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Donald D. Clayton

Clemson University, claydonald@gmail.com

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ANALYTIC APPROXIMATION OF CARBON CONDENSATION ISSUES IN TYPE II SUPERNOVAE

DONALD D. CLAYTON

Department of Physics and Astronomy, Clemson University, Clemson, SC, USA; claydonald@gmail.com
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ABSTRACT

I present analytic approximations for some issues related to condensation of graphite, TiC, and silicon carbide in oxygen-rich cores of supernovae of Type II. Increased understanding, which mathematical analysis can support, renders researchers more receptive to condensation in O-rich supernova gases. Taking SN 1987A as typical, my first analysis shows why the abundance of CO molecules reaches an early maximum in which free carbon remains more abundant than CO. This analysis clarifies why O-rich gas cannot oxidize C if ^{56}Co radioactivity is as strong as in SN 1987A. My next analysis shows that the CO abundance could be regarded as being in chemical equilibrium if the CO molecule is given an effective binding energy rather than its laboratory dissociation energy. The effective binding energy makes the thermal dissociation rate of CO equal to its radioactive dissociation rate. This preserves possible relevance for the concept of chemical equilibrium. My next analysis shows that the observed abundances of CO and SiO molecules in SN 1987A rule out frequent suggestions that equilibrium condensation of SUNOCONs has occurred following atomic mixing of the He-burning shell with more central zones in such a way as to reproduce roughly the observed spectrum of isotopes in SUNOCONs while preserving $\text{C/O} > 1$. He atoms admixed along with the excess carbon would destroy CO and SiO molecules, leaving their observed abundances unexplained. The final analysis argues that a chemical quasiequilibrium among grains (but not gas) may exist approximately during condensation, so that its computational use is partially justified as a guide to which mineral phases would be stable against reactions with gas. I illustrate this point with quasiequilibrium calculations by Ebel & Grossman that have shown that graphite is stable even when $\text{O/C} > 1$ if prominent molecules are justifiably excluded from the calculation of chemical equilibrium.

Key words: atomic processes – ISM: abundances – ISM: general – meteorites, meteors, meteoroids – supernovae: general – supernovae: individual (SN 1987A)

1. INTRODUCTION

The problem historically of condensing carbon SUNOCONs in the interiors of Type II supernovae is that most of the synthesized carbon is bathed in more abundant oxygen and was long presumed to be oxidized by it. Only the convective He-burning shell has more carbon than oxygen. In models based on equilibrium condensation therefore, only that He-burning (He/C/O) shell could support carbon condensates (graphite or SiC). But isotopic measurements on those carbonaceous SUNOCONs (“SUPERNOVA CONDENSATES” Clayton 1978) reveal in their bulk (e.g., Amari et al. 1992; Zinner 1998; Clayton & Nittler 2004) diagnostic excess isotopes, ^{12}C , ^{15}N , and ^{28}Si (see Figure 10 of Deneault et al. 2003), and ^{44}Ti (Nittler et al. 1996; Clayton 1975) and trace-element isotopes $^{95,97}\text{Mo}$ (Meyer et al. 2000; Deneault et al. 2003). These overabundant isotopes in the SUNOCON mineral structure suggest that the bulk of the SUNOCON mass condensed from gas having $\text{O/C} \gg 1$ within the ^{12}C -rich and ^{28}Si -rich inner zones of SN II. That impression earns hydrodynamic support from a calculation (Deneault et al. 2003) showing (their Figure 2 and online movie) that the desired isotopic zone is compressed by the reverse shock from the H envelope and should therefore condense grains rapidly to greater size than the average interior SUNOCONs. Taken together, this evidence suggests that carbon SUNOCONs condensed primarily from that compressed matter. I will oversimplify the known carbon-based SUNOCON specimens because this paper is not about their isotopic data but rather about carbon condensation, about lack of microscopic mixing prior to condensation, and about the possibility of employing chemical-equilibrium calculations to help define the stable mineral fields for them. The hydrodynamic instabilities within SNII cause *overtorn of massive fluid fingers*

in the radial flow rather than to *atomic scale mixing* of those fluid elements with surrounding SN matter. Microscopic mixing ultimately requires diffusion, which is too slow (Deneault et al. 2003). Carbon SUNOCONs are primarily two types of graphite (“low density” and “high density”; Croat et al. 2003) and silicon carbide (Clayton & Nittler 2004). A special chemical challenge within graphite is the frequent occurrence of ^{44}Ti -rich TiC spheres imbedded within the larger graphite SUNOCONs (Croat et al. 2003), proving SN provenance.

On the other hand, the substantial abundances of ^{13}C and of ^{14}N coupled with ^{26}Al -rich aluminum (Zinner 1998) and ^{18}O -rich oxygen (Amari et al. 1995) point to additions of He-burning shell material to the SUNOCONs. The question is “added how?” Unquestionably the suite of high-precision isotopic ratios in individual SUNOCONs provides incomparably precise data concerning the fluid post-collapse history of supernovae. New understanding must follow a correct description of how the SUNOCONs condensed and assembled, however, rather than on the nucleosynthesis map for those anomalous isotopes. Nucleosynthesis is understood very much better than condensation and assembly, so another attempted discussion of isotopes (Deneault et al. 2003; Travaglio et al. 1999) will not be the goal of this paper. To assume that the SUNOCONs condensed in equilibrium from a gaseous mixture containing each of the diagnostic isotopes requires that the appropriate supernova zones have mixed at the atomic level prior to condensation (Nittler et al. 1996; Travaglio et al. 1999; Zinner 1998; Fedkin et al. 2010) and that only microscopic mixtures having bulk $\text{C} > \text{O}$ can support carbon condensation. The assumption of the putative isotopic mixing is motivated by hard isotopic evidence, but the second assumption (microscopically mixed zones having $\text{C/O} > 1$) is, I maintain, a folktale. I discount that latter

assumption on four grounds: (1) there is insufficient time available (Deneault et al. 2003) prior to the onset of condensation to mix gases microscopically, because growth of such large SUNOCONs must begin during the first year; (2) assuming condensation to follow chemical equilibrium is unjustifiable in SNII; (3) the gaseous abundance ratio $C > O$ is no longer required in order to condense carbon SUNOCONs (Clayton et al. 1999; Cherchneff & Dwek 2009; Clayton 2011), so gaseous mixtures need not be limited by that perceived requirement; (4) I show in Section 3 that observed abundances of CO and SiO molecules in SN1987A rule out microscopic mixing with the He/C/O shell prior to condensation, at least in SN 1987A.

The perceived mismatch of C/O chemical ratio with isotopic compositions has been known for about two decades and has frustrated the drawing of scientific knowledge about supernovae from these exciting SUNOCONs. The big implications for supernovae and for nucleosynthesis require a dynamic and self-consistent theory for condensation in rapidly expanding supernova cores. The attempted circumvention of the isotopic mismatch has postulated molecular mixing of carefully balanced portions of the He-burning shell with portions of deep ^{28}Si -rich and ^{44}Ti -rich interiors (e.g., Fedkin et al. 2010). Such microscopic mixing could, if it did occur, enable graphite, TiC and SiC to be stably condensed within thermal-equilibrium models of condensation having $C > O$ and appropriate isotopic compositions. Fedkin et al. (2010) have posited microscopic mixing with the He/C/O shell followed by equilibrium condensation to account for the ^{44}Ti -rich TiC spheres imbedded within graphite (Croat et al. 2003). The kinetic point of view of TiC might propose instead that $(\text{TiC})_n$ clusters may form in the gas (Cherchneff & Dwek 2010) while graphite is condensing to encase those clusters, followed by solid-state diffusion and amalgamation of TiC inclusions within hot forming graphite. These two suggestions illustrate differing approaches to the TiC subgrains.

Igniting the debate over carbon condensation Clayton (1998) and Clayton, Liu & Dalgarno (1999) introduced a kinetic theory by which carbon can condense thermally in gas having more abundant oxygen. That theory is noteworthy in having every reaction from the initial $O > C$ gas to macroscopic graphite included in a kinetic network, even though most of the cross sections and the isomeric transitions from linear chains to carbon rings are not accurately known. It was an *existence proof*. Rare carbon-ring molecules were not prevented from formation despite rapid oxidation of their molecular precursors. It rests on an affirmative answer to this *gedanken experiment*: will a small graphite grain grow larger (until free carbon is depleted) if tossed into a hot gas containing significant carbon abundance but more abundant oxygen?

That initial theory has been amplified during the past decade by several studies: (Clayton et al. 2001; Deneault et al. 2003, 2006; Cherchneff & Dwek 2009). More recently Clayton (2011) has reviewed this work and clarified its basis. Not only does C condense in O-rich gases, but oxides may condense *simultaneously*. Nozawa et al. (2003) and Cherchneff & Dwek (2009, 2010) have published noteworthy studies of molecules formed in low-metallicity supernovae using large reaction networks, but they did not address the contentious issue of microscopic mixing prior to condensation of solids. To the contrary, they reported molecular abundances in completely mixed supernova models as well as in unmixed ones.

Despite the success of kinetic nucleation and growth of carbon in oxygen-rich supernovae, kinetic theory cannot easily clarify

which mineral phases should be abundant and stable against gaseous attack in the temperature range 2200–1600 K, where the bulk of mineral condensation is expected to occur. To identify the most stable condensates in a given chemical composition requires some sort of partial equilibrium calculations for that composition. This has not been possible because the oxidizing composition of the supernova mantle gases does not even admit carbon condensates. Equilibrium condensation sequences by Fedkin et al. (2010) illustrate the C/O constraint by presenting tables of equilibrium inner-zone condensates. However, in Section 4 I will call attention to graphite in a restricted O-rich equilibrium calculated by Ebel & Grossman (2001). I will present in Section 2.4 a scheme that may circumvent the inapplicability of equilibrium chemistry. It is based on an artificial adjustment of the dissociation energy of the CO molecule, made not arbitrarily but numerically such that the radioactive dissociation of CO by Compton electrons yields the same stationary ratio for $n_{\text{CO}}/n_{\text{C(g)}}$ as does the CO thermal equilibrium using the revised binding energy. With that revised binding energy, here called B^*_{CO} , it is suggested that thermal equilibrium may validly identify the most stable condensates. A similar restriction exists for SiO molecules. In addition to this adjustment, it proves to be necessary to rule out the presence of the dioxide molecules CO_2 and SiO_2 that would be abundant in chemical equilibrium but for which dynamic formation paths in supernovae do not exist.

Chemical equilibrium is not a valid guide to what mineral phases will actually condense dynamically within supernova interiors. The supernova expansion is simply too rapid for equilibrium condensation to apply. Both temperature and density fall too rapidly with time. That environmental condition not only invalidates the basic equilibrium assumption, but also deals brutally with the equilibrium property by which atoms must depart one condensed phase to form different ones as temperature declines. The scientific value of equilibrium mineral composition is instead that it identifies which mineral phases would be *stable* against gaseous attack in the environment. Equilibrium cannot mandate their condensation, but can confirm that when kinetic chemical paths suggest a plausible reaction route to a stable condensate that it will probably exist. With that understanding equilibrium calculations can support a kinetic map to quasiequilibrium condensation of carbon SUNOCONs within O-rich gas. I address the quasiequilibrium in Section 4.

It was highly significant that dust and CO and SiO molecular vibrational lines in SN 1987A were detected early from the young supernova remnant (Petuchowski et al. 1989; Spyromilio et al. 1998). For discussion of this history see the introduction by Cherchneff & Dwek (2009). I show in Section 3 that the abundances of those molecules rule out molecular scale mixing prior to condensation of SUNOCONs in SN 1987A. Recent astronomical evidence also adds urgency to the need to understand carbon condensation in interior shells of supernovae. Herschel telescope observations (Matsuura et al. 2011) of SN 1987A seem to imply the existence of 0.4–0.7 solar masses of dust condensed within its interior shells. Such large mass may be difficult to account for without regarding the carbon abundance interior to the He shell to be among the “condensable elements,” despite its being bathed by more abundant free oxygen.

Radioactivity within supernovae creates many unique consequences for astronomy (Diehl et al. 2011). Chemically the most significant consequence of intense radioactivity and the basis of this paper is that CO molecules are destabilized. A high CO abundance is no longer possible within the first year of ^{56}Co

activity, so CO formation is not able to prevent a large abundance of free carbon atoms. High-energy electrons created locally by Compton scattering of the gamma radiation disrupt those CO molecules (Liu & Dalgarno 1995; Clayton 2011). The dissociative reaction is inelastic scattering: $\text{CO} + e \rightarrow \text{C} + \text{O} + e^*$. Although the lifetime τ_{CO} of a CO molecule against disruption by fast electrons is of order 10^6 s in the supernova expansion near 2000 K, which is not chemically fast, there exist so many CO molecules that radioactive disruption breaks apart a large number per unit time, maintaining a source of free carbon. That C must be recaptured. It is similar in this way to the ^{56}Co radioactivity itself; its half-life (77 days) is also not short, but so many ^{56}Co nuclei exist within SNII that the activity of gamma-ray creation is sufficiently intense that Compton electrons allow the CO molecule to be stable only for about 10^5 – 10^6 s. If the zone in question is abundant in He or Ne, moreover, the Compton electrons instead partially ionize those noble gas atoms and their collision rate with CO causes its dissociation (see Section 3). By either route, radioactivity liberates free carbon.

The flux and spectrum of newly injected Compton electrons (Clayton & The 1991) yields the lifetime of a CO molecule in an interior zone. In a gas of pure CO the *mean energy per ion pair* is defined as the energy of primary electrons divided by the number of pairs produced. Its value is almost independent of the initial high energy of the injected electrons because each initial electron energy, in the end, degrades through similar trees of energy loss; but the relevant suprathreshold electron flux stands in proportion to the initial electron input energy. Liu & Victor (1994) calculated the mean energy per ion pair in pure CO gas and obtained the result $\Delta E = 32.3$ eV deposited per dissociated pair, which agrees well with the measurement of 32.2 eV by Klots (1968). So the efficiency of energetic electrons for dissociating CO seems well established. A lifetime τ_{CO} near one week is typical in SN 1987A at early times, but would be longer in those supernovae synthesizing less ^{56}Co and at times greater than about 8 months.

2. THE FUNCTION $n_{\text{CO}}(t)$ AND THE EFFECTIVE BINDING ENERGY OF CO

The interior core of C and O resulting from completed He burning in massive stars is a mix of C and O atoms having bulk $\text{C}/\text{O} < 1$ (where intent is clear I will use the ratio of chemical symbols in this way). Post-explosive cooling of such matter will attempt to associate C and O into CO molecules. Liu & Dalgarno (1995) applied radioactivity to a model of SN 1987A to show that the fast Compton electrons reduced the total mass of CO molecules surviving the cooling expansion from about 0.1 solar masses of CO to about 0.01 solar masses between days 100 and 200. Simultaneously, the radiative association $\text{C} + \text{O} \rightarrow \text{CO} + \gamma$ continues to form new CO, with rate coefficient $k_{\text{CO}} = 3.3 \times 10^{-17} \text{cm}^3 \text{s}^{-1}$ (Lepp et al. 1990). The associated replenishment of CO abundance between days 100 and 200 has slowed the abundance decline of CO by a factor about three, making the large observed decline consistent with the CO lifetime τ_{CO} owing to radioactivity being in the range 5–10 days in SN1987A.

The reaction $\text{C} + \text{O} \rightarrow \text{CO} + \gamma$ is one of the crucial reactions of chemical astrophysics. Its rate k_{CO} is intrinsically slow because quantum mechanics requires not only rearrangement of electronic shells but also simultaneous creation of a photon during the collision; nonetheless, the huge product $n_{\text{C}}n_{\text{O}}$ in the He-exhausted mantle ensures a robust growth term for the CO abundance until it is reversed by radioactive dissociation. The

function n_{CO} will have a single maximum during the first year when the growth of large carbon grains must begin, but n_{CO} may again increase at longer times when radioactive destruction weakens (Liu & Dalgarno 1995; Cherchneff & Dwek 2009).

Evidently the abundance of CO within that zone during expansion attempts to balance these creation and destruction effects, doing so exactly at the time of maximum n_{CO} . The mass of ejected CO in SN1987A is much less than it would have been if the expansion of the supernova interior had oxidized all hot C bathed in O; therefore, a large abundance of free C necessarily remains in the ejected gas. Observations of CO in SN 1987A confirmed its abundance there to be much lower than if all C were oxidized (Spyromilio et al. 1988; Petuchowski et al. 1989; Liu & Dalgarno 1995), implying either free C or condensed C.

This paper attempts to improve analytic understanding of the abundance of CO molecules in SN 1987A. That problem is an exercise in numerical modeling (Liu & Dalgarno 1995; Gearhart et al. 1999; Clayton et al. 2001, 2006; Cherchneff & Dwek 2009); but understanding the numerical complexity of those results can be helped a great deal by analytic demonstrations of key physical points. Insight starts from evaluating the stationary CO abundance at the moment $t = t_{\text{max}}$ when n_{CO} reaches its maximum. The leading creation and destruction terms for CO then balance, so that $dn_{\text{CO}}/dt = 0$ at that time. Hence

$$dn_{\text{CO}}/dt = n_{\text{C}(\text{g})}n_{\text{O}}k_{\text{CO}} - n_{\text{CO}}/\tau_{\text{CO}} = 0 \quad (1)$$

at t_{max} , so that the maximum abundance reached by CO is

$$n_{\text{CO}}(t_{\text{max}}) = n_{\text{C}(\text{g})}n_{\text{O}}k_{\text{CO}}\tau_{\text{CO}}. \quad (2)$$

This amount is equal to that formed during its last mean lifetime τ_{CO} against radioactive dissociation. The time t_{max} of the maximum occurs later for larger values of τ_{CO} , which means for SNII expansions that t_{max} would occur at cooler temperature for larger τ_{CO} . In SN 1987A, in which the radioactivity was intense because the nucleosynthesis yield of ^{56}Ni was $0.075 M_{\text{sun}}$, the short value early of τ_{CO} near 10^5 s caused $n_{\text{CO}}(t_{\text{max}})$ to occur early, while the gas was still too hot for dust to form. The amount of CO thereafter declines while the gas cools to temperatures at which carbon chains can form and isomerize to rings (Clayton et al. 1999).

But if other SNII have created much less ^{56}Ni than has SN 1987A, τ_{CO} will be longer and the abundance $n_{\text{CO}}(t_{\text{max}})$ will be larger in those SNII. The maximum of Equation (2) forms only if radioactivity remains intense; after it has decayed to low levels and τ_{CO} becomes long another greater secondary maximum can grow if free C still exists. Cherchneff & Dwek (2009) show in their Figure 4 a huge rise of such CO abundance after 600 days in their $20 M_{\text{sun}}$ mixed model, which results from the neutralization of Compton-electron-produced He^+ after the radioactivity has weakened. That late rise may not actually happen, however, because C may not remain free but may have condensed as graphite grains earlier than 600 days, in which case free C would be diminished, unavailable for late association with O. The condensation of the large carbon SUNOCONs necessarily begins during year one while the density is large and ^{56}Co radioactivity is still intense. Because this work focuses on large SUNOCON condensation, which must start during the first year, we will not consider here what occurs after radioactivity has decayed. Figures 10 and 11 of Cherchneff & Dwek show their results in unmixed zones, wherein t_{max} for CO appears to occur near 180 days. It may then decline monotonically if carbon condensation had been included in those models. Both problems must be solved simultaneously.

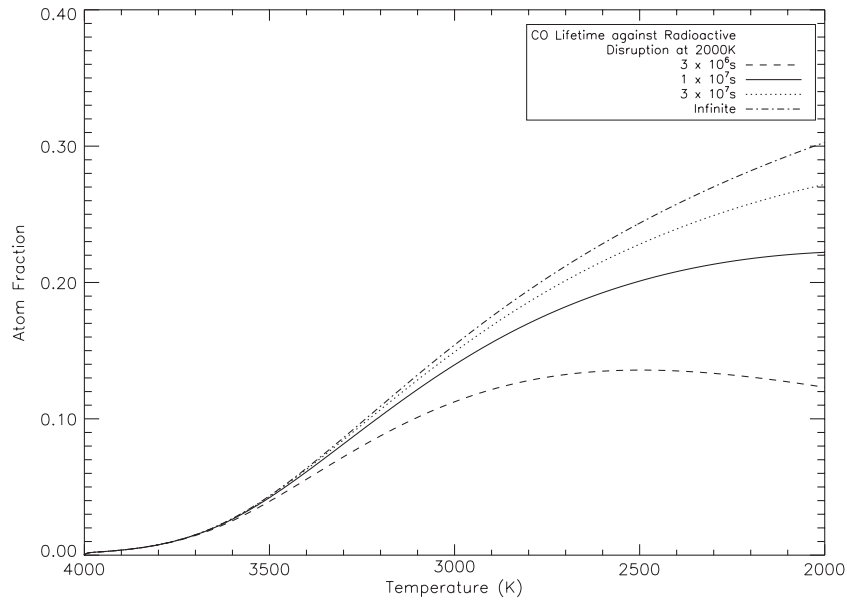


Figure 1. Atom fraction of CO molecules in the C/O shell as a function of time (from Deneault et al. 2006) for C/O = 2/3 and differing values of the CO dissociation lifetime owing to radioactivity. If radioactivity intensifies, τ_{CO} shortens, and the CO abundance curve lowers. For $\tau_{\text{CO}} = 3 \times 10^6$ s (bottom curve), Compton electrons cause CO abundance to reach a maximum near $T = 2500$ K. In SN 1987A, $\tau_{\text{CO}} = 10^5$ s to 3×10^6 s, more intense than even the bottom of these curves.

There exist additional creation and destruction channels for CO molecules than Equation (1) displays (Liu & Dalgarno 1995; Cherchneff & Dwek 2009). Inclusion of all possibilities requires a full network, but the leading terms shown in Equation (1) appear to be an adequate simplification for understanding the early CO abundance. The reaction-rate tables in Cherchneff & Dwek (2009) suggest that after significant O_2 has formed, the reaction $\text{O}_2 + \text{C} \rightarrow \text{CO} + \text{O}$ becomes a faster way to convert free C into CO; but I omit it at early times in Equation (1) because CO grows faster by radiative association than O_2 at early times. Essential additional collisional destruction mechanisms occur in two circumstances: first, if T is so high that thermal dissociation of CO is faster than radioactive dissociation; second, if He, Ne, or Ar is overabundant in the shell in question. In that case destruction of CO by He^+ , Ne^+ , or perhaps Ar^+ is faster than direct destruction by Compton electrons (see Section 3). If so the lifetime τ_{CO} in Equation (1) must be shortened appropriately, usually dramatically, lessening n_{CO} . It should also be noted that Cherchneff & Dwek (2009) suggest a different CO-destroying sequence for formation of the C_2 and C_3 molecules that initiate the linear carbon chains (Clayton et al. 1999, 2001). They suggest that C_2 and longer linear carbon chains are created much earlier (near 5000 K) by hot destruction of the small CO abundance by the endoergic reaction $\text{CO} + \text{C} \rightarrow \text{C}_2 + \text{O}$ rather than by radiative association of free C. Neither do I evaluate that possibility here except to remark that fast photodissociation of C_n will counteract this source to a significant degree. My goal is a simplified understanding of the abundances for the uninitiated about O-rich carbon condensation.

2.1. Examples at $t = t_{\text{max}}$ of $n_{\text{C(g)}}$, n_{O} , and n_{CO} if No Solid C has Condensed

I next draw inferences from published numerical evaluations of $n_{\text{CO}}(t)$ because they demonstrate the robustness of free C being more abundant than CO, a cornerstone of C condensation.

Deneault et al. (2006) integrated the time-dependent equations numerically within an expanding SN shell of pure C+O gas having C/O = 2/3 in bulk. Their result, reproduced in Figure 1, is instructive. The atom fraction $n_{\text{CO}}(t)$ used there is

defined as the number of CO molecules in a given volume divided by the total number of atoms in that same volume; and in this pure C+O zone, $n_{\text{CO}}(t)$ begins at zero and can grow no greater than 0.4 (which would be achieved for C/O = 2/3 if a representative five atoms ($2\text{C} + 3\text{O}$) form two CO molecules and one free O atom, giving CO the maximum atom fraction $n_{\text{CO}} = 2/5 = 0.4$). Figure 1 shows the evolution of $n_{\text{CO}}(t)$ from $t = 0$ to $t = 10^7$ s for some differing values of the radioactive dissociation lifetime τ_{CO} for CO molecules. Consider these published examples and others derived below to gain understanding of the high abundance of free carbon even though C/O < 1.

The topmost of the curves in Figure 1, the dot-dashed infinite- τ_{CO} case (zero radioactive dissociation), shows that as t advances to 10^7 s the CO abundance fraction has grown steadily in this example to $n_{\text{CO}}(t) = 0.3$ as temperature simultaneously has fallen. n_{CO} has not yet reached its maximum possible CO atom fraction (0.4 for C/O = 2/3). The atom fraction $n_{\text{CO}}(t) = 0.3$ at 10^7 s represents 3 CO molecules per ten atoms ($4\text{C} + 6\text{O}$ if C/O = 2/3), leaving a free-C atom fraction $n_{\text{C}} = 1/10$ and a free-atom ratio $n_{\text{O}}/n_{\text{C}} = 3.0$. In this evaluation $n_{\text{CO}}/n_{\text{C}} = 3.0$, showing that CO can exceed free C in the absence of radioactive dissociation. Interestingly nonetheless, free C remains abundant at $t = 10^7$ s even in the absence of radioactivity. The first 10^7 s are inadequate to oxidize all free C owing to the quantum slowness of the radiative association reaction that forms CO. Chemical equilibrium certainly could not apply in SNII interiors at $t = 10^7$ s even in the absence of radioactivity because in that equilibrium state all C would be oxidized. Therefore, the correct way to regard the effect of radioactivity in SNII is that it significantly *increases* the abundance of free C rather than *causes all* free C. The kinetic rates used for this calculation are given by Clayton et al. (1999, 2001). The model takes free C to associate radiatively into linear carbon chains $\text{C}_2, \text{C}_3, \dots, \text{C}_N$ up to a critical length C_N , where N is the shortest linear chain that rapidly and spontaneously makes an isomeric transition to a closed-ring molecule C_{Nr} . The closed-ring molecule C_{Nr} is important to this model because closed-ring molecules are, like graphite, much more resistant to oxidation than are linear carbon chains. The isomerization into ringed carbon provides the seed nucleus

for growth of carbon grains in O-rich gas. This can continue only as long as free C exists, because given enough time at high temperature, carbon must eventually oxidize, considering that if chemical equilibrium is achieved all carbon becomes CO. Clayton's (2011) second necessary condition for carbon condensation in O-rich supernovae states: *Chemical reaction networks associating C atoms into carbon solids must be kinetically faster than their oxidation.* That condition cannot be met except while abundant free C still exists.

The bottom curve of Figure 1 adds radioactivity using the moderate lifetime $\tau_{\text{CO}} = 3 \times 10^6$ s (30 \times longer than the initial radioactive lifetime in SN 1987A). Using this lifetime τ_{CO} one sees that t_{max} for n_{CO} occurs near $T = 2500$ K, and that maximum is very broad and slowly declining as T approaches 2000 K. From Equation (2) the value of that maximum is $n_{\text{CO}}(t_{\text{max}}) = n_{\text{C}} n_{\text{O}} k_{\text{CO}} \tau_{\text{CO}}$, which must therefore approximate the atom fraction $n_{\text{CO}}(t_{\text{max}}) = 0.13$ shown in Figure 1. The atom fractions for C and O are therefore required by mass balance to be $n_{\text{C}} = 0.27$ and $n_{\text{O}} = 0.47$ if bulk C/O = 2/3. Clearly at t_{max} the atom fraction n_{C} exceeds n_{CO} by a factor 2.1 (most C is free) and $n_{\text{O}}/n_{\text{C}} = 1.7$ even with this slow dissociation rate for CO. Despite modest O richness of that computation, $n_{\text{C}}/n_{\text{CO}} = 2$, more free C than CO.

These computed examples assume C, O, and CO to be the only species. They demonstrate that having more O than C does not cause most carbon to become CO. That belief has caused many to doubt that C can condense in O-rich gas.

The abundances at t_{max} can be found for arbitrary values of bulk O/C with a little algebra. Choosing bulk abundances similar to those for completed He burning, and letting bulk oxygen exceed bulk carbon in abundance by the factor $R = O/C$, let bulk oxygen density be O and bulk carbon density be $C = O/R$. If condensed carbon is not yet significant, mass conservation among gaseous n_{O} , n_{CO} , and n_{C} requires

$$n_{\text{O}} + n_{\text{CO}} = R(n_{\text{C}} + n_{\text{CO}}), \quad (3)$$

where n are the gaseous number densities of those species. The vanishing of Equation (1) is solved after some algebra by the quadratic equation

$$n_{\text{CO}}^2 - [(1 + 1/R)O + (k_{\text{CO}} \cdot \tau_{\text{CO}}) - 1]n_{\text{CO}} + O^2/R = 0. \quad (4)$$

Solving for n_{CO} requires knowing the dissociation lifetime τ_{CO} at the time of maximum CO density, and that can be achieved only by a full numerical integration. But because that maximum is broad, the estimation for τ_{CO} is not extremely sensitive. Using as an example CO radioactive lifetime $\tau_{\text{CO}} = 20$ days = 3×10^6 s, $O/C = R = 2$, and $O = 1 \times 10^{10}$ cm $^{-3}$ at $t = t_{\text{max}}$ yields $n_{\text{O}} = 8.37 \times 10^9$ cm $^{-3}$, $n_{\text{C}} = 3.37 \times 10^9$ cm $^{-3}$, $n_{\text{CO}} = 1.63 \times 10^9$ cm $^{-3}$. Free n_{C} exceeds n_{CO} by the factor 2.1, showing most carbon to be free despite oxygen being twice as abundant as carbon. Because this is at maximum, other times n_{CO} is even smaller. This result has only weak dependence on the value of τ_{CO} .

Even with a more O-rich composition $O/C = R = 100$ but the same $\tau_{\text{CO}} = 20$ days, free n_{C} exceeds n_{CO} by the factor 1.7 at t_{max} . Such large O/C value in some inner supernova shells still yields $n_{\text{C}} > n_{\text{CO}}$, showing that free carbon robustly exceeds CO if the CO Compton electron lifetime is shorter than two months. Readers must appreciate that the dominance of free C over CO is the driver for C condensation in supernovae. There still exists the instinct among those influenced by chemical equilibrium that, if $O > C$, n_{CO} will greatly exceed $n_{\text{C(g)}}$,

and these examples attempt to rebalance chemical instincts in profoundly radioactive supernova interiors.

In following examples, I will take bulk oxygen $O = 1 \times 10^{10}$ cm $^{-3}$ at $t = t_{\text{max}}$ as a comparison condition. The bulk carbon density $C = O/R$ may differ. A unit volume at that time retains its bulk contents if it is taken subsequently as a coexpanding reference frame. I do this for simplicity among comparisons.

2.2. Solutions at $t = t_{\text{max}}$ for $n_{\text{C(g)}}$, n_{O} , and n_{CO} if $n_{\text{C(s)}}$ has Condensed

Important changes happen to n_{CO} after enough graphite nuclei have been formed that they begin to significantly deplete the free carbon. The linear carbon chains themselves are of such low abundance (Clayton et al. 2001, Figure 2) that they play no role in carbon mass balance. Oxidation of C_n by free O prevents their abundance from growing large. For example, Clayton et al. (2001, Figure 2) displays fractional abundance of linear C_{10} to be about 10^{-22} at $O/C = 5 = R$. Isomerization from linear chain to carbon rings forms graphite nucleations that are less rapidly oxidized and that serve for carbon capture chains that deplete free carbon as they grow in size and number. For the sake of example, if atom density is 10^{10} cm $^{-3}$ and $R = 5$, the density of C_{10} rings would be $n_{\text{C}_{10}} = 10^{-12}$ cm $^{-3}$, so that if the lifetime against isomerization is assumed to be $\tau = 1$ s, the rate of appearance if C_{10} rings would be $dn_{\text{C}_{10r}}/dt = 10^{-12}$ cm $^{-3}$ s $^{-1}$. During the first 10^7 s of expansion that rate of ring creation could generate 10^{-5} graphite nucleations in the comoving volume that initially held $n_{\text{C(g)}} = 1.6 \times 10^9$ cm $^{-3}$. Evidently those graphite grains could grow to contain up to 10^{14} atoms each, a radius $a = 10$ μ m, by depleting all of the carbon. If the isomerizing chain is taken to be C_8 rather than C_{10} , its 100-fold greater abundance could result in 10^{12} -atom graphite spheres, comparable to the largest found in meteorites. This rather fanciful calculation has a scientific point. It illustrates that the numbers seem reasonable for growing the rare micron-sized graphite SUNOCONs that are discovered in meteorites. Population control (Clayton et al. 2001, Section 3.2; Clayton 2011) is also illustrated in that if the nucleations were not rare, they could exhaust $n_{\text{C(g)}}$ long before growing to discovered meteoritic sizes. For that very reason the He-burning shell (wherein $C > O$) could not grow large graphite spheres, exactly opposite to instincts honed on equilibrium chemistry. There is poetry in the effect of oxidation, which was anticipated to make carbon condensation impossible in O-rich gas, but which actually enables graphite to grow large. This example may assist visualization of requirements for large graphite spheres grow in O-rich gas. Clayton (2011) has reviewed the necessary conditions for this to happen.

Whenever a significant fraction of bulk carbon has been able to condense at that time t_{max} at which n_{CO} would have reached a maximum in the absence of condensation, the condensed fraction $n_{\text{C(s)}}$ of solid carbon will have depleted carbon from both gas phases, $n_{\text{C(g)}}$ and n_{CO} . As a result, n_{CO} could steadily decline owing to depletion of free C onto growing graphite grains. Comparing solutions at the same reference time t_{max} at which n_{CO} would have reached maximum in the absence of condensation, bulk oxygen $O = 10^{10}$ cm $^{-3}$ at the reference time. Equation (3) expressing mass balance must be altered to $n_{\text{O}} + n_{\text{CO}} = R(n_{\text{C(g)}} + n_{\text{CO}} + n_{\text{C(s)}}$), where $n_{\text{C(s)}}$ is the number density of solid condensed carbon atoms; but Equation (1) is no longer correct because dn_{CO}/dt no longer vanishes when condensation begins; rather both it and $dn_{\text{C(g)}/dt}$ must be negative when $dn_{\text{C(s)}/dt}$ is positive owing to mass balance. Although modeling requires a full numerical integration, the consequences can be

illustrated by a simple approximation: assume that depletion from the gas occurs in the ratio Equation (2), $dn_{\text{CO}}/dn_{\text{C(g)}} = n_{\text{CO}}/n_{\text{C(g)}} = n_{\text{O}}k_{\text{CO}}\tau_{\text{CO}}$, so that Equation (2) remains valid for the gas ratio, and by representing the number of solid (S) carbon atoms as being a factor Ξ greater than the density of gaseous carbon; namely, $n_{\text{C(S)}} = \Xi n_{\text{C(g)}}$ in the enlarged Equation (3). The quadratic equation (4) would then become

$$n_{\text{CO}}^2 - [(1 + 1/R)\text{O} + (1 + \Xi)(k_{\text{CO}}\tau_{\text{CO}})^{-1}]n_{\text{CO}} + \text{O}^2/R = 0. \quad (5)$$

An example evaluation having about 99% of carbon condensed ($\Xi = 100$), but with no oxygen condensed and no significant oxidation rate of the condensed carbon, and using the same parameters as above where no solid carbon existed, $\tau_{\text{CO}} = 20$ days, $\text{O}/\text{C} = R = 2$, and $\text{O} = 1 \times 10^{10} \text{ cm}^{-3}$ at the same time t_{max} at which the purely gaseous nebula achieves maximum CO density, yields $n_{\text{O}} = 1.0 \times 10^{10} \text{ cm}^{-3}$, $n_{\text{C(S)}} = 4.92 \times 10^9 \text{ cm}^{-3}$, $n_{\text{C(g)}} = 4.9 \times 10^7 \text{ cm}^{-3}$, $n_{\text{CO}} = 2.8 \times 10^7 \text{ cm}^{-3}$. Free $n_{\text{C(g)}}$ would still exceed n_{CO} by the factor 1.8 at t_{max} , but both would be smaller by a factor of roughly 70 than in the previous example having no condensed carbon. Although the approximations can be criticized, this calculation nonetheless suggests how n_{CO} and $n_{\text{C(g)}}$ are both depleted by condensing graphite.

Numerical models with condensation have been computed by Deneault et al. (2006) to evaluate the kinetic rate of growth of graphite (and SiC) solids. Observationally, such supernovae would show a faster rate of decline of the abundance of CO molecules than does the purely gaseous-molecule SN nebula because condensation (increasing $n_{\text{C(S)}}$) slows the rate of C+O association leading to CO in Equation (1). Depletion of free carbon occurs faster than the radioactive depletion lifetime of CO, which remains τ_{CO} . It follows that the time of maximum CO abundance will occur earlier whenever carbon is depleting onto solids. A numerical integration such as Deneault et al. (2006) is required to compute the rate of carbon condensation to yield $\Xi(t)$, but considerable physical understanding can be achieved by considering additional numerical examples.

That carbon depletion overwhelmingly occurs onto grains if a significant fraction of carbon already exists in grains is illustrated by the following rough estimate. The rate of depletion of gaseous carbon onto grains is $dn_{\text{C(g)}}(\text{S})/dt = -n_{\text{C(g)}}v_{\text{C}}\Sigma$, where $\Sigma = \sum_j A_j$ is the sum of the cross-sectional areas of existing graphite grains and v_{C} is the average thermal velocity of free carbon atoms, and (S) denotes that the carbon depletion is into solids (S). The ratio of that rate of depletion onto grains to the rate of depletion by associating C with O, $dn_{\text{C(g)}}(\text{CO})/dt = -n_{\text{C(g)}}n_{\text{O}}k_{\text{CO}}$, is large. Dividing out the common factors $n_{\text{C(g)}}v_{\text{C}}$ reveals the ratio of rates to be $dn_{\text{C(g)}}(\text{S})/dn_{\text{C(g)}}(\text{CO}) = \Sigma/[n_{\text{O}} 10^{-22} \text{ cm}^2]$, where 10^{-22} cm^2 is the approximate value of the C+O radiative association cross section. If bulk $C = 10^9 \text{ cm}^{-3}$ ($R = 10$) at the reference time t_{max} of Section 2.1 examples, having half of C contained in grains could be represented by $n_{\text{G}} = 5 \text{ cm}^{-3}$ grains of radius $0.1 \mu\text{m}$ containing 10^8 C atoms each, in which case the depletion ratio $dn_{\text{C(g)}}(\text{S})/dn_{\text{C(g)}}(\text{CO}) = (5 \text{ cm}^{-3})(10^{-9} \text{ cm}^2)/(10^{10} \text{ cm}^{-3})(10^{-22} \text{ cm}^2) = 5000$; that is, free carbon overwhelmingly sticks to existing graphite grains if it is already half condensed. If the sample five grains are taken instead to be tenfold smaller, i.e., $a = 0.01 \mu\text{m}$, $n_{\text{C(S)}}$ in grains would amount to only 0.05% of carbon, but nonetheless enough that 92% of $n_{\text{C(g)}}$ depletes onto grains. Understanding rapid depletion onto grains follows also from the lifetime of free carbon against depletion, $\tau_{\text{C(S)}} = (v_{\text{C}} \Sigma)^{-1} = 5000\text{s}$ using again the example of five grains cm^{-3} of $0.1 \mu\text{m}$ each. This lifetime is much less than the CO lifetime $\tau_{\text{CO}} = 10^6 \text{ s}$ against Compton

electrons. These results show that one can expect $n_{\text{C(g)}}$ to deplete more rapidly than n_{CO} whenever at least 10^{-3} of C is condensed. The rate of destruction of CO still depends on its lifetime τ_{CO} . If depletion of free C is either small or not included, Figure 4 of Cherchneff & Dwek (2009) shows the large late increase in ejected CO abundance that would occur after radioactivity ceases to actively dissociate CO.

Of course, the assumptions made for this example are not accurate. For one thing, condensed graphite oxidizes at a nonzero rate, creating CO. The example takes that rate to be negligible. Some researchers suspect it could be rapid enough to prevent graphite condensation in expanding O-rich gas. Clayton (2011, p. 164) highlighted this issue by listing it among the key issues for future research; namely, *5.7 How does gaseous O and/or O₂ attack condensing graphite?* Even a slow rate of oxidation for small graphite grains would provide a second source term for CO molecules in Equation (1). That source term need not be very large to exceed the association of free carbon with oxygen, invalidating the assumptions leading to Equation (5). What prevents carbon from reaching oxidized chemical equilibrium, however, is the quenching associated with expansion and cooling of the supernova gas, which is too fast for chemical rates to keep up. Therefore, in the end, metastable graphite simply survives oxidation.

2.3 Expansion, Decreasing Density, and Decaying Radioactivity

The stationary condition, Equation (1), for the CO abundance at t_{max} would not remain a solution as time passes owing to expansion and to the temporal weakening of ^{56}Co radioactivity. Because of the rapid expansion, each number density n declines as t^{-3} in addition to its changes owing to chemical reactions. The radioactive lifetime τ_{CO} is not altered by instantaneous expansion, only by the decay of the radioactivity owing to the time required for expansion. The radioactive lifetime τ_{CO} is proportional to $\exp(t/111 \text{ days})$, so if τ_{CO} were 10 days at $t_{\text{max}} = 3 \text{ mos}$, it will lengthen to $\tau_{\text{CO}} = 118 \text{ days}$ at $t = 1 \text{ yr}$. These aspects of the temporal response of n_{CO} can be displayed. Let N_{CO} and N_{C} be the numbers of CO and C in a comoving volume so their numbers do not change owing to expansion (similarly to the atom fractions). The association rate $\text{C} + \text{O} \rightarrow \text{CO}$ must contain the oxygen number density however, $n_{\text{O}}(t) = N_{\text{O}}/(t_{\text{max}}/t)^3$, since collision rate is proportional to the flux of O within which C moves. In that comoving volume, the energy per CO ion pair remains unaltered by lower density; therefore τ_{CO} changes only owing to the exponential radioactivity decline of ^{56}Co ; say $\tau_{\text{CO}}(t) = \tau_{\text{CO}}(t_{\text{m}})e^{(t-t_{\text{m}})/\tau_{56}}$, where τ_{56} is 111 days. So the terms of Equation (1) have the temporal form

$$dN_{\text{CO}}/dt = K[(t_{\text{max}}/t)^3 - \exp(-(t - t_{\text{max}})/\tau_{56})], \quad (6)$$

where $K = N_{\text{C}}N_{\text{O}}k_{\text{CO}}$. Equation (6) approaches zero as $t \rightarrow t_{\text{max}}$, as it must. As time advances past t_{max} , at which $dN_{\text{CO}}/dt = 0$, the shape of this rate of change for N_{CO} is easily evaluated. It initially becomes strongly negative owing to rapid decrease of the factor $(t_{\text{max}}/t)^3$ causing N_{CO} to decline. The decline steepens, then becomes less steep and eventually levels off at a smaller value of N_{CO} , accounting for much its shape. See Figure 7 of Liu & Dalgarno (1995), Figure 1 of Clayton et al. (1999), or Figure 4 of Deneault et al. (2006). Note that if the nucleations of ringed C_n as the seeds needed for rapid graphite growth already exist at 100 days, their capture of C provides another loss term to n_{C} . That reduction of n_{C} also drives down CO,

which follows n_C down while it maintains a near constant ratio n_{CO}/n_C , as Equation (5) demonstrated. This may be part of the observed rapid decline of CO abundance between days 100 and 300 in SN 1987A (Liu & Dalgarno 1995). Keep in mind that the *unmixed* CO shell immediately under the He-burning shell is necessarily the location of the observed CO molecules (see Section 3), and it can contain up to 0.3 solar masses of carbon bathed in oxygen in a 25 solar mass SNII, which could associate up to 0.7 solar masses of CO molecules, some 70 times more than actually observed. The corresponding quantity is three times smaller in 15 solar mass SNII, but still much more than observed. So it is the *smallness* of the observed CO mass that must be understood, presenting a challenge especially to those who expect that almost all C must emerge oxidized.

2.4. Effective Binding Energies of Molecules in Thermal Equilibrium

In thermal equilibrium among C and O atoms and CO molecules, the ground state ratio of the number of CO molecules to the number of C atoms is given by statistical mechanics:

$$n_{CO}/n_C = n_O(h^2/2\pi M kT)^{3/2} \exp(B_{CO}/kT), \quad (7)$$

where $M = 12 \times 16/(12+16)$ amu is the reduced mass of C and O and $B_{CO} = 11.1$ eV is the CO binding energy. The equilibrium ratio n_{CO}/n_C depends linearly on the free-oxygen abundance, but at $T = 2000$ K it would always be much greater than unity if oxygen were more abundant than carbon ($n_O/n_C > 1$). The ratio n_{CO}/n_C is actually much smaller in young SNII interiors, however, owing to CO dissociation by Compton electrons. We showed in the preceding examples that $n_{CO}/n_C < 1$ at $t = t_{max}$ in the steady state between CO formation by association and dissociation owing to high flux (Clayton & The 1991; Liu & Dalgarno 1995) of energetic Compton electrons that will exist in almost all SNII. That steady-state balance is expressed by Equation (1) with τ_{CO} being the fast-electron dissociation lifetime. Equation (1) establishes a ratio less than unity, typically $n_{CO}/n_C = 1/2$.

In a state of thermal equilibrium, a steady state would exist between association and *thermal* dissociation; namely

$$n_{CO}/n_C = n_O k_{CO} \tau_{th}, \quad (8)$$

where $\tau_{th}(T)$ is the thermal dissociation rate of CO at the ambient temperature.

Despite radioactive dissociation I suggest that LTE might nonetheless be employed meaningfully if the binding energy B_{CO} is artificially reduced to a value to make the thermal-equilibrium ratio n_{CO}/n_C close to the known dynamic ratio (Equation (2)). That will be the case if B_{CO} is given the value that produces thermal dissociation rate at temperature T equal to the rate of electron-induced dissociation owing to radioactive effects.

Setting Equations (7) and (8) equal to one another and dividing out the oxygen abundance yields the value B^*_{CO} of the “effective binding energy” given by

$$\exp(B^*_{CO}/kT) = k_{CO} \tau_{CO} (h^2/2\pi M kT)^{-3/2}. \quad (9)$$

Near $T = 2000$ K, when condensation will be occurring, and using $\tau_{CO} = 10^6$ s for the sake of numerical example, that solution (Equation (9)) would be $B^*_{CO} = 6.3$ eV. At $T = 1800$ K

it would be $B^*_{CO} = 5.7$ eV. This procedure yields the binding that CO would have in order that its thermal dissociation rate τ_{th} equal $\tau_{CO} = 10^6$ s. One could even evaluate Equation (9) at every time step and for every value of τ_{CO} . Doing so would emulate this important effect of radioactivity in an equilibrium cooling curve while allowing CO molecular abundance to remain a valid participant in an equilibrium calculation. We discuss in Section 4 how equilibrium condensation might be validly useful for understanding mineralogy of SNII grains (SUNOCONs).

I acknowledge a weak point here; I have assumed that O atoms remain undepleted for the sake of these approximations. But Cherchneff & Dwek (2009) found (see Figure 10(b)) that by $t = 300$ days about 10% of O has been converted to O_2 , which exceeds the CO abundance after 250 days and continues to grow O_2 until it comprises most of bulk O by 900 days. Also, O_2 provides another source term for CO in Equation (1) through the reaction $C + O_2 \rightarrow CO + O$. In a complete analysis these affect both the rate of formation of CO molecules and the rate of oxidation of linear C_n chains. Thus, the analysis here is not accurate after $O_2/O > 10^{-4}$; but I think the main lessons of analysis will remain. I speak of early times because to grow a graphite grain containing 10^{11} C atoms seems to require that its growth begins early, when the density is greater.

3. MICROSCOPIC MIXING AND THE OBSERVED CO AND SiO ABUNDANCES IN SN1987A

Surprisingly, the controversy over the physical circumstances of the condensation of carbon SUNOCONs is constrained by the observations of significant masses of CO and SiO molecules in Type II supernovae. SN 1987A has provided the best data, but it appears typical of SNII. Larger early masses of CO (Petuchowski et al. 1989) and perhaps SiO declined to about $2 \times 10^{-3} m_{sun}$ of CO and $5 \times 10^{-4} m_{sun}$ of SiO owing to the dissociative effects (Liu & Dalgarno 1995, 1996; Cherchneff & Dwek 2009, 2010) of Compton electrons created by the ^{56}Co gamma radiation diffusing from the interior (Clayton and The 1991). Those final CO and SiO masses will now be shown to pose severe constraints on the common hope (Zinner 1998; Travaglio et al. 1999) that the He-burning shell in Type II SN can microscopically mix with the deep ^{15}N -rich, ^{28}Si -rich, and ^{44}Ti -rich Si/S inner shell prior to condensing the graphite and SiC SUNOCONs that have been discovered in carbonaceous chondrites. Mixing those two shells would destroy the SiO molecule and mixing of He-burning shell with the C/O shell would destroy the CO molecules formed therein.

3.1. The Destructive Role of He and Ne on CO and SiO Molecules

That a significant abundance of He and/or Ne greatly increases the rate of radioactive dissociation of CO and SiO has been known for a long time (e.g., Lepp et al. 1990; Cherchneff & Dwek 2009). The new emphasis here is the constraint that this threat imposes on the circumstances of SUNOCON condensation. Microscopic mixing prior to SUNOCON condensation has been the solution proposed for some time (Nittler et al. 1996; Travaglio et al. 1999; Zinner 1998). It is implausible because insufficient time for such mixing exists (Deneault et al. 2003), and also because SN remnants (e.g., Cas A) are observed to have differing compositions in differing zones. I call attention here to another obstacle, the problem that mixing the helium-burning shell (where $C > O$) with the inner shells would also mix

He, its most abundant element (sometimes therefore called the He/C/O shell), into those shells. Significant He admixed into other shells would rapidly destroy any CO and SiO molecules located there. He atoms are rapidly ionized by the Compton electrons to about the 1% level. Those He⁺ ions would destroy CO by the fast dissociative charge-exchange reaction $\text{CO} + \text{He}^+ \rightarrow \text{He} + \text{C}^+ + \text{O}$, whose fast rate given by the UMIST database (Woodall et al. 2007) is $k_{\text{He}^+} = 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The lifetime of the CO molecule against this reaction is $\tau_{\text{CO}} = (k_{\text{He}^+} n_{\text{He}^+})^{-1}$; therefore, if the He atom fraction following mixing is β and the He ionization fraction is typically $\text{He}^+/\text{He} = 0.01$ in radioactive SNII, then $\tau_{\text{CO}} = (0.14\beta)^{-1} \text{ s}$ at a time when the number density of atoms is 10^{10} cm^{-3} . If the admixed He atom fraction β is greater than 10^{-4} this lifetime τ_{CO} is shorter than the 10^5 s early lifetime of CO against Compton electrons in SN1987A. This must be true of any substantial admixtures of the He/C/O shell into any other shell, especially if the mixing is to yield a bulk C/O > 1, because He is the most abundant element of the He/C/O shell. For this reason the abundance n_{CO} will essentially vanish not only in the He-burning shell but also in all inner shells admixed significantly with matter from the He-burning shell. These He-polluted shells will not eject enough CO to account for $2 \times 10^{-3} m_{\text{sun}}$ of observed CO. That CO mass necessarily has originated within the He-free *unmixed* C/O shell. Thus, it would be necessary to assume that the postulated microscopic mixing of the He/C/O shell avoids the C/O shell immediately beneath it.

Similarly the reaction $\text{He}^+ + \text{SiO} \rightarrow \text{Si}^+ + \text{O} + \text{He}$ would destroy SiO if the SiO forming zone is microscopically admixed with He/O/C shell matter. That fast chemical reaction rate (Woodall et al. 2007) is $k_{\text{He}^+} = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Therefore, He/C/O shell matter cannot have mixed into the bulk of any shell responsible for the SiO molecules. In a little noted remark, Liu & Dalgarno (1994) stated almost two decades ago, “The SiO mass would be drastically reduced to the order of $10^{-9} m_{\text{sun}}$ if SiO were mixed with helium.”

I call attention to this destruction with respect to postulated molecular mixing that has been hypothesized to precede SUNOCON condensation. The core Si/S/O shell, near where fusion during oxygen burning builds the ²⁸Si and ⁴⁴Ti excesses that characterize carbon SUNOCONs (Nittler et al. 1996; Zinner 1998; Clayton & Nittler 2004), is also the only location of a Si abundance sufficiently great to form the $10^{-3} m_{\text{sun}}$ of SiO molecules observed early in SN 1987A. See Figure 10(b) of Cherchneff & Dwek (2009). Necessarily *the SiO molecular mass observed in SNII is created within the Si/S/O core*. As a consequence it can be inferred that the SUNOCON condensation zone (Si/S/O) had not been mixed with the He/O/C shell prior to condensation.

The ONeMg shell immediately atop the SiSO shell, which is actively burning carbon, synthesizing Ne and Mg at explosion time, faces a similar mixing constraint. It cannot be the main source of SiO molecules because its second most abundant element, Ne, is ionized to 1% or so by the Compton electrons. Electron-hungry Ne⁺, like He⁺, is rapidly destructive of SiO molecules via analogous reactions to those above with He⁺; namely $\text{SiO} + \text{Ne}^+ \rightarrow \text{Ne} + \text{Si}^+ + \text{O}$ and $\text{SiO} + \text{Ne}^+ \rightarrow \text{Ne} + \text{SiO}^+$ followed by dissociative recombination $\text{SiO}^+ + e \rightarrow \text{Si} + \text{O}$ (Liu & Dalgarno 1994, 1996). It can be concluded that the adjacent Si/S/O shell, where the SUNOCONs originate, and the O/Ne/C shell have not mixed microscopically with one another, for doing so would also destroy the SiO molecules formed in the Si/S/O shell.

These consequences derived from observed molecular abundances of CO and SiO in SN 1987A thereby attest negatively to the suggestion of molecular-level mixing of supernova shells prior to their SUNOCON condensation. To salvage the unphysical hypothesis of mixing He/C/O and Si/S shells at the atomic level prior to condensation, one must now resort to a more restrictive postulate; namely, that those shells finely mix in portions that condense the SUNOCONs but do not mix at all in other portions that yield the observed SiO abundance. The finely mixed portions and the totally unmixed portions must have comparable masses. Inasmuch as atomic-scale mixing of supernova interiors during their first year also seems physically impossible, it seems advisable to discard that hypothesis. It has been stimulated not only by an “apparent chemical need” but also by injudicious wording by supernova modelers that has referred to turbulent transposition of fluid masses within the radial flow as “mixing,” and supported unintentionally by chemical modelers who postulate “complete mixing” of compositions in order to compare numerical results from differing chemical reaction codes. More circumspect wording would be helpful.

Finally, note that Cherchneff & Dwek (2010) also describe the He⁺ ion as hindering formation of linear carbon chains C_n . Their reactions with C_n have much the same effect as oxidation by free O (Clayton et al. 2001); namely $C_n + \text{He}^+ \rightarrow C_{n-1} + \text{He} + \text{C}^+$. But free O and He⁺ only slow in this way the progression to larger C_n ; their reactions with C_n lower the chain abundances, but do not destroy them (Clayton et al. 2001). Even at low abundance, when a ringed isomer of C_n is reached, depletion of free C by their capture of C atoms seems capable of growing rare large graphite SUNOCONs, as found in meteorites. Only if He/O > 10 (taking He⁺/He = 0.01) do the He⁺ reactions compete with oxidation. That condition appears to limit the importance of He⁺ reactions to the He/C/O shell and to the alpha-rich freezeout (Woosley et al. 1973) in the core.

One hears doubts about the carbon chains providing nucleations for SUNOCON growth because linear C_n is of such low abundance—very much lower than that of CO molecules (e.g., Cherchneff & Dwek 2009, p. 659). That situation is exactly the one required to grow very large SUNOCONs. Were seed carbon condensation nuclei too numerous, they would condense many small graphite particles instead of a few large ones as observed. The low abundances of linear C_n provide *population control*, the restriction of the grain population necessary for a very few large particles to exhaust free carbon (Clayton 2011, Section 5.5, p. 163). Concerns about the low abundance of C_n are relevant for their contribution to optical opacity, which places emphasis on the numbers of grains, but not for the rare existence of large micron-sized SUNOCONs.

It seems more likely that the SUNOCONs are composite grains that initially condense in ²⁸Si-rich and ⁴⁴Ti-rich inner zones, especially if compression of that matter by the reverse shock from the H envelope occurs (Deneault et al. 2003), and later acquire many small grains of graphite, CN, SiN, and AlN from the He/C/O shell, as described by Deneault et al. (2003). These composites then apparently remained hot long enough to anneal to single crystals. But this type of accumulation needs careful study by modelers of molecular chemistry, modelers of post-explosive turbulent grain transport, and researchers of SUNOCON inhomogeneities (e.g., Croat et al. 2003). Attempting to argue this here is far beyond the scope of this paper. Although these isotopic questions ultimately require explanations, it is not my responsibility to do so here.

My attempt is to focus researchers on understanding the issues of condensation of carbonaceous grains.

3.2. Nonradioactive SNII and CO and SiO Molecules

SN 1987A is the prototype for studies of core-collapse supernovae because so much observational information exists about it. In SN 1987A substantial molecular masses of CO and SiO were observed. In SN 1987A the radioactivity was intense because the nucleosynthesis yield of ^{56}Ni was large, $0.075 M_{\text{sun}}$, producing a short value of τ_{CO} near 10^5 s (Liu & Dalgarno 1995; Clayton 2011). The ^{56}Co decay (in both SNIa and in SNII) was the historic source of most ^{56}Fe in the galaxy via the radioactive chain $^{56}\text{Ni} \rightarrow ^{56}\text{Co} \rightarrow ^{56}\text{Fe}$. Iron was revealed thereby to be a rare “radiogenic element,” a realization that impacted a great many issues of astrophysics (Clayton 1999). One must express caution about assuming SN 1987A to be typical of all SNII.

Solar system SUNOCONs did not arise from SN 1987A of course, but rather from a lengthy history of presolar galactic SNII, having differing masses, differing yields of ^{56}Ni , and differing turbulent histories. Some supernovae within that spectrum could therefore have produced differing SUNOCONs than SN 1987A would have done. Perhaps some fraction of SNII could succeed to mix microscopically and yield the SUNOCONs but little CO and SiO, whereas another fraction similar to SN 1987A does not mix microscopically and produces SiO and CO molecules but no SUNOCONs. Such arguments cannot be addressed here, but they seem likely to collapse from implausibility. The most extreme possibility with respect to these issues is very massive core-collapse supernovae whose radioactive cores are consumed by fallback into a central black hole. Lacking the radioactive chain $^{56}\text{Ni} \rightarrow ^{56}\text{Co} \rightarrow ^{56}\text{Fe}$ in the ejected mass could leave the CO and SiO molecules stable. The arguments of this paper disappear for such an event, which would eject a very large mass of CO gas.

4. APPROACH TO CHEMICAL EQUILIBRIUM

Because free carbon exists in supernova interiors even when $\text{C/O} < 1$, it may condense carbon SUNOCONs (Clayton et al. 1999, 2001; Deneault et al. 2003, 2006; Clayton 2011) by depletion of liberated C onto graphite nucleations. The mineralogy of the final condensates is awkward to judge with kinetic networks, however, because the favored final minerals depend on the local chemical abundances and on the binding energies of various competing solids. This dependence exists if sufficient chemical reactions can occur between solids and the gaseous species to allow their modification into more stable solids. The validity of that assumption underlies the idea of chemical equilibrium; but it might not be valid in SNII. Inability to change mineral chemistry may leave them frozen in the first forms to be created by the kinetic growth of solids. I call attention to this issue without solving it. Whether mineral grain A, formed kinetically before $T = 2000$ K, can be altered to more stable mineral grain B during the remaining expansion will depend on details of that alteration.

If sufficient gas reactions do allow changes of mineral phases, I express in this section possible grounds for using thermodynamic equilibrium to guide the identification of thermodynamically stable solids despite the disequilibrium of SNII interiors. Computed equilibria do not identify *what will occur*; they identify which condensed phases would be stable in a global thermal equilibrium (which cannot be achieved in supernovae because of insufficient time). Calculations of mineral equilibrium within

hot gases have been employed to calculate the first mineral phases to condense in a historical but incorrect model of the early solar system containing hot gases whose temperature was slowly lowered in successively cooler states of thermal equilibrium (Grossman 1972); and also in models of slowly cooling carbon-star ejecta (Lodders & Fegley 1997). Such a picture of quasistatic cooling in equilibrium is unworkable in supernova II interiors for two major reasons: (1) the supernova state changes are too rapid for establishment of equilibrium; (2) oxygen’s greater abundance than carbon throughout their evolved cores would cause equilibrium calculations to find that carbon exists in the chemical form of oxidized carbon monoxide, a stable final product owing to its very large (11.1 eV) dissociation energy. Point (2) motivates common opinion that carbon cannot condense from O-rich gas (e.g., Nittler et al. 1996; Zinner 1998). The resulting stalemate may be overcome if it can become scientifically accepted that C can condense within O-rich gas, and this paper aims to be another step toward that goal.

Reaction kinetics above show that $n_{\text{CO}}/n_{\text{C}}$ does not change greatly from its value near 0.5 at t_{max} as the temperature falls further (except at later times when radioactivity weakens and abundant CO can grow (Cherchneff & Dwek 2009)). Both n_{CO} and n_{C} decline if ringed-carbon nucleations capture free C as they grow into graphite grains. Computed chemical equilibria will, on the other hand, be dominated by CO molecules, so they might seem useless. Section 2.4, Equation (9) demonstrated how that dominance of CO can be correctly cured in equilibrium by using an effective binding energy B_{CO}^* rather than its laboratory binding energy in order to endow the CO molecule with its actual dissociation rate in SNII rather than its thermal dissociation rate. Reducing equilibrium abundances of n_{CO} in this way corresponds to what actually occurs in SNII and allows carbon to be considered among equilibrium condensed phases.

One may then examine in what structures carbon would condense in a thermal equilibrium in which CO were kept small by the forgoing modification of its binding energy. That computational experiment has already been done by Ebel & Grossman (2001), and I call attention to their interesting but little known results for the general subject of the present paper. Ebel & Grossman (2001) showed almost immediately after the introduction of our theory for carbon condensation in O-rich gas that although $\text{C/O} > 0.98$ is required in order that graphite be a stable mineral (i.e., that graphite would condense in thermal equilibrium), if the CO molecule is excluded from final products graphite appears abundantly in stable chemical equilibrium provided that $\text{C/O} > 0.49$. That new stability boundary, which allows carbon condensation in O-rich gas up to $\text{O/C} = 2$, occurs because the modified chemical quasiequilibrium computations would in that case form a large abundance for the CO_2 molecule instead of the excluded CO molecules. That explains why excess free carbon can make graphite only if $\text{C/O} > 0.5$. Already this result, surprising for many, demonstrates that the old rule-of-thumb, that graphite can condense only if $\text{C} > \text{O}$, is not valid when the CO molecular abundance is not allowed grow large.

But this result too is unphysical for young supernova interiors for a different reason; namely, in SNII there are no sufficiently fast chemical paths to the formation of CO_2 . I know of no work that expects CO_2 to be made abundantly in SNII. In their study of molecular reactions, Cherchneff & Dwek (2009) list three-body reactions of significance at higher density, $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$, and reactions between minor gas components, $\text{CO} + \text{SiO} \rightarrow \text{CO}_2 + \text{Si}$; but their computed abundances for CO_2 are negligible (see their Figure 10(b)) in comparison

to the huge amount called for by the thermal quasiequilibrium calculation in which abundant CO_2 is allowed.

From these considerations we conclude that not only CO but also CO_2 must be excluded from having significant abundance in final products of thermal equilibrium in SNII. Very similar issues occur for the abundance of the SiO molecule in SNII (Liu & Dalgarno 1994; Cherchneff & Dwek 2009, 2010). The abundance of SiO is also, like that of CO, roughly 1% of the maximum value it might have had if all Si oxidized. Both gaseous oxides have small abundances owing to radioactive dissociation by the Compton electrons (and by He^+ in SN zones containing He). To simulate the effect of radioactivity in calculated equilibrium abundances one may also adjust the effective binding energy of SiO to be near 6 eV.

Because *all* molecules are physically constrained to be of low abundance in SNII, Ebel & Grossman (2001) recalculated an equilibrium that *excluded all molecules*. This situation is technically a chemical *quasiequilibrium*, because complete equilibrium is prevented by an external constraint (on abundances of CO, CO_2 , SiO, and SiO_2). If those steady-state molecular abundances are constrained to be small, say perhaps 1% of the demands of chemical equilibrium, it is preferable to eliminate them entirely from chemical equilibrium calculations, in which their large equilibrium abundances otherwise would have excessive influence on the mass balances of C and O.

Ebel & Grossman (2001) found that when all gaseous molecular species (in particular CO, CO_2 , SiO, SiO_2) are prevented from forming, graphite becomes an abundant equilibrium condensate below 2110 K in a cooling O-rich gas of solar composition (O/C = 2.35). Their Figure 6 shows their result. Graphite condensation would be followed by condensation of solid silica (SiO_2) at 1860 K, and by various other oxygen-bearing phases. Note that quasiequilibrium stability allows graphite and silica to condense simultaneously from the same gas. These path-breaking results by Ebel & Grossman (2001) show that graphite condensation in an O-rich gas is not contrary to chemical equilibrium but is quite consistent with a quasiequilibrium having restricted molecular abundances. The concept of carbon condensation in O-rich gas is rendered more plausible by their results. Their quasiequilibrium calculations also remind us that chemical condensates other than carbon are simultaneously occurring. The surprising stability of silica at high temperature found by Ebel & Grossman (2001) suggests relevance of detailed proposals by Cherchneff & Dwek (2010); in particular, the formation of molecular clusters $(\text{SiO})_n$ followed by further oxidation to the stable SiO_2 solids. In the same spirit, one seeks understanding of the common TiC subgrains discovered within graphite SUNOCONs and studied by Croat et al. (2003). Kinetic pathways to those TiC condensates do exist, and the chemical equilibrium calculations may exert influence on the understanding of observed SUNOCONs. Their Figure 6 shows that despite graphite condensation, TiC is not among the quasiequilibrium condensates, where Ti condenses as oxides.

4.1. The Scientific Thrust: Equilibrium Application to Kinetic Condensation

The preceding paragraph illustrates that the concept of chemical quasiequilibrium may have relevance as part of a multi-pronged path to understanding thermal condensation. Owing to severe restriction on molecular abundances, the condensing system might be describable as a *quasiequilibrium*. Various quasiequilibrium possibilities include the following type: two abundance pools, say A and B, contrast in that all reactions

within A must be kinetically computed, along with the kinetic rate at which atoms transfer from the A pool into the B pool. The B pool macroscopic structures may be in equilibrium with each other under the exchange of atoms of the A pool. To illustrate, if a cluster of $(\text{SiO})_n$ molecules joins a graphite grain, little can be expected to happen because they form no joint condensate that would be stable above 1500 K. Quasiequilibrium suggests that they will simply re-separate. Many readers may recognize the example of the Si-burning quasiequilibrium of nucleosynthesis (e.g., Clayton 1968, Chapter 7), in which the A pool consists of free nucleons and alpha particles and all nuclei having $A < 28$, whose abundances must be calculated by kinetic reaction rates, whereas the B pool consists of all nuclei having $A > 27$ and in which those B nuclei are in equilibrium with one another under exchanges of p , n , α . The abundances of the B nuclei can then be successfully computed from quasiequilibrium. This success greatly clarified the burning conceptually. Woosley et al. (1973) showed that this is preceded by smaller quasiequilibrium clusters that merge as the system evolves.

In the supernova condensation chemistry, all free atoms and molecules would be in pool A, totally out of equilibrium owing to external constraints. Pool A includes the linear carbon chains C_n that provide the nucleations of ringed C_n upon which macroscopic grains grow by accretion of free C atoms. None of these species are in quasiequilibrium. The pool B, whose macroscopic graphite grains grow by carbon capture chains from the ringed C_n , may exist to some degree in a chemical quasiequilibrium with the other grain condensates under reactions with gaseous atoms and molecules. Even if a quasiequilibrium is not established, it validly delimits the mineral stability fields. The free molecules of pool A are unlikely to be abundant enough to have a significant effect on the mass balance of those chemical elements because they are externally constrained to be rare. The mass balance of each chemical element is probably dominated by condensates in pool B. Such a picture endows chemical quasiequilibrium with enough plausibility to make its results relevant, even if they are not exact. Consider some examples.

In true quasiequilibrium the condensates would necessarily gain and lose gas particles at equal rates, thereby maintaining a carbon vapor pressure even after free C has been depleted into grains; e.g., $G_{n+1} \rightarrow G_n + C$, where G_n is a graphite grain. Ebel & Grossman showed in their Figure 7, which is based on the SNII O/Si zone composition (O > Si > Mg > C), that if large molecular abundances are excluded by radioactivity, graphite and SiO_2 liquid would both become stable below 2240 K despite the zone M5 huge O/C = 300 ratio. The small graphite abundance seen in their Figure 7 is simply a consequence of that zone's small bulk carbon abundance; but essentially all C has turned to graphite. Their Figure 7 also shows that graphite would become unstable below 1940 K to the transition to MgCO_3 . Whether that transition would actually happen in SNII would require a dynamic calculation to ascertain whether graphite grains can kinetically evolve to MgCO_3 below 1940 K in the time available. Such reciprocal reactions, if they occur in SNII, allow a condensed mineral phase to transform to more stable phases as the temperature declines. As another example, condensed silica (SiO_2) becomes unstable to pyroxene (MgSiO_3) below 1700 K. But does sufficient flux of MgO molecules occur in SNII to drive that transition? Suppose only for sake of illustration that kinetic reactions seed the expanding gas with separate MgO and SiO_2 grains. These might transform to pyroxene in quasiequilibrium by MgO vapor pressure joining the SiO_2 solids and/or by SiO_2

or SiO molecular vapor pressure joining the MgO solids. Given a long time at $T = 1600$ K, this would indeed happen, but vapor pressure is probably too slow in the rapid cooling of SN. In reality it seems more likely that the pyroxene growth would happen, if at all, on condensed liquid silica as gaseous $(\text{MgO})_n$ molecular clusters are absorbed by it. If so, the amount of pyroxene would perhaps grow only to the amount called for by the chemical potentials of quasiequilibrium, making it appear that quasiequilibrium had been established even though it had not. Once a solid condensate exists in SNII, it may be able to change composition only by adding more elements to it and letting hot equilibration do its work. In any case, this Figure 7 from Ebel & Grossman's calculations confirms that graphite can be stably condensed in that O/Si/Mg/C O-rich SNII zone provided that its molecular abundances are constrained to be small. Their Figure 7 seems to this writer to demolish the belief that carbon SUNOCONS cannot condense if $O > C$. So despite justifiable doubt about the validity of quasiequilibrium, calculations of that state, as Ebel & Grossman have done, may nonetheless provide a mineral guide to what the hot chemistry of SN grain growth is likely to provide if sufficiently fast kinetic pathways exist. It is evident that quasiequilibrium calculations within supernova zones can be usefully iterated with kinetic flows to help infer what is likely to condense there.

4.2. Summary Remarks

The main criticism of chemical equilibrium abundances is that one cannot just assume that whenever equilibrium calls, nature will find a way to follow, as it would do if unlimited time were available at given temperature and density. Supernova interiors expand and cool rapidly, quenching many reaction paths. So the state of chemical quasiequilibrium can never *predict* the condensate minerals within supernovae. But when kinetic reactions suggest, as they do, that graphite, SiC, TiC, and MgSiO_3 , for example, can be produced via direct kinetic paths, chemical equilibrium calculations can confirm or deny those phases to be thermodynamically stable within supernova shells having more oxygen than carbon. Existence of a plausible path for formation plus stability against equilibrium chemical reactions can render that SUNOCON mineral plausible. Graphite SUNOCONS already merit that degree of acceptance.

What is the motivation for this discourse? At stake within the present sea of doubt over carbon condensation in O-rich gas is finding a recipe for scientific progress. Progress in deciphering the enormous information content of SUNOCONS will accelerate when a consensus can be reached on where and how carbon can condense within supernovae. Those that model SNII chemistry need the energetic science by the meteoritic community to decide what has happened. Reaching consensus will be the appropriate time to address the isotopic evidence of the incorporation of atoms from the He-burning shell into the SUNOCONS from the Si-rich core. The isotopes within SUNOCONS present a great opportunity to diagnose the dynamics of young supernova remnants (e.g., Deneault et al. 2003). In the present work, I have attempted analytic demonstrations of some central issues relevant to the chemistry of the condensation problem, hoping that clearer understanding of those features can lessen resistance to a dynamic description of supernova chemistry and hydrodynamics. The evaluation must ultimately be numerical rather than analytic; but the willingness to work with a specific picture does depend on that picture seeming to be analytically plausible.

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