

# QUANTUM EFFECTS IN COSMOCHEMISTRY: COMPLEXATION ENERGY AND VAN DER WAALS RADII. D. W. Mittlefehldt<sup>1</sup> and T. L. Wilson<sup>1</sup>, <sup>1</sup>NASA, Johnson Space Center, Houston, Texas 77058 USA.

**Introduction:** The subject of quantum effects in cosmochemistry was recently addressed [1] with the goal of understanding how they contribute to Q-phase noble gas abundances found in meteorites. It was the pursuit of the Q-phase carrier of noble gases and their anomalous abundances that ultimately led to the identification, isolation, and discovery of presolar grains [2]. In spite of its importance, Q-phase investigations have led a number of authors [3] to reach conclusions that do not seem to be supported by quantum chemistry. In view of the subject's fundamental significance, additional study is called for. Two quantum properties of Q-phase candidates known as endohedral carbon-cage clathrates such as fullerenes (Fig. 1) will be addressed here. These are complexation energy and instability induced by Pauli blocking (exclusion principle).

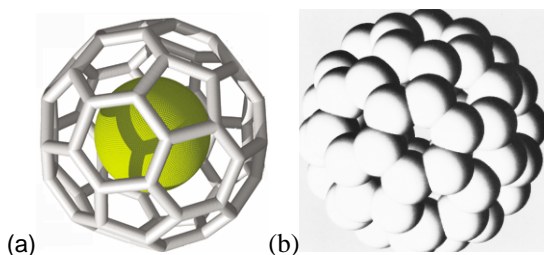


Figure 1. Endohedral fullerenes containing trapped noble gases are candidates for Q-phase. (a) A model illustrating the covalent carbon bonds; (b) a more realistic image with carbon atoms depicted.

**What is Q-phase?:** Originally dubbed “Q” for quintessence [4,5], Q-phase is the carrier of the planetary noble gases, as opposed to the solar and extrasolar (also cosmic or interstellar) noble gases. The term *planetary* derives from the close similarity of Q-gas abundance to that for Ne, Ar, and Kr in the atmospheres of the Earth and Mars.

The general consensus of opinion today is that Q-phase is a carbonaceous carrier that derives from two broad areas of the chemistry and physics for carbon. (1) The first, conservative school of thought is that Q-phase is a two-dimensional structure of conventional hexagonal carbon material such as graphite in which noble gases are entrapped through active capture and sorption [6,7]. (2) The second school of thought is that Q-phase is a three-dimensional structure of endohedral carbon cages like the fullerenes in Figure 1, carbon onions, or some class of carbon nanotubes known as SWNTs (single-walled nanotubes) or MWNTs (multi-walled nanotubes) [8-16].

The second category, described as the issue of “fullerenes from space,” is promising but controversial. In spite of claims to the contrary [3, 8], carbon-cage Q-phase *per se* has not been definitively confirmed or identified in meteorites [8-16]. There was one serendipitous candidate that predates fullerene chemistry [17] which noted that Q-phase must contain a powerful form of bonding in order to survive the highest temperatures involved.

Q-phase contains a noble-gas abundance pattern that is anomalous compared with the Sun (Fig. 2), as well as in comparison with the extrasolar (cosmic or interstellar) abundance.

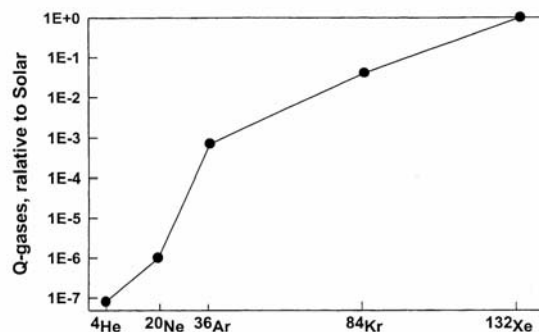


Figure 2. Elemental abundance of Q-gases relative to solar abundance of <sup>132</sup>Xe, as a function of mass. Adapted from Hohenberg *et al.* [6].

**Van der Waals Properties:** Our earlier study [1] of carbon-cage clathrates Q@C<sub>60</sub> (Q = He, Ne, Ar, Kr, and Xe) made use of the Lennard-Jones model of fullerene. This is an atom-atom potential method [18-23] which visualizes the C<sub>60</sub> molecule as 60 carbon atoms distributed evenly on a sphere of Van der Waals radius  $r_{C_{60}} = 3.56 \text{ \AA}$  with each carbon C having a Van der Waals radius  $r_C = 1.75 \text{ \AA}$ , leaving a cavity of  $r_{cav} = 1.81 \text{ \AA}$ . The geometry is illustrated in Figure 3 for Ar@C<sub>60</sub>. The volume ratio ( $V_Q/V_{C_{60}}$ ) then becomes 0.97, 0.69, 1.19, 1.31, and 1.75 for Q = He, Ne, Ar, Kr, and Xe respectively.

Surprisingly, Ar@C<sub>60</sub> is the most stable; not surprisingly Xe@C<sub>60</sub> is the most unstable. That instability has been corroborated experimentally when Xe@C<sub>60</sub> was not found but Xe@C<sub>70</sub> was [24-25]. The overlap for Ar@C<sub>60</sub> is readily seen in Figure 3, where the Pauli Exclusion Principle takes effect (called Pauli blocking in Monte Carlo physics) because the electron levels are all filled and Pauli's rule is being violated.

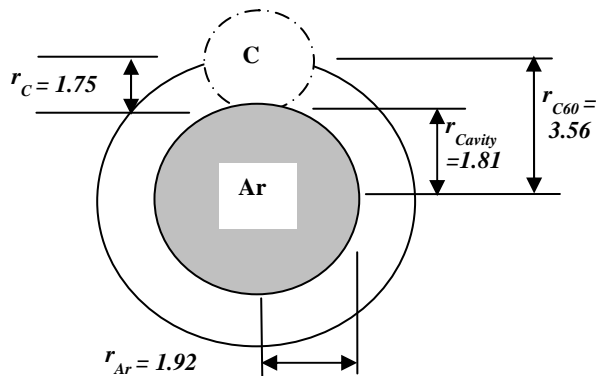


Figure 3. The Van der Waals radii in Å of C and Ar with cavity radius  $r_{Cavity}$  for the Ar@C<sub>60</sub> complex. Not to scale.

**Complexation energy:** Ironically, Ne has a more stable endohedral complexation energy than He, where complexation energy is the energy required to form the molecular complex Q@C<sub>60</sub>, with a positive endohedral potential. From Figure 4, the endohedral complexation energy of He and Ne distinguishes them from Ar, Kr, and Xe – a characteristic possibly mimicked in the Figure 2 Q-gas abundances. In addition, the Van der Waals radii of He and Ne do not overlap with the C<sub>60</sub> shell, while Ar, Kr, and Xe do [21].

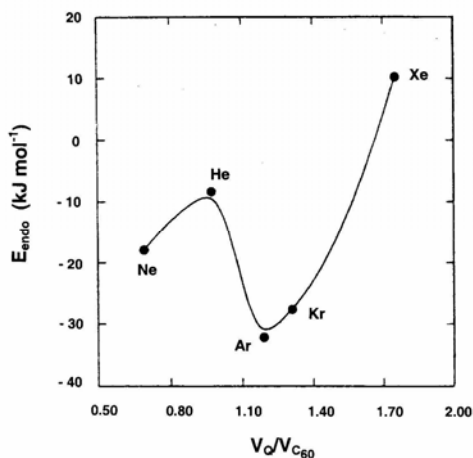


Figure 4. Comparison of complexation energy  $E_{endo}$  with Van der Waals volume ratio ( $V_Q/V_{C60}$ ). Adapted from Son and Sung [21].

From this brief discussion of the Van der Waals properties of Q@C<sub>60</sub>, it is not at all evident what is the compelling correlation with the abundances in Figure 2 if Q@C<sub>60</sub> is the Q-phase carrier of the planetary noble gases. The data in Figure 2 would seem to indicate that Xe@C<sub>60</sub> is the most stable while the Van der Waals radii for Xe@C<sub>60</sub> indicate it is the most unstable due to the exceedingly large overlap with a volume ratio of 1.75.

The resolution of this circumstance may be quite simple: As the Van der Waals radii begin to overlap and the exclusion principle takes effect, the Q-phase carbon cage might evolve into Q@C<sub>n</sub> where C<sub>n</sub> is one of the larger fullerenes with  $n > 60$ , or a carbon onion is produced. Nature may solve the endohedral entrapment of Xe by building a larger carbon cage or a multi-walled structure. In [24-25] this was experimentally observed to be the case, and may be the object discovered in [17] - both in contradiction with statements made in [3].

**Conclusions:** Endohedral carbon cages are viable candidates for Q-phase, and may provide additional insight about the presolar nebula. We know that planetary noble gases are characterized in part by depletions in light gases relative to heavy ones as compared to the Sun (Fig. 2). Complexation energy and Pauli blocking (Fig. 3 and 4) offer additional insight into this process.

**References:** [1] Wilson, T.L., and Mittlefehldt, D.W. (2006) *LPSC XXXVII*, 1386. [2] Ott U. (2002) in *Noble Gases in Geochemistry and Cosmochemistry*, D. Porcelli, C.J. Ballentine, R. Wieler, eds. *Rev. Mineral. Geochem.* **47**, 71-100. [3] Becker L., Poreda R. J., and Bunch T.E. (2000), *Proc. Nat'l. Acad. Sci.*, **97**, 2979. [4] Lewis R. S., Srinivasan B., and Anders E. (1975), *Science* **190**, 1251-1262. [5] Papanastassiou, D.A., and Wasserburg G.J. (1971), *Earth Plant. Sci. Lett.* **11**, 37-62. [6] Hohenberg C.M., Thonnard N., and Meshik A. (2002), *Meteoritics & Planet. Sci.* **37**, 257-267. [7] Wacker J.F. (1989), *Geochim. Cosmochim. Acta* **53**, 1421-1433. [8] Harris P. J. F. and Vis R. D. (2003), *Proc. R. Soc. Lond. A* **459**, 2069-2076. [9] Harris P. J. F., Vis R. D., and Heymann, D. (2000), *Earth Plant. Sci. Lett.* **183**, 355-359. [10] Vis R. D., Mrowiec A., Kooyman P.J., Matsubara K., and Heymann, D. (2002), *Meteoritics & Plan. Sci.* **37**, 1391-1399. [11] Vis R. D. and Heymann D. (1999), *Nucl. Instr. Meth. Phys. Res. B* **158**, 538-543. [12] Heymann D. (1998), *LPSC XXIX*, 1098. [13] Heymann D. (1997), *Ap. J.* **489**, L111-L114. [14] Heymann D. (1995), *LPSC XXVI*, 595-596. [15] Heymann D. (1986), *J. Geophys. Res.* **91**, E135-E137. [16] de Vries M.S., et al. (1993), *Geochem. Cosmochem. Acta* **57**, 933-938. [17] Smith P.P.K. and Buseck P.R. (1981), *Science* **212**, 322-324. [18] Bug A. and Wilson A. (1992), *J. Phys. Chem.* **96**, 7864-7869. [19] Pang L. and Brisse F. (1993), *J. Phys. Chem.* **97**, 8562-8563. [20] Jimenez-Vázquez H.A. and Cross R.J. (1996), *J. Chem. Phys.* **104**, 5589-5593. [21] Son M.-S. and Sung Y.K. (1995), *Chem. Phys. Lett.* **245**, 113-118. [22] Breton J., Gonzalez-Platas J., and Girardet C. (1993), *J. Chem. Phys.* **99**, 4036-4040. [23] Zhang Y. and Xu Z. (1995), *Amer. Mineralogist* **80**, 670-675. [24] Giblin D.E., et al. (1997), *J. Am. Chem. Soc.* **119**, 9883-9890. [25] Saunders M., et al. (1994), *J. Am. Chem. Soc.* **116**, 2193-2194.