O_2 gas. The overall slope is much shallower than either diffusion slope (~0.511) or isotope exchange at 700ºC (~0.529).

3) With additional gas molecules, e.g. N_2, CO_2, He, the NMD effect for O_2 does not vanish but its temperature and pressure dependencies are affected.

Conclusion: New data further support that the NMD effect is largely controlled by the nature of molecular collisions during thermal diffusion and such effect may be considerable in natural environments, e.g. planetary atmosphere and solar nebulae.

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