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A STUDY OF THEORIES CONCERNED WITH THE FORMATION OF PRIMARY RADIOACTIVE PARTICLES IN A NUCLEAR FIREBALL

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The application of nucleation-condensation and coagulation theories to the formation of radioactive fallout particles in a nuclear fireball is reviewed. It is concluded that, due to inherent complexities in the mathematical formulation of the theories and to the lack of accurate input data, these theories are not well adapted to the development of a simple model of radioactive particle formation. As an alternative, a semi-empirical "kinetic" model of primary particle formation is presented. Suggestions are made as to how this model can be used to furnish input for a more sophisticated computer-programmed model of radioactive fallout formation.

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NAVAL ORDNANCE LABORATORY
SILVER SPRING, MARYLAND

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A Study of Theories Concerned with the Formation of Primary Radioactive Particles in a Nuclear Fireball

This report is concerned with the formation of radioactive fallout particles resulting from nuclear explosions. Previous reports have described laboratory investigations of the formation processes of radioactive particles. This report reviews the application of vapor condensation and particle coagulation theories to the problem of primary particle formation in a cooling nuclear fireball. On the basis of this study, a simplified model of primary particle formation is outlined and recommendations are made for the elaboration of the model by laboratory measurements and computer programming. Eventual incorporation of secondary particles into this described temperature-time history of the radionuclide composition and particle size distribution will provide (via DELFIC) a description of local fallout as a function of quantity of secondary particles injected (or height of burst).

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ROBERT ENNIS
Captain, USN
Commander

Albert Lightbody
A. LIGHTBODY
By direction

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INTRODUCTION

This report is concerned with the formation of radioactive particles in the cooling fireball of a nuclear explosion. The first part of this report is a review in which the physical-chemical processes occurring during the particle formation period are studied and in which the more important reports in the literature dealing with this subject are considered and their applicability to the formulation of a model of radioactive fallout particle formation is evaluated. The second part of the report outlines a simplified "kinetic" model of particle formation and discusses how this model can be used as an aid and guide in the construction of a more sophisticated, computerized model.

In this report the emphasis is upon "primary particles", i.e., those particles which are formed wholly by the condensation of vapor within the fireball and which are distinguished from the secondary particles which are formed from non-vaporized environmental material swept into the cooling fireball. Of particular interest is the possibility of formulating a model to predict the radiochemical composition of the primary particles as a function of the particle size distribution.

PARTICLE FORMATION BY VAPOR CONDENSATION

Throughout the discussion that follows we shall be concerned only with the formation of particles in a fireball which initially contains nothing but vaporized materials, both inert and radioactive, and into which no material is injected subsequent to the explosion. This situation is realized in the case of an air burst high enough above the ground so that no surface or other environmental material enters the fireball.

A theory of the nucleation and growth of liquid drops by condensation of a cooling vapor has been developed by Volmer, Becker and Doring, Frenkel, and others. Summaries of the development and present state of the theory are given by several authors. (1, 2, 3) The general features of the theory are as follows. As a vapor is cooled, the colliding vapor molecules have an increasing tendency to stick together to form small groups of molecules (or nuclei). Because the vapor pressure of such small droplets is quite high compared with the bulk liquid, the small droplets tend to evaporate as fast as they form until a comparatively high degree of supersaturation of the vapor is reached. At this point, a series of chance molecular collisions will produce nuclei of a sufficient size to be

stable. Once past this "potential barrier", the nuclei, by virtue of their lower vapor pressure, will grow rapidly in size via vapor condensation. The size of these critical nuclei at the potential barrier will vary with the conditions and characteristics of the vapor, but will in general be of the order of a few tens of molecules.

This theory, while simple in concept, is difficult to formulate in precise mathematical terms. In order to solve the basic differential equations, a simplifying assumption was made. In the actual case of vapor condensation, the droplets will continue to grow and the vapor will be depleted as the condensation process proceeds. However, for the solution of the equations, a steady state was assumed in which droplets are removed from the system after they have attained a certain size and the loss of material is compensated for by the arbitrary addition of single molecules to the vapor.

Another disadvantage of the Becker-Doring and Frenkel treatments is the occurrence of a constant whose nature and value is not known. Becker-Doring and Frenkel have assumed that the value of this constant is zero. On the other hand, Lothe and Pound have associated this constant with translational and rotational partition functions of the critical nuclei (4). However, the predictions of nucleation rates made using the Lothe-Pound approach appear to be several orders of magnitude too large.

An additional criticism has been concerned with the use of values for vapor pressures and surface tensions which have been measured for the bulk liquid and which may be significantly in error when applied to the very small nuclei. Also the effect of the latent heat, relea ed by the condensation of the vapor molecules, on the stability of the small droplets has been ignored. In spite of these shortcomings, the theory has been reasonably successful in predicting critical values of supersaturation required to initiate condensation of pure vapors and initial condensation rates.

In the application of nucleation theory to the vapors of a cooling fireball, additional difficulties arise of which the most important is the extreme sensitivity of the rate of nucleation to the degree of supersaturation. For example, Strickland-Constable (1) calculates that an increase in the supersaturation of water vapor from $P/Po = 4$ to 6, increases the nucleation rate by a factor of 10^{14}. Stewart estimates that the high-temperature rates of condensation of iron and of silica increase by a factor of 10^4 by an increase in the degree of supersaturation of 0.44 and 0.68% respectively (5). When one considers that vapor pressures are a logarithmic function of temperature, and that the temperature in a nuclear fireball at the condensation temperature can be falling as much as one to three hundred degrees a second, it can be seen that any calculations of the nucleation rate can be grossly in error.

Additional uncertainties arise because the theory was developed for the condensation of a vapor consisting of a single species. The vapors in a fireball are a complex mixture of various molecular

species which can interact with one another either in the vapor or liquid phases. Also the vapors are mixed with neutral air molecules whose effect on the condensation rate is not known. Another factor affecting the nucleation rate which would be difficult to evaluate is the intense radiation due to radioactive decay within the fireball.

In view of the gross uncertainties which seem to accompany the application of nucleation theory to the case of the cooling fireball, it is pertinent to question what useful information can be obtained from it. In general, the quantities which are determined by nucleation theory are the degree of supersaturation required to initiate nucleation, the size of the critical nucleus, and the rate of initial condensation. The quantities which are of interest in primary particle formation are the times and temperatures over which particle growth occurs (which will affect the radiochemical composition of the particles) and the final particle size distribution.

The time and temperature of particle formation can be estimated without recourse to nucleation theory from a knowledge of the vapor concentrations of the major refractory constituents in the fireball and their high-temperature equilibrium vapor pressures. It would be desireable to use nucleation theory to predict the size of the initial condensate particles, but, as has been pointed out above, any predictions of this nature will be quite inaccurate. Moreover, if one considers the coagulation rate of small particles, it seems that the final size-distribution of the primary particles will be determined by the coagulation process and will be largely independent of the size-distribution of the initial condensation nuclei.

PARTICLE GROWTH BY COAGULATION

According to classical theory, developed largely by Smoluchowski, the coagulation of very small particles is due to collisions caused by their Brownian motion. This is a very effective mechanism for small particles but its importance decreases rapidly as the particles increase in size. For particles larger than about 0.1μ in diameter, coagulation via Brownian movement becomes very slow and collisions caused by the turbulent flow of the suspending medium become increasingly important.

In order to estimate the effect of coagulation on the particle size of the primary particles, some calculations have been made of coagulation rates under conditions similar to those found in a cooling fireball. The expression,

$$\frac{1}{n} - \frac{1}{n_o} = \frac{4RT}{3\eta N}\left(1 + \frac{A\ell}{r}\right) t$$

was used in which n is the number of particles per cubic centimeter at time t, n_o is the number at t=o, η is the viscosity of the air and N is Avogadro's number. The factor, $\left(1 + \frac{A\ell}{r}\right)$, is the Cunningham

correction factor for small particles in which ℓ is the mean free path of the air molecules, r is the radius of the particles and A is a constant.

If one assumes a mass concentration of 3×10^{-8} g/cm^3 at a temperature of 2500°C in the fireball and an initial particle radius of 0.001 μ, then the concentration of initial particles will decrease by a factor of 10^8 (from 2×10^{13} to 2×10^5 particles/cm^3) and particle radii will increase by a factor of 10 to 0.01μ in about 0.01 sec. These conditions correspond approximately to one ton of condensed particles distributed evenly throughout a fireball of about 1500 ft. diameter and would probably represent an upper limit of particle concentration. If one assumes an initial particle concentration smaller by a factor of 10^3, then it takes about 1 sec. for the particle concentration to decrease by a factor of 10^2, from 2×10^9 to 2×10^7, and about 10 sec. to decrease by a factor of 10^3 to 2×10^6 particles/cm^3.

Although these estimates are crude, they do indicate that, because of the rapid coagulation of the very small particles, the final particle size-distribution will be largely determined by the coagulation process and will be more or less independent of the size of the particles formed during the initial condensation period. As a first approximation one might ignore nucleation theory and construct a model of particle formation based primarily on coagulation theory. However, difficulties arise here too. Although the coagulation of the very small particles by Brownian movement probably can be calculated to a fair degree of accuracy, the collision mechanism changes as the particles increase in size. For particles larger than about 0.1μ, Brownian motion ceases to be effective and collision of the particles is effected by turbulent flow of the air. The theory of coagulation in a turbulent medium has been developed (for a review see ref. 3, chapter 5). However, an important parameter is the degree of small scale turbulence or eddy diffusion of the carrier gas and, in the case of a nuclear fireball, this parameter is not adequately known.

An important restriction to keep in mind regarding either nucleation or coagulation theory is that, in their simple forms, they furnish information only on the size of the average or mean of the distribution of particle sizes. If a particle size-distribution as a function of time is desired, the mathematics become very complex and the equations can only be solved by use of a computer. For example, Beeckmans has used a computer to solve Smoluchowski's equations for the coagulation of uncharged aerosols. His solutions contain not only the term for Brownian motion but also terms for turbulence and differential sedimentation (6).

Hidy also reports numerical solutions by use of a computer for the coagulation of monodisperse and polydisperse sols consisting of spherical particles (7). Rosinski and Snow have studied the condensation of vaporized meteoric material in the high atmosphere.

The particles dealt with are quite small (5-100 A in dia.) and their initial state is a mono-molecular vapor. This computer program applies when the quenching of the vapor is quite rapid and the condensation is not limited by nucleation but is due to the coagulation of the vapor molecules (8). Courtney has used a computer to solve about 100 simultaneous equations (based on the classical liquid drop theory of nucleation described above) in order to describe the non-steady-state nucleation of water vapor (9).

APPLICATION OF NUCLEATION AND COAGULATION THEORIES TO PRIMARY PARTICLE FORMATION

Despite the formidable difficulties involved in the use of nucleation-coagulation theory, some attempts have been made to apply it to studies of the formation of primary particles in nuclear fireballs. In 1956 Stewart used the Frenkel equation of the steady-state nucleation theory and coagulation theory to study the formation of primary particles in the fireball of a hypothetical 20 kt nuclear explosion (5). His treatment was, of necessity, quite simple not only because of the limitations and assumptions inherent in these theories but also because of the lack of data on the concentrations and chemical reactions of the vaporized constituents and on the degree of small scale turbulence within the fireball.

Despite the crudeness of the treatment, Stewart was able to draw some general conclusions. First, the condensation process occurs over a very short time period (about 200-400 msec depending upon the concentrations of the vaporized material in the fireball). Second, the growth of the particles is predominantly by a coagulation rather than a condensation process. Stewart gives an expression for the modal, or most frequent, particle size (about 0.01μ for a 20kt air burst with 1000kg of iron) and, having assumed a log-normal distribution, an expression for the particle size distribution. These solutions are quite approximate and are of doubtful value for a realistic description of the primary particle sizes.

Edvarson has extended the work of Stewart; the main difference being that the coagulation process has been treated in a more detailed fashion (10). Edvarson started by applying the Becker-Doring equation for homogeneous nucleation to the fireball problem and he came to the conclusion, "that any attempt to calculate the particle size spectrum resulting from the combined nucleation-condensation process must be extremely uncertain." He was, however, able to make an order of magnitude estimate of the size of the primary particles formed by the combined nucleation-condensation process during the cooling of the fireball of a 20 kt air burst (0.1 ton Fe vaporized). The diameters of the particles were of the order of 0.001 to 0.003μ.

However, Edvarson was concerned mainly with the growth of the primary particles by coagulation. For this process he developed a computer program which allowed him to calculate a particle size distribution. He also came to the conclusion that the coagulation

process was most important and that, "under these circumstances the particle volume distribution attains quite rapidly a form which is to a good approximation independent of the initial distribution".

Recently Nathans, et al. (11), have applied the theory of self-preserving size-distributions (of Freidlander and Wang (12) to the formation of primary particles in nuclear air bursts. This theory is based on the hypothesis that the particle size-distribution in a system coagulating by Brownian motion reaches a form, after a sufficiently long time, which is independent of the initial distribution.

Nathans, et al., calculated the shapes of particle size-distributions by starting with various assumptions about the coagulation mechanism and then compared the results with a log-normal distribution normalized so that all the distributions have the same value for the geometric mean diameter. The work of Stewart and Edvarson was used to determine the particle size conditions at the start of the coagulation process.

Nathans, et al., also measured the size-distributions for particles collected from a series of nuclear air bursts. These distributions followed a log-normal law. The particle size spectra calculated by use of the theory of self-preserving size-distributions have the same general shape as the measured size spectra except that the standard deviations are larger and the maximum size of the calculated distribution are about one-quarter the measured values.

One of the major difficulties associated with formulating a detailed model of primary fallout particle formation, such as Edvarson's, is the lack of data with which to test the completed model. There are little data available on the complete size distribution of the primary particles formed in nuclear air bursts. However, there is one feature of the known particle sizes from nuclear air bursts that seems to be incompatible with Edvarson's model and that is the existence of large numbers of particles in the 5-20 μ range. The growth mechanisms postulated cannot account for so many particles growing to such a large size in the time available during the cooling of the fireball. Edvarson suggests that the large particles are due to a very uneven distribution of condensing material within the fireball. Most models assume an even distribution of vapor material throughout the volume of the fireball and it is probable that this assumption can lead to large errors. Unfortunately there seems to be no data available on the degree of heterogeneity of the distribution of vaporized material within a fireball. There is also the possibility that high temperatures persist longer in the center of the fireball and this, combined with a high concentration of vapor near the center, would allow the growth of larger particles.

Another effect on particle coagulation rates which is difficult to evaluate is the contribution of the high degree of turbulence in the fireball. Turbulence can greatly accelerate the coagulation

of particles larger than about a half micron in diameter. Again there seems to be no adequate data on the intensity of local, small scale turbulence. Edvarson didn't introduce any expression for turbulence into his particle formation model. He did consider the effect of turbulence but concluded that it would not be important and that, "turbulence can at most be a distortion of the high-volume part of the distribution". Stewart introduced a factor for the effect of turbulence into his simple model of particle formation, but, because of a lack of data, was only able to make a rough estimate of its magnitude.

Stewart also considered the effect of ionization due to the radioactivity in the fireball on the condensation process. He calculated that only a small fraction of the total molecules would be ionized and that because of the rapid ion-electron recombination rate, the condensation process would be between neutral atoms in the presence of ions. In general, nuclei formation might be facilitated but the coagulation process might be hindered.

UPTAKE OF RADIOACTIVITY BY PARTICLES

This report so far has been concerned only with the formation of primary particles by the condensation and coagulation of the inert or non-radioactive materials in the fireball. An adequate fallout formation model also requires knowledge of the condensation behavior of the radioactive components in the fireball. These components are in such small concentrations compared with the inert components that they would not affect the main course of particle formation. However, the manner in which the various radioactive species partition themselves in the fallout particles has an important effect on the final distribution of radioactivity in fallout.

The process would be comparatively simple if all the radioactive species behaved similarly. However there are large differences in the chemical nature of the various radioactive species and the amounts of the various radioelements are rapidly changing due to decay. These differences manifest themselves in different degrees of reactivity at different temperatures between the vaporized radioactive species and the inert material forming the bulk of the fallout particles. Some of the radioactive species are refractory and co-condense with the refractory inert materials. Other radioactive species have greater volatilities and condense later at lower temperatures or, as in the case of the rare gases, do not condense at all. These differences in condensation times lead to the phenomenon of radiochemical fractionation in which particles formed, or exposed in the fireball, at early times are enriched in the refractory and depleted in the volatile radioelements relative to the particles which are formed, or enter the fireball, at later times.

To quantitatively describe this process, Miller first proposed a "thermodynamic" model (13). He assumed that the fallout formation process could be divided into two phases. The first phase occurs above the melting point of the inert material forming the fallout particles and the second phase occurs below the melting point. During the first phase, the vaporized radioelements, or oxides, partition themselves between the vapor and the liquid substrate material according to Henry's law. Miller assumed that local equilibrium is attained either throughout the volume of the small particles or in the surface layers of the large particles. He does not consider that diffusion of the condensed radioelements in the substrate matrix is important in determining the uptake. Miller also considers the possibility of compound formation between the radioactive species and constituents of the liquid substrate.

During the second phase, those radioelements which have not yet condensed, either sublime directly onto the surfaces of the particles or react chemically with constituents of the particles. Because of a lack of thermodynamic data, Miller was forced to assume ideal behavior (Raoult's law) in his calculations. Subsequent measurements of Henry's law constants for oxide vapor-molten silicate systems have shown that the assumption of ideal behavior can be grossly in error.

Norman and his co-workers have made laboratory measurements of Henry's law constants and diffusion constants of important radioelements or their oxides in silicate systems at high-temperatures (14, 15). Their first model describing the uptake of the vaporized radioactive species is a more sophisticated version of the thermodynamic model (16). They assumed that the outer layers of the particles quickly became saturated with the condensing radioactive species and that the amount of uptake of each species was determined by Henry's law. Following the saturation of the outer layers of the particles, the rate of uptake of additional radioactive material was governed by the rate at which the condensed material in the surface layer diffused into the interiors of the particles. Heft has successfully used Norman's Henry's law constants to describe the distribution of radioactivity in fallout from an underground cratering shot in Nevade (17). Norman has also given some consideration to the role of condensation coefficients and gas diffusion on the radioactive vapor uptake process (18).

Adams, et al., have investigated the rate determining mechanisms that govern the uptake of radioactive vapors by inert substrate materials at high temperatures (19). These authors measured the rates of uptake of several radioactive species by comparatively large spherical particles of either a silicate or a calcium ferrite. In general, they found that an important parameter in the uptake process was the condensation coefficient, (α). When α was about 0.1 to 1.0, the reaction of the vapor with the substrate material was quite rapid and the rate of uptake was determined by the rate at which the radioactive vapors diffused through the surrounding air

to the surfaces of the substrate particles. When $\alpha < 10^{-2}$, the uptake rate was governed by a relatively complicated function of three parameters: the condensation coefficient, Henry's law constant, and the diffusion constant of the condensed radioactive species within the substrate material. In this case, the uptake rates were appreciably slower than would be predicted by the simple Henry's law-diffusion constant model described above.

OUTLINE OF A SIMPLIFIED MODEL OF RADIOACTIVE PARTICLE FORMATION

The discussion so far has shown that there are two major difficulties associated with the application of theory to the formation of primary fallout particles. The first difficulty lies in the complexities of the theories themselves. For the straightforward, non-computer, solutions of the basic equations, simplifying assumptions are required which severely vitiate the theory when applied to condensation in the fireball. If restrictive, simplifying assumptions are to be avoided, then it is necessary to set up a rather elaborate computer program. There is also the difficulty that nucleation-condensation theory was originally formulated to describe the steady-state condensation of a pure vapor and is not adequately developed for a situation such as that which prevails in a nuclear fireball which involves a complex mixture of reactive vapors of variable degrees of volatility and large amounts of inert gas, all existing in a region of rapidly falling temperatures and high radiation fields.

The second difficulty lies in the lack of input data. Measurements of the surface tensions and vapor pressures of very small particles of the size and composition of the condensation nuclei have not been made. Data on the actual local concentrations of vaporized material in the fireball as a function of time and temperature are not available. Little is known of the degree of small scale turbulence within the fireball which is required for calculating the coagulation rates of the larger particles. And finally, few measurements are available on the complete size-distribution of primary particles in an air burst which could be used to check the validity of any particle formation model.

In addition to these difficulties in formulating an accurate model of particle formation and growth, there are problems associated with the construction of a mathematical model of the uptake of the radioelements by the growing particles. As mentioned above, a complete model would require knowledge of the diffusion constants of the radioelements in air and in the inert particles as well as the Henry's law constants and condensation coefficients for all combinations of the important radioactive species and various substrate materials. Some measurements of these quantities have been made, especially in silicate systems, but there still remains a significant lack of data and work in this field is difficult and slow.

Also, the question arises, in view of the scarcity of reliable input data on vapor concentrations, temperature distributions and degrees of turbulence within nuclear fireballs, whether or not a sophisticated model of fallout particle formation would be appropriate. There is also the goal of keeping the model simple enough so that it can easily be incorporated as a module into an over-all fallout formation and distribution computer program.

In view of these considerations, it appears that some compromises might be made. On this basis, the following discussion will outline a scheme for combining some of the data which is available on sizes and radiochemical compositions of primary radioactive particles with some concepts derived from theory in order to develop a semi-empirical and simple "kinetic" model of particle formation in a cooling fireball. The basic information which will be used is as follows.

First, from observations of airborne, radioactive debris, it is known that primary particles from air bursts can be as large as 10 or 20μ in diameter (20). Also some data have been obtained on the radiochemical composition of primary particles as a function of particle size. These data are usually presented in discussions on the subject of radiochemical fractionation of fallout (21, 22).

Second, from theoretical considerations described above, it is probable that the condensation of the primary particles occurs over a short interval of time (from about 1/2 to 3 sec depending upon yield and vapor concentration) and that the initial condensate particles are quite small (about 0.001 to 0.003μ in diameter). After the initial condensation, particle growth occurs primarily by coagulation. On the basis of this information, a simplified model of primary particle formation is proposed.

First, it will be assumed that at a time and temperature determined by the vapor concentration of the most refractory of the major inert constituents of the fireball and by the rate of cooling of the fireball, all the refractory material, both inert and radioactive, co-condense more or less instantaneously to form the initial primary radioactive particles. After this initial condensation, only the volatile and relatively volatile radioactive species remain in the vapor state. The particles will continue to grow by coagulation and different groups of particles will grow at different rates.

Coincidently with the coagulation process, the fireball will be cooling and successive radioactive species will condense on the surfaces of the growing particles. It will be assumed that each radioactive species will condense over a very short period of time and at a temperature where the condensation coefficient of the particular radioactive species relative to the substrate material of the primary particles becomes appreciable.

This assumption can be justified by measurements in this laboratory which have suggested that, in the case of oxide and silicate systems, the initial rate of uptake of a vapor by a substrate material will be proportional to its saturation concentration in the substrate material, i.e., its Henry's law constant. Henry's law constants for a variety of radioactive species in a silicate matrix as a function of temperature are available (14). These data indicate that, under conditions approximating those in a fireball, Henry's law constants can change by an order of magnitude over a temperature drop equivalent to a time interval of 1 to 4 seconds. Even when the condensation coefficient of a condensing vapor is unity, a certain time is required for the vapor molecules to strike the particle surfaces and condense. This time will be inversely proportional to the total amount of particle surfaces available and, in the fireball if the particles are not too diffuse, this time will be of the order of 1 to 3 seconds.

This computational procedure for the condensation of the radioactive species will lead to a radiochemical composition of the primary particles which is dependent upon particle size, i.e., the fractionation effect. In the calculational model one can vary parameters such as the time schedule of particle growth and radioactive vapor condensation and thereby vary the degree of fractionation. By comparing the calculated degree of fractionation with the observed fractionation of airborne nuclear debris samples, one can decide which values for the parameters give the best results and thereby gain some knowledge of the conditions prevailing during the particle formation process.

In order to test this simple model, the following calculational scheme was tried. First, equilibrium vapor pressure curves for several refractory materials which are likely to be the major inert components of a fireball were plotted as a function of temperature. Second, the time-temperature curves of the fireballs from nuclear explosions of varying yields were plotted. These plots enable one to estimate an approximate condensation temperature and time for the refractory components of the fireball for various assumed yields and vapor concentrations.

Third, the radioactive species were divided into three groups. The first group consisted of the refractory isotopes such as Zr, Nb, Ce and Sr, which were assumed to co-condense completely with the refractory inert materials forming the initial particles. The second group consisted of those isotopes which were considered to be of intermediate volatility such as Mo, Cs, and Ag. These species were assumed to condense upon the surfaces of the particles existing at an intermediate temperature. The third group, the volatile species such as Xe, Kr and I, was assumed to condense at a low temperature after the growth of the particles had ceased.

Finally, a schedule of particle growth was constructed. It was assumed that the radius of the initial condensate particles was 0.01μ. The particles were then divided into three groups initially of 10^8 particles each. The particles of each group were assumed to grow at different rates. The particles of each group attained radii of 0.03, 0.3 and 1.0μ respectively at the time of intermediate temperature when the radioactive species of intermediate volatility condensed. The final radii of the particles of the three groups were 0.1, 1.0 and 10.0μ respectively at the time when the volatile radioelements condensed.

The relative amounts of the various radioelements at the different condensation times were obtained from the Bolles-Ballou compilation (23). Because of the rapid decay of the early fission products into various daughter species, it was necessary to divise a bookkeeping system to keep track of the amounts of the various radionuclides which had condensed into the particles and the amounts which remained in the vapor state at the different condensation times. The refractory radioactive species, which were assumed to co-condense with the refractory inert materials, were distributed equally throughout the volumes of the 0.01μ particles. At the intermediate stage of condensation, the total surface area of the three size groups of particles was calculated and the radioactive species of intermediate volatility were assumed to condense equally upon all the available surfaces. Similarly, at the final stage of particle growth, the total particle surface area of the three groups was again computed and the remaining vaporized radioactive species were condensed equally on all the available surfaces. These calculations were performed for three different combinations of bomb yield and initial vapor concentration. These conditions are summarized in Table I. The particle growth schedule and numbers of particles at each stage of growth are summarized for the three groups in Table II.

TABLE I

Fireball Conditions

Yield (mt)	Metal conc. in Fireball (g/cm^3)	Initial Condensation		Intermediate Condensation		Final Condensation	
		T(°K)	t(sec)	T(°K)	t(sec)	T(°K)	t(sec)
0.2	1×10^{-9}	2860	6	2200	9	1200	16
1.0	3×10^{-9}	2950	13	2150	19	1300°	28
10.0	3×10^{-11}	2600	41	2050	50	1300	74

TABLE II

Particle Radii and Numbers in Each Size Groups

Condensation Time	SMALL GROUP		INTERMEDIATE GROUP		LARGE GROUP	
	Radius(μ)	Number of Particles	Radius(μ)	Number of Particles	Radius(μ)	Number of Particles
Initial Condensation	0.01	10^9	0.01	10^9	0.01	10^9
Intermediate Condensation	0.03	3.7×10^7	0.10	10^6	0.30	3.7×10^4
Final Condensation	0.10	10^6	1.0	10^3	10.0	1

This calculational process led to radiochemical fractionation between the three particle size groups. As the particles increased in size, the ratio of surface area to volume decreased and the larger, faster growing particles picked up less of the later condensing, more volatile radioelements relative to their mass than did the smaller, slower growing particles. The degrees of fractionation resulting from the different initial conditions could be computed and these results compared with those obtained from measurements on actual bomb debris in order to test the validity of the assumptions upon which this model is based.

These computations were performed for several of the more important fission chains occurring in radioactive debris. The results of the calculations were then compared with fractionation data from averages of actual fallout collections tabulated by Lai and Freiling (24). The results have been presented in the form of "r" values. These "r" values are a computational device designed to indicate the relative composite volatility of various fission chains (including all the individual members of each chain) which are normalized to take into account the varying amounts of each chain formed in fission. In the scheme used by Freiling (21), the fission chain including ^{95}Zr was chosen as the reference chain for refractory material. All the members of this chain exhibit refractory behavior and would be expected to condense at early times. The chain ending with ^{89}Sr was chosen as the reference chain for volatile behavior as it contains the non-condensable species ^{89}Kr and the volatile species ^{89}Br which are predominant during the time of fallout formation.

The "r" values for several fission chains were computed for each of the three particle size groups. The manner in which these "r" values are plotted against the "r" values of the reference chains, results in a slope of zero for any chain exhibiting refractory behavior like that of ^{95}Zr and a slope of unity for any chain exhibiting volatile behavior like that of ^{89}Sr. Fission chains exhibiting intermediate behavior will give values intermediate between zero and unity depending upon their degree of volatility. The data are summarized in Table III.

TABLE III

"r" Value Slopes

	Lai and Freiling: observed values			This Report: calculated values			
	Air	Coral Surface	Silicate Surface	0.2 mt	2 mt	10 mt	
^{89}Sr	1.00	1.00	1.00	1.00	1.00	1.00	Py definition
^{137}Cs	.90±.09	1.0	1.0-1.2	1.12	1.14	1.16	
^{90}Sr	.92±.08	.73	.5-.7	.81	.76	.65	
^{140}Ba	.62±.04	.6	.5-.6	.65	.58	.44	
^{91}Y	.56±.03	.54	.4-.5	.60	.56	.51	
^{111}Ag	.80±.05	-	-	.59	.61	.66	Semi-Vol: Ag, Ru, Rh, Pd
				1.18	1.20	1.29	Semi-Vol: Ag, Volatile: Ru, Rh, Pd
^{136}Cs	.67±.08	-	.4-.8	.59	.61	.66	Semi-Vol: Cs
				1.18	1.20	1.32	Volatile: Cs
^{115}Cd	.80±.06	-	-	.59	.61	.66	Semi-Vol: Ag, Rh, Pd
				.88	.73	.69	Semi-Vol: Ag, Volatile: Rh, Pd
^{103}Ru	-	-	.5	.34	.51	.66	Semi-Vol: Mo, Tc, Ru
				.37	.62	1.00	Semi-Vol: Mo, Volatile: Tc, Ru
^{99}Mo	.30±.05	-.10	-.02-.04	.02	.03	.08	
^{144}Ce	.17±.20	.08	0.0-.2	0.0	0.0	0.0	
^{95}Zr	0.0	0.0	0.0	0.0	0.0	0.0	Ey definition

The "r" values for .200 mt, 1 mt and 10 mt fireballs have been compared with the Lai and Freiling values for nuclear debris from air, coral surface and silicate surface bursts. The first point to notice is that, in most cases, the calculated values are roughly independent of yield. Secondly, when comparing the calculated values with those reported by Lai and Freiling, it is seen that the discrepancies are rather moderate considering the crudeness of the model used in the calculations.

In calculating the "r" values for the fission chains 103, 111 and 115, there was uncertainity as to whether to classify the oxide vapors of Ru, Rh, Pd and Tc as volatile or semi-volatile. Calculations were made with these oxides in both categories and a significant difference was observed in the case of the 111 chain but not with the 103 and 115 chains. Also it is interesting to observe the behavior of ^{136}Cs. This is a shielded nuclide and exists only as cesium during the condensation process. Two values were calculated for cesium. The first assuming that cesium oxide was semi-volatile (condenses about 2100°K) and the second that it was volatile (condenses $<$1200°K). It is seen that the values computed assuming semi-volatility agree well with the value for air bursts reported by Lai and Freiling.

The tabulated calculations are rough approximations and are presented for heuristic purposes only. That these data correlate well with actual fallout data is striking and suggests that the proposed model has some validity and, because of its simplicity, might easily be adapted into a computerized model of fallout formation.

To refine this kinetic model it would be necessary to have better data on the concentrations of the major inert materials in the fireball, the time-temperature relations in the cooling fireball, a growth rate rule for the primary particles and a better knowledge of the temperatures at which the rates of uptake of the various radioactive species on various substrate materials become appreciable. Also the computational steps should be increased to include more groups of particle sizes and more time intervals over shorter temperature drops. Increasing the number of computational steps would require setting up a simple computer program for these calculations.

CONCLUSIONS AND RECOMMENDATIONS

Arguments have been presented in this report which demonstrate the difficulties involved in formulating an accurate mathematical model of fallout particle formation. As an alternative to employing condensation and coagulation theory alone, a kinetic model has been proposed to describe primary radioactive particle formation which is semi-empirical and relies on a minimum of theory. Although the crude calculations presented above give results which are in agreement with radiochemical data from actual radioactive debris, it is not suggested that this simple model be used to explain the whole phenomenon of fallout particle formation. Rather the kinetic model

hould be used as an aid in furnishing estimates for input data for more sophisticated models. These data would apply to such parameters as a time scale for the particle growth process (which is related to the degree of local vapor concentrations and turbulence within the fireball) and condensation times and temperatures of the various radioactive components.

If one were to proceed on this basis, there are two areas in which further work is required. The first involves the acquisition of data on the temperature of condensation of the vaporized radioactive species. A considerable body of useful information has already been accumulated, mainly in the measurements of Henry's law constants and diffusion constants in silicate matrices by Norman,et al. and of rates of radioactive vapor uptake by silicate and calcium ferrite substrate particles by Adams, et al.

There is a more or less complete lack of data on the uptake of the radioactive species by other substrate materials of interest such as iron and aluminum oxides. Experimental measurements have shown that for many radioactive vapor species there can be gross differences in condensation behavior upon different substrates (19). To fill this lack of information, work is in progress at the Naval Ordnance Laboratory on the measurement of the relative rates of co-condensation of different radioactive species with a variety of inert materials which have been vaporized by a high-powered laser beam.* This laser method furnishes only qualitative data on vapor condensation but it has the advantage over more quantitative methods in being able to produce data more quickly on a larger number of vapor-substrate combinations.

All of these data can be used in conjunction with the simple kinetic model described above. This model can be programmed to yield a variety of solutions for different postulated fireball conditions, and by comparing the calculated results with measurements on actual radioactive debris from nuclear explosions of known characteristics, information can be obtained for the further development of a more comprehensive model.

The second area in which further work is required is the development, or elaboration, of a practical computational model for the total process of fallout formation. This will involve not only the process of primary particle formation, but also the introjection of secondary particles into the fireball. It will be necessary to describe the interactions between the large, secondary particles, which are swept into the fireball, with either the primary particles or uncondensed radioactive vapors. Except for the physical-chemistry of the uptake reactions between the radioactive vapors and the secondary particle substrate materials, this is essentially an aerodynamical problem.

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A computerized model which might prove adequate for this purpose is the NRDL water-surface burst fallout model which was developed under DASA sponsorship. This model consists of a cloud module and a transport and deposition module. The cloud module is concerned with the evolution and size-distribution of particles formed in the fireball by condensation and coagulation. This model has terms taking into account coagulation parameters such as Brownian movement, turbulence and gravitational settling. In order to incorporate into this model the various features and input data described above, it would be necessary to expand the model's capability somewhat. This modification would include introducing an initial dual size distribution consisting of the small primary particles and the large secondary particles. Each distribution can be introduced at the appropriate point in the time-temperature history and the redistribution by agglomeration of the small, radioactive particles by the large, inert particles can be calculated. Also several condensation temperatures can be specified, each one for a particular radioactive species. The final result of both the laboratory and computer programming work which has been suggested would be a computer program, or numerical laboratory, in which a radioactive species could be tracked from the vapor phase, through condensation onto small particles, and via agglomeration with, and scavenging by larger particles, ultimately into radioactive fallout.

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