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CONDENSATION ONTO GRAINS IN THE OUTFLOWS FROM MASS-LOSING RED GIANTS

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ABSTRACT

We describe the conditions under which molecules condense onto already formed grains in the outer circumstellar envelopes of mass-losing red giants. Although there are a number of uncertain parameters, it is clear that condensation is particularly effective for species which can bind most tightly to the grains and in envelopes with large amounts of dust. For example, we can explain the presence of both ice and water vapor in the unusual circumstellar envelope of the mass-losing, oxygen-rich star, OH 231.8+4.2 (the "Rotten Egg"). In most stars with cool outflows, SiO is probably depleted onto grains, while condensation onto grains is not important for such well-studied species as CO, HCN, and H_2.

Models for the circumstellar envelope around OH 231.8+4.2 indicate a substantial mass-loss rate (10^{-4} to 10^{-5} $M_\odot$ yr^{-1}). Because this object is found in an open cluster (M46), we can deduce an initial mass for the central star of 3 $M_\odot$ from the turnoff point from the main sequence. The large amount of circumstellar material is consistent with a model in which we are witnessing an intermediate-mass star in the process of shedding enough material to become a stable white dwarf with less than a Chandrasekhar mass.

Subject headings: interstellar: grains — stars: circumstellar shells — stars: mass loss

I. INTRODUCTION

Mass loss from red giants is important both in the evolution of these stars and in replenishing the interstellar medium (see Zuckerman 1980). Grains form in the outflows from these stars, and radiation pressure on this dust is probably essential in driving the matter to infinity in most stars (see Jura 1984*a*). Therefore, a detailed understanding of the interaction between the gas and dust is critical for developing models of the outflows.

The formation and evolution of grains and their role in driving the mass loss is a very complex phenomenon; here we address just one aspect of this problem. Specifically, the question of grain formation is ignored, and we concentrate instead on subsequent condensation onto the grains as the matter flows to infinity. That is, after grains nucleate near the stars, they grow in part because of adsorption of gas-phase species, and here the adsorption process is discussed quantitatively.

The picture we envision is very simple. The grains and molecules are formed near the star in some quasi-equilibrium process. However, after the matter flows further away from the star, there are relatively few chemical reactions, and the abundances tend to "freezeout" (McCabe, Smith, and Clegg 1979; Lafont, Lucas, and Omont 1982; Glassgold and Huggins 1984) until photodissociation by ambient interstellar radiation becomes important (Goldreich and Scoville 1976; Jura and Morris 1981; Huggins and Glassgold 1982). The additional physical process considered in this paper results from the cooling of the grains as they flow away from the star; molecules that initially do not condense onto the grains can do so far from the star. We show that for some species this effect can be quite important in determining their gas-phase abundances in the outer circumstellar envelope.

One of the major motivations of this work is to understand the physical conditions and molecular abundances in the outflows from these stars so that one can refine models for stellar evolution and the enrichment of the interstellar medium. For example the unusual oxygen-rich star, OH 231.8+4.2, has both H_2O and OH masers (Turner 1971; Morris and Knapp 1976; Genzel and Downes 1977; Morris and Bowers 1980; Morris, Bowers, and Turner 1982; Bowers and Morris 1984) and an infrared absorption feature at 3.1 μm characteristic of ice (Soifer *et al.* 1980); here, we explain how water can be found in both the gas and solid phases. Also, we address the question of why, for many stars, the observed amount of thermal SiO is much less than predicted on the basis of simple models for freezeout chemistry (Morris *et al.* 1979).

A further motivation for this work is to help understand gas-grain interactions in general. This is important for the interstellar medium where condensation onto grains is an extremely important process in determining the gas-phase abundances which control the gas temperature and molecular composition.

In § II, we sketch the basic physical model, while in § III detailed numerical results are presented. Section IV describes our general conclusions. It should be emphasized that since many of the important physical parameters such as sticking probabilities and binding energies onto circumstellar grains are not well known, our calculations are only suggestive and are not, by themselves, decisive demonstrations that a particular element should be substantially depleted.

II. MODEL FOR CONDENSATION ONTO GRAINS

We consider the outer circumstellar envelope where the material has already been accelerated to its terminal outflow velocity, v. The gas-phase density, n_X, of species X is governed by the equation of continuity with sources and sinks. The sink term is condensation onto grains while the source term is thermal evaporation from the grains. The expected drift velocities of the grains through the gas are usually less than 5 km s^{-1}, and therefore sputtering is assumed to be unimportant (see Draine and Salpeter 1979). We also ignore the chemical production and destruction of molecules, and we may therefore write:

$$\partial/\partial r(f_X v) = -f_X(n_{gr}\sigma_{gr} v_{dr})\alpha + (1 - f_X)R_{evap}(T_{gr}) \, . \quad (1)$$

In equation (1), f_X is the fraction of species X that is in the gas phase, n_{gr} is the density of grains, σ_{gr} is the grain cross section, v_{dr} is the drift velocity between the grains and the gas, α is the sticking probability of molecules onto the grains, and $R_{evap}(T_{gr})$ is the rate of evaporation of a single molecule off a grain of temperature T_{gr}. Because the grains are driven supersonically through the gas (Goldreich and Scoville 1976), the rate of gas-grain collisions is governed by v_{dr}.

In principle we ought to consider a range of grain sizes. But because the amount of depletion depends upon one parameter, the integrated value of $n_{gr}\sigma_{gr}v_{dr}$, and because relatively little is known about the many parameters that are involved, we asume a single grain size. One result of this assumption is that we neglect grain-grain collisions and the possible resulting desorption of mantle material. That is, the speed of a grain through the gas depends upon its size (see eq. [9] below) and if all the grains are the same size, there are no grain-grain collisions. In any case, because the rate of grain-grain collisions depends upon deviations from the average grain velocity, this effect might be small for all but the extreme grain sizes.

Now consider the source term in equation (1). For classical evaporation we generalize the results of Léger (1983) who gives a rate for CO evaporating from a grain for temperatures in the range of interest (30–300 K) as:

$$R_{evap}(T_{gr}) = 3 \times 10^{13}\ \mathrm{s}^{-1} \exp{(-T_{bind}/T_{gr})} \, .$$

In equation (2), kT_{bind} is the binding energy of the molecule onto the grain. While different species have different (usually larger) coefficients in front of the exponential compared to the rate for CO (see, for example, Léger, Jura, and Omont 1984), by far the most important term is the exponential. The rate of classical evaporation is generally so large that unless $T_{gr} \leq T_{bind}/50$, condensation onto grains is not important. Therefore, in describing the condensation process, we only consider variations in T_{bind} for different substances and ignore variations among species of the constant coefficient in equation (2). Of course it is possible for some species to become chemically incorporated into the grains, in which case the source term in equation (1) is unimportant, but in the absence of any useful information, we ignore this process. Also, it should be emphasized that T_{bind} is a function of the grain material and can only be roughly estimated from current knowledge.

To compute the grain temperatures in the outer circumstellar envelope, we assume the usual balance between heating by absorption of photons from the central star (perhaps reprocessed by dust grains very near that star) and reradiation in the infrared. A convenient way to express the dust temperature for material whose radiative cross section varies as ν^p is (Sopka *et al.* 1984):

$$T_{gr} = \left(\frac{r}{D}\right)^{-2/(4+p)} \left(\frac{h}{k}\right) \left[\left\{\frac{c^2}{[8\pi h g(p)]}\right\} \int \nu^p F_\nu \, d\nu\right]^{1/(4+p)} . \quad (3)$$

In equation (3), D is the distance to the star from the Sun, h and k are Planck's and Boltzmann's constants, c is the speed of light, F_ν is the flux received at Earth and $g(p)$ is the integral:

$$g(p) = \int (y^{(3+p)})/(e^y - 1) dy \, . \quad (4)$$

To within 10%, for $p > 0$, $g(p) = (p + 3)!$ Equation (3) shows that T_{gr} can be expressed as a power law with r.

We present a simplified solution to equation (1) which captures the essential results. Since slight changes in T_{gr} lead to very large changes in R_{evap}, there is some characteristic condensation radius, r_0, such that for $r < r_0$, there is effectively no condensation while for $r > r_0$, almost every molecule that sticks onto the grain remains there. We estimate r_0 from the condition that the characteristic flow time (r/v) is equal to the evaporation time R_{evap}^{-1}. With this simplification ($R_{evap} = \infty$ for $r < r_0$), the solution to equation (1) for species X in the region $r > r_{0,X}$ is:

$$f_X(r) = \exp{\{-\delta[(1/r_{0,X}) - (1/r)]\}} \, . \quad (5)$$

In equation (5), δ is a scale length constructed from parameters in equation (1). Specifically, if $n_{gr} = \dot{N}_{gr}/(4\pi r^2 v)$ for a spherically symmetric outflow, then:

$$\delta = \alpha \dot{N}_{gr}\sigma_{gr} v_{dr}/(4\pi v^2) \, . \quad (6)$$

Let $f(\infty)$ denote the fraction of a species that remains in the gas phase. We define a parameter τ_{UV} which is a rough measure of the geometrical column-density of grains between r_0 and ∞: between r_0 and ∞:

$$\tau_{UV}(r_0) = \dot{N}_{gr}\sigma_{gr} Q_{UV}/(4\pi r_0 v) \, , \quad (7)$$

where $Q_{UV} \approx 1$. Therefore,

$$f(\infty) = \exp{[-\alpha(v_{dr}/v)\tau_{UV}(r_0)/Q_{UV}]} \, . \quad (8)$$

Furthermore, we may write (see, for example, Kwan and Hill 1977) that:

$$v_{dr} = [Q_{IR} L_* v/(\dot{M}c)]^{1/2} \, . \quad (9)$$

In equation (9), Q_{IR} is the intensity-weighted average ratio of optical to geometric cross section for the grains in the outer circumstellar envelope, L_* is the luminosity of the central star, and $\dot{M}$ is the mass-loss rate. For those stars in which radiation pressure on the grains controls the radial momentum in the outflow, we may write that:

$$\dot{M}v = \beta L_*/c \, , \quad (10)$$

where β is a parameter which is usually of order unity or less (Jura 1983*b*, 1984*a*). Finally,

$$f(\infty) = \exp{[-\alpha\tau_{UV}(r_0) Q_{IR}{}^{1/2}\beta^{-1/2} Q_{UV}{}^{-1}]} \, . \quad (11)$$

We use equation (11) to estimate depletions of different substances.

As a general rule, we expect that depletion onto grains is most important for large values of the parameter $\tau_{UV}(r_0)$. This number is large when there are a large number of dust grains and when the binding energy of the molecule onto the grain, kT_{bind} is sufficiently large that r_0 (see eq. [7]) is small.

Another route for the removal of molecules from the gas phase is photodissociation by ultraviolet photons in the ambient interstellar medium. Whether condensation or photodissociation actually dominates the decrease in molecules beyond a radius r_0 depends upon $\tau_{UV}(r_0)$. If this ultraviolet optical depth is small, photodissociation usually dominates. However, if the ultraviolet optical depth at r_0 is large, condensation can be important.

An important uncertainty is the sticking probability of molecules onto grains. For very low gas and grain temperatures, we may adopt $\alpha = 1$ (see Léger 1983). Because the grains may have typical temperatures of $\sim$100 K and the temperature equivalent to the collision between the gas phase molecule and the supersonically streaming grain may be as large as $\sim 10^4$ K, it is not clear that the sticking probability is nearly unity. The appropriate values of α range between 0.1 and 1 (Burke and Hollenbach 1983). However, because we are generally concerned with the situation where $kT_{\rm bind}$ is much greater than the kinetic energy of the adsorbed molecule, the larger values of α are probably appropriate. Since α for a given molecule depends only upon the grain composition and the drift velocity of the grains, α may be taken as a constant for a given circumstellar envelope.

III. NUMERICAL APPLICATIONS

In Table 1, we list condensation temperatures for pure substances. We consider species in Table 1 that are of interest because of their high cosmic abundances, because they are observable in a circumstellar envelope, or because they can be useful for comparing circumstellar and interstellar gas-phase abundances. It should be emphasized that our values of $T_{\rm bind}$ are sensitive to the nature of the grain onto which the molecule is condensing, and the results in Table 1 are at best only roughly representative of the true values of this quantity. For some molecules of interest, such as SiS, we are unable to find appropriate values of $T_{\rm bind}$, and we cannot make any quantitative estimate of the depletion.

In order to assess the potential importance of condensation of a particular molecule onto grains in a circumstellar envelope, we consider a characteristic condensation radius of 10^{16} cm and a typical outflow velocity of 15 km s^{-1} to give a flow time of 6.7×10^9 s. Using equation (2), we find that condensation is important for $T_{\rm gr} \leq T_{\rm bind}/54$. Since this critical temperature is only logarithmically dependent upon the assumed condensation radius, we adopt it as the criterion for the occurrence of significant adsorption. (For example, even for an outflow time of 7×10^{10} s, the temperature at which condensation becomes important is $T_{\rm bind}/56$, only slightly different from the above result.) One must then estimate the grain temperature as a function of radius around the star in order to determine which species are likely to condense.

a) IRC +10216

This object is perhaps the best studied mass-losing carbon-rich star. Here, we describe our results as much as possible in terms of observed parameters, such as angle, ϕ, on the sky, and we rely as little as possible on the (uncertain) distance to this object. From Kwan and Linke (1982), the momentum in the mass loss is equal to the momentum in the radiation so we may adopt $\beta = 1$. According to Jura (1983*a*), the ultraviolet optical depth can be inferred from the angular distribution of molecules such as HCN, and it seems appropriate to adopt $\tau_{\rm UV}(20'') = 2$ (see, for example, Huggins, Glassgold, and Morris 1984), with $\tau_{\rm UV}$ varying as ϕ^{-1}. From Kwan and Linke (1982) we take $Q_{\rm IR} = 0.02$, and therefore it is likely that $Q_{\rm UV} = 1$. With these parameters and from equation (11), if $\alpha = 0.1$, then condensation is important, that is, $f(\infty) < 0.5$, for $\phi_0 < 0\overset{\prime\prime}{.}82$, where ϕ_0 is the angular radius corresponding to the projected distance r_0 on the sky. If $\alpha = 1$, condensation is significant for $\phi_0 < 8\overset{\prime\prime}{.}2$.

We can now estimate the materials which will condense from the temperature distribution of the grains and from the criterion that $T_{\rm gr} = T_{\rm bind}/54$. From the data compiled by Sopka *et al.* (1984) applied to equation (3), we have $T_{\rm gr} = 290\phi^{-0.37}$, where ϕ is measured in arcsec. Consequently, from this temperature profile, we find that substances with $T_{\rm bind} > 16{,}800$ K and $T_{\rm bind} > 7200$ K can be significantly depleted onto grains in the outflow for $\alpha = 0.1$ and $\alpha = 1.0$, respectively. This means that relatively volatile molecules such as CO, HCN, and H_2 should remain in the gas phase, regardless of α, but there should be some significant depletion of more refractory species such as SiO. In Table 2 we list the depletions of various substances in the envelope of this star predicted using equation (1). These results indicate that there are observable species in the circumstellar outflow for which condensation onto grains is important. Because, for a given envelope, the only parameter which determines the relative amount of condensation is $T_{\rm bind}$, we do not list the degree of depletion onto grains for every species listed in Table 1.

TABLE 1

CONDENSATION TEMPERATURES OF DIFFERENT SPECIES

Substance	$T_{\rm bind}$	Reference
H_2	500	1
N_2	890	2
CO	1030	2
CH_4	1110	2
H_2S	2420	3
C_2H_2	2640	3
HCN	3690	2
NH_3	3750	2
H_2O	6070	2
K	10200	3
Zn	16000	3
SiO	29500	4
Sr	43200	3

REFERENCES.—(1) Hollenbach and Salpeter 1971. (2) Léger, Jura, and Omont 1984. (3) *Handbook of Chemistry and Physics 1982–1983*. (4) Nuth and Donn 1982.

TABLE 2

PREDICTED GAS PHASE DEPLETIONS AROUND IRC +10216

Substance	$f(\infty)$, $\alpha = 0.1$	$f(\infty)$, $\alpha = 1$
N_2	1.0	1.0
CO	1.0	1.0
HCN	0.99	0.93
NH_3	0.98	0.85
K	0.84	0.17
Zn	0.55	2.5×10^{-4}
SiO	0.064	$<10^{-10}$
Sr	1.6×10^{-4}	$<10^{-10}$

Finally, we note that our results for IRC +10216 should be representative of carbon-rich stars with substantial amounts of circumstellar dust. Similar depletions might also be found for oxygen-rich stars since the temperatures and amounts of dust often are quite similar to those used to describe IRC +10216.

b) OH 231.8+4.2

This is an extremely interesting oxygen-rich star with the unusual property among late-type evolved stars of having observable quantities of both gas phase and solid phase water.

We now compute the amount of condensation around this star in a fashion similar to that used above for IRC +10216. From the data compilation of Sopka *et al.* (1984) applied to equation (3), we adopt $T_{\rm gr} = 85\phi^{-0.37}$. An important question regarding this star is the appropriate value of β, the ratio of momentum in the mass loss compared to the momentum in the radiation. First, there is some uncertainty about the outflow velocity from this star. The OH maser emission exhibits a full width of 100 km s^{-1} indicating perhaps an outflow velocity of 50 km s^{-1}. This object is an highly anisotropic bipolar nebulae (Cohen and Frogel 1977), and it is quite possible that the outflow velocity varies with polar angle. That is, the bulk of the matter may flow outward near the equatorial plane with a substantially smaller velocity. Using the 7 m telescope at Bell Labs, Knapp and Morris (1984) report a line width of 137 ± 50 km s^{-1} for $J = 1$–0 emission from CO, consistent with the velocity extent of the OH. Zuckerman *et al.* (1984) used the 45 m Nobeyama telescope with much higher spatial resolution and a somewhat higher signal-to-noise ratio and found only a 30 km s^{-1} line width for the same CO transition from this star. This is consistent with the width of the ^{13}CO $J = 1$–0 line measured by Knapp (1984). Ukita and Morris (1983) report a line width of 30 km s^{-1} for an emission line from H_2S. In all cases except that of OH, the signal-to-noise ratio is too small to determine with any confidence whether the observed emission is sitting on top of a 100 km s^{-1} plateau. Therefore, while there is still considerable uncertainty, it seems that the bulk of the outflowing mass from OH 231.8+4.2 may have a relatively low speed of 20 km s^{-1}.

With an outflow speed of 20 km s^{-1} and a distance of 1300 pc, the 400 μm observations of Sopka *et al.* (1984) imply a dust loss rate of 2×10^{-6} $M_\odot$ yr^{-1} (1.3×10^{20} gm s^{-1}). Since the observed OH probably results from the photodissociation of H_2O, we write:

$$\dot{M}_d = \tau_{UV}(r)(4\pi r v)/\chi , \qquad (12)$$

where χ is the opacity per gram. If we adopt $\tau_{UV} = 2$ at the radius where photodissociation occurs (Huggins and Glassgold 1982), if this radius is 9.7×10^{16} cm (corresponding to 5″ at 1300 pc; Morris, Bowers, and Turner 1982), if $v = 20$ km s^{-1} and if $\chi_{UV} = 10^5$ cm^2 g^{-1} (corresponding to $\chi = 20$ cm^2 g^{-1} at 400 μm, and χ varying as $\lambda^{-1.1}$ from 400 μm to 1500 Å [see Sopka *et al.* 1984]), then $\dot{M}_d = 5 \times 10^{19}$ g $s^{-1} \approx 8 \times 10^{-7}$ $M_\odot$ yr^{-1} which is somewhat lower than the dust loss rate derived by Sopka *et al.* (1984). This mild discrepancy could be accounted for if v were indeed somewhat larger than 20 km s^{-1} (as it may well be in the OH maser region), or if χ is somewhat smaller than assumed.

We may also estimate the total amount of gas being lost by this star. If the outflow velocity is 20 km s^{-1}, then from measurements of the CO line emission, the hydrogen loss rate derived by Knapp and Morris (see also Morris 1975, 1980) should be scaled to 9×10^{-6} $M_\odot$ yr^{-1}. This value assumes a carbon-to-hydrogen molecule ratio of 3×10^{-4} and that all the carbon is contained within CO. This estimated minimum mass loss rate is only a factor of 3–10 greater than the mass loss rate of dust which, if accurate, is quite remarkable and is inconsistent with the assumed carbon abundance used to derive this result. That is, for a high mass-loss rate, we would expect CO to be stronger than observed. For lack of more information, we assume that the mass loss rate is between 10^{-5} and 10^{-4} $M_\odot$ yr^{-1}.

It should be noted that a relatively low hydrogen abundance in an oxygen-rich environment is not unprecedented in astrophysics. There exists at least one nova, DQ Her, where the hydrogen is extremely depleted relative to CNO yet [O] > [C] (Williams *et al.* 1978). Also, there exists a class of objects, the RT Ser stars (Payne-Gaposchkin 1964) which resemble novae but have outflow velocities of less than 50 km s^{-1}, not all that different from the outflow velocity inferred for OH 231.8+4.2.

In any case, if the total mass loss rate is 10^{-5} $M_\odot$ yr^{-1} and if $v = 20$ km s^{-1}, then because the luminosity is 4×10^3 $L_\odot$ (Kleinmann *et al.* 1978), we find that $\beta = 3$. For $M = 10^{-4}$ $M_\odot$ yr^{-1}, $\beta = 30$. We consider both cases in our calculations for the amount of circumstellar ice.

An unusual feature of OH 231.8+4.2 is that $\dot{M}_{\rm dust} \approx L/(vc)$ in contrast to the more usual result that for mass-losing red giants, $\dot{M}_{\rm dust} \approx 0.01L/(vc)$. This very large amount of dust for the amount of radiation means that it is particularly easy to condense material onto grains, because there is a large amount of cold dust near the star. This result need not violate the hypothesis that radiation pressure on grains is responsible for driving the matter to infinity if the star is evolving rapidly (Jura 1984*b*).

If the distance to this star is 1300 pc, if depletion of H_2O occurs at $T = 112$ K which obtains at $\phi = 0\overset{''}{.}5$ ($r_0 = 1.1 \times 10^{16}$ cm), if the dust loss rate is 1.3×10^{20} g s^{-1} (Sopka *et al.* 1984), and if $v = 20$ km s^{-1}, then the column density of refractory dust from the condensation radius to infinity, $\dot{M}_{\rm dust}/(4\pi r v)$ is 5×10^{-4} g cm^{-2}. Since absorption in the ice feature has an opacity between 1 and 2×10^4 cm^2 g^{-1} (Bertie, Labbé, and Whalley 1969; Léger *et al.* 1979), the ice optical depth could be as large as 5–10 if condensation were to occur at r_0 and if there is as much mass in ice as there is in refractory dust in the outflow (see Table 4 for the results of a more exact calculation). The observation of a deep ice feature with $\tau \approx 2$ is consistent with our model. Also, as indicated in Table 4 (see below), we still expect an appreciable amount of H_2O and OH to survive in the gas phase beyond the condensation radius. Therefore, we can understand how there are both water and ice in the circumstellar outflow. Finally, as described by Hagen, Tielens, and Greenberg (1983), the data are fully consistent with the unusually narrow ice feature observed toward OH 231.8+4.2 because the mantle of condensed ice is relatively pure H_2O since other molecules condense at different grain temperatures and, therefore, at different radii in the wind.

For a mass-loss rate between 10^{-5} and 10^{-4} $M_\odot$ yr^{-1}, the analysis by Ukita and Morris (1983) implies that $[H_2S]/[H_2]$ is between 5×10^{-6} and 5×10^{-7}, or perhaps 0.2 to 0.02 of all the sulfur is contained within this molecule in the gas phase. Because we expect only a small fraction of this molecule to condense onto grains, it seems that (*i*) the abundances toward OH 231.8+4.2 are quite anomalous, (*ii*) that simple models of "freezeout" gas phase chemistry which predict that most of the sulfur is contained within H_2S are not correct, or (*iii*) that the analysis of the H_2S data requires a more sophisticated treatment.

c) Ice in Oxygen-rich Stars

We now consider the general question of the presence of ice in oxygen-rich circumstellar outflows. Even though much of the oxygen is in the form of H_2O (Goldreich and Scoville 1976), this molecule normally does not condense onto grains sufficiently to produce an observable absorption feature at 3.1 μm (Merrill and Stein 1976). Here, we follow the procedure described above for computing $f(\infty)$ for circumstellar envelopes of representative stars. For the stars of interest, we take $Q_{\rm IR} = 0.02$, $Q_{\rm UV} = 1$, $p = 1.3$, and $\alpha = 1$. We adopt $\beta = 1$ unless otherwise specified, and the temperature profiles are computed from equation (3) using data from Sopka *et al.* (1984) and Werner *et al.* (1980). We ignore the variability of the stars and simply use the quoted fluxes. Finally we adopt

$$\tau_{UV}(1'') = \chi_{UV}\dot{M}_d/[4\pi r(1'')v] . \qquad (13)$$

TABLE 3

ASSUMED PROPERTIES OF MASS-LOSING OXYGEN-RICH STARS

Star	d (kpc)	T (1″)	τ_{UV} (1″)	β	v (km s^{-1})	$\dot{M}_d$ (M_0 yr^{-1})	r_0(Ice) (10^{16} cm)	Reference
OH 231.8+4.2	1.3	85	13	3, 30	20	10^{-6}	0.93	1
VY CMa	1.5	270	4.7	1	39	8×10^{-7}	23	1
IRC +10011	0.48	169	2.0	1	24	6×10^{-8}	2.1	1, 3
NML Cyg	2.0	220	5.2	0.2	23	7×10^{-7}	18	1
α Ori	0.2	574	1.1	0.01	15	10^{-8}	23	1
OH 26.5+0.6	0.7	130	7.0	2	15	7×10^{-8}	1.5	2, 3
OH 32.8−0.3	5.0	71	4.4	2	18	1.4×10^{-6}	2.2	2, 3

NOTE.—The optical depth at 1″,τ_{UV}, is derived using eq. (13) with the mass loss rate in dust and outflow velocity taken from the references. We assume that $\beta = 1$ for IRC+10011 and VY CMa. Other values of β are discussed in the text or are from detailed analysis of particular stars: NML Cyg (Morris and Jura 1983) and α Ori (Mauron *et al.* 1984).

REFERENCES.—(1) Sopka *et al.* 1984. (2) Werner *et al.* 1980. (3) Bowers and Hagen 1984.

In equation (13), $\dot{M}_d$ is the mass-loss rate of dust, χ_{UV} is the opacity per gram of the dust, assumed equal to 10^5 cm^2 g^{-1}, v is the outflow velocity of the dust, and $r(1'')$ is the physical separation from the star corresponding to 1″ at the assumed distance. Our estimated ultraviolet optical depths are consistent with the observed OH angular sizes and the model for the photodissociation of H_2O by Huggins and Glassgold (1982). In Table 3 we list the assumed parameters for the different stars.

Table 4 shows our estimates for depletion around the different stars. To determine the amount of ice, we assume that the mass-loss rate of H_2O equals the mass-loss rate of dust, and we use equation (5) to compute the optical depth in the ice feature:

$$\tau(3.1\ \mu m) = \frac{\chi(H_2O)\dot{M}_d}{(4\pi r_0 v)}\left\{1 - \left(\frac{r_0}{\delta}\right)\left[1 - \exp\left(\frac{-\delta}{r_0}\right)\right]\right\}. \quad (14)$$

If r_0 is taken to be the radius where $T_{gr} = T_{bind}/54$ and $\chi(H_2O) = 2 \times 10^4$ cm^2 g^{-1}, then one arrives at the optical depths and values of r_0 shown in Table 4. For the red giants we consider, r_0 ranges between 10^{16} and 3×10^{17} cm. The implication of these results is that in most cases, $\tau(3.1\ \mu m)$ is small. The ice feature is unusually strong in OH 231.8+4.2 because of the large amount of dust compared to the total luminosity. We predict a strength of $\tau(3.1\ \mu m) = 0.02$ toward OH 26.5+0.6, a value consistent with the upper limit of Forrest *et al.* (1978), while we predict an ice feature toward OH 32.8−0.3 ($\tau \approx 1$) which is roughly consistent with the detection by Roche and Aitken (1984). Finally, we do not attempt to reproduce the ice feature detected toward M1-92 (Eiroa, Hefele, and Zhong-yu 1983) since we have so little information about the mass loss from this star.

TABLE 4

CONDENSATION PARAMETERS FOR OXYGEN-RICH STARS

Star	$f(\infty)_{H_2O}$	$f(\infty)_{SiO}$	$\tau(H_2O)$
OH 231.8+4.2:			
$\beta = 3$	0.11	$<10^{-10}$	3.3
$\beta = 30$	0.49	$<10^{-10}$	1.5
VY CMa	0.94	1.4×10^{-2}	2.9×10^{-3}
IRC+10011	0.92	3.3×10^{-3}	5.0×10^{-3}
NML Cyg	0.76	1.1×10^{-8}	2.2×10^{-2}
α Ori	0.98	0.26	3.0×10^{-5}
OH 26.5+0.6	0.85	3.6×10^{-5}	2.3×10^{-2}
OH 32.8−0.3	0.17	$<10^{-10}$	1.9

d) SiO

This molecule is particularly interesting to consider because it has been studied extensively in circumstellar envelopes (Morris and Alcock 1977; Morris *et al.* 1979; Wolff and Carlson 1982), and it is generally found to have a mean gas-phase abundance a factor of 10^2–10^3 smaller than predicted by equilibrium models for "freezeout" chemistry near the photosphere of the star. It is often thought that the silicon is incorporated into grains either as silicates around the oxygen-rich stars or as SiC around the carbon-rich stars. However, the detailed kinetics of this process are uncertain. SiO maser emission usually arises close to the photosphere of the star, and the usual models require a gas-phase abundance of this species that contains most of the cosmically available silicon (see, for example, Langer and Watson 1984). Therefore, depletion onto grains during the outflow is a distinct possibility.

In this paper, we do not discuss the formation of grains. It is likely that significant amounts of silicon are incorporated into grains, but the efficiency of this process is quite uncertain because it does not proceed at thermodynamic equilibrium. Even if SiO does survive beyond the region where grains form, it can still be incorporated into grain mantles by simple adsorption.

One piece of evidence in favor of condensation of SiO onto grains in the outer envelope is from observations of IRC +10216. In the $J = 2$–1 line of SiO, Olofsson *et al.* (1982) have measured an upper limit to the size of the SiO emitting region of 15″; this is consistent with a relatively large gas-phase abundance near the star and then a very sharp decrease in the gas-phase concentration.

In order to consider these questions in more detail, we have estimated the degree of condensation of SiO for different stars, and the results are shown in Tables 2 and 4. Except for α Ori, we expect that the depletion of this molecule is very substantial. For α Ori, $\tau_{UV}(r_0) \ll 1$, and it is therefore quite possible that photodissociation of this molecule occurs quite close to the star (see Jura and Morris 1981). The absence of detectable radio SiO emission (Lambert and Vanden Bout 1978) may be a consequence of both adsorption and photodissociation.

Current large-beam observations of SiO are unable to determine whether there is a high abundance concentrated toward the central star or whether there is a low abundance with roughly an r^{-2} distribution of the material. Future observations with millimeter wave interferometers may distinguish between these two possibilities.

e) Minor Elements: K, Sr, *and* Zn

We now consider species which may be largely atomic in the outflows (see Tsuji 1973) and which are quite interesting for comparing interstellar and circumstellar depletions. Hagen, Stencel, and Dickinson (1983) have used optical observations of strontium to derive total amounts of circumstellar matter and therefore mass loss rates from late-type stars. One difficulty with this analysis is that it assumes that strontium has a gas-phase abundance equal to its cosmic value. This assumption is not necessarily valid in view of the strong depletion of this material in the interstellar medium (see Hagen, Stencel, and Dickinson 1983). Around α Ori, for example, even assuming that the grains do not form closer to the star than 1″ (Bloemhof, Townes, and Vanderwyck 1984) and using the parameters described in Table 3, we find that $f(\infty)$ for strontium is 0.25. Therefore, even if the grains do not incorporate strontium when they form, this element can be significantly depleted onto the grains in the outflow from the star.

Potassium is of interest because observations of this element around α Ori have been used to determine the mass-loss rate from this star (Jura and Morris 1981; Mauron *et al.* 1984). By applying equation (11) to this species and using the parameters in Tables 1 and 3, we find that $f(\infty) = 0.9$ for α Ori. Around this star, most of the potassium should remain in the gas phase, and this element can be used to study the overall gas loss rate.

Finally, zinc is probably mostly atomic in the outflows from stars (Tsuji 1973), and so it is of interest to compute its degree of condensation in an outflow. As we can see from Table 2, we do not necessarily expect a large depletion of this element; this is particularly noteworthy since zinc is generally undepleted in the interstellar gas (York and Jura 1982).

IV. CONCLUSIONS

In the outflows from red giants, condensation onto grains can be important in determining the abundances of molecules that survive in the gas phase. This effect is most important where there is a large amount of dust and for materials that can be tightly bound to the grains. Volatile species such as CO, HCN, and H_2 should generally remain in the gas phase, but more refractory molecules such as SiO can be largely condensed onto the solid material. Species with intermediate binding energies such as H_2O usually remain in the gas phase, but this is not always the case. The detection of ice around OH 231.8+4.2 is a consequence of the unusually large amount of cold material surrounding this star.

Since mass-losing red giants are the main source of matter ejected into the interstellar medium, it is instructive to compare our inferred circumstellar depletions with those observed in interstellar regions (see Spitzer and Jenkins 1975). Hydrogen is expected to be found in the gas phase because its binding energy is so low. Also, because carbon, nitrogen, and oxygen are primarily contained within CO and N_2, these elements are predicted not be be depleted, as is found in the interstellar gas (York *et al.* 1983; Jenkins and Shaya 1979; Jenkins, Jura, and Loewenstein 1983). On the other hand, we might expect silicon to be substantially contained within SiO and therefore significantly depleted as observed.

One difficulty is with sulfur which is generally not substantially depleted in the interstellar gas. From simple theoretical models, we might expect sulfur to be carried as SiS and CS in carbon-rich stars and as H_2S in oxygen-rich stars. Although we do not expect H_2S to be substantially depleted, the observed abundance of this molecule in OH 231.8+4.2 is not high enough to account for a solar abundance of this element. At the moment we cannot explain this result.

Finally, zinc and potassium may not be substantially depleted in the outflows from red giants, and they are also generally undepleted in the interstellar medium. The rough correlation that we infer between interstellar and circumstellar depletions (see Field 1974) suggests that similar processes govern the depletion in both environments.

We note that there is a substantial difference between evolved stars and protostars. Large amounts of ice are quite unusual in the outflows from oxygen-rich stars. The more common detections of ice in protostellar sources may reflect the presence of large amounts of material at large distances from the central star. That is, for an evolved object, the material is moving a high velocities (>10 km s^{-1}) even far ($>10^{16}$ cm) from the central star while around accreting stars, the velocities at large distance should be much lower so there can be much more cool matter. It should be interesting to investigate models for mass-accreting protostars with an analysis similar to that described here for mass-losing evolved stars.

We point out that in some outflows, it is possible that almost all of the H_2O is depleted onto grains and therefore photoproduction of OH is negligible so that some extremely red mass-losing oxygen-rich giants do not have associated OH masers.

Finally, we note that it has not been previously pointed out that OH 231.8+4.2 is within 12′ of the center of the open cluster M46 (= NGC 2437) which has a diameter of 27′ (Cuffey 1941). The physical association between the two systems is almost certainly real because of agreement of their radial velocities (both have $v_{\rm LSR} = 25$–30 km s^{-1}) and independent estimates of the distance of ~ 1.4 kpc (Bowers and Morris 1984; Cuffey 1941). We can use this result to estimate the mass of the progenitor star which must have just recently evolved off the main sequence, although, since OH 231.8+4.2 is a bipolar nebula, its evolution may be somewhat complex because it may be a binary (Morris 1981; Cohen 1984). In any case, since the spectrum of the stars at the turnoff point of M46 is A0 (Harris 1976; Mermilliod 1981) with stellar luminosities of $\sim 200\ L_\odot$, we estimate the main-sequence mass of the progenitor of OH 231.8+4.2 to be 3 $M_\odot$ (see, for example, Becker 1981). Since the mass-loss rate from OH 231.8+4.2 is between 10^{-5} and $10^{-4}\ M_\odot$ yr^{-1}, and since the mass-losing episode has lasted for at least 10^3 yr, it seems that this star has lost at least 0.01 to 0.1 $M_\odot$. It is entirely possible that during the entire mass-losing phase, OH 231.8+4.2 loses more than 1 $M_\odot$, and we may be witnessing an example of an intermediate-mass star evolving into a stable white dwarf with less than a Chandrasekhar mass.

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