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OFFICE MEMORANDUM

TO : R. W. Spence, J-11 Group Leader

DATE: November 16, 1953 *M-7140*

FROM : J. L. Magee, J-11 Consultant

SUBJECT: Mechanisms of Fractionation

SYMBOL: J - 11-5

CLASSIFICATION CANCELLED

DATE 11-7-58

For The Atomic Energy Commission

H.F. Canell
Chief, Declassification Branch

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I. Introduction

In this report we shall be concerned with the mechanisms involved in fractionation as measured in samples obtained "early," i.e. from drone planes during the cloud rise or from manned aircraft a few hours later. Fractionation at later stages involves more meteorology than bomb phenomenology and will not be considered.

The problem of fractionation has not been solved and this report only presents some ideas on the subject. In view of its hasty preparation, no claim can be made even for a complete tabulation of effects. A key problem is the formation of the precipitate in the cloud, and at first an attempt is made to describe this mechanism. The treatment of this process is, of course, for certain idealized conditions, but application to a bomb cloud is also discussed. The entire history of the precipitate from formation to sample measurement is traced for fractionation effects.

II. Detailed Mechanism of Condensation

1. Condensation by self-nucleation in a homogeneous super-saturated gas

There is a well-established theory for the formation of a precipitate in a homogeneous super-saturated gas at constant temperature¹. According to

¹ This theory is frequently called The Becker-Doring theory; it is conveniently summarized in a symposium on nucleation phenomena: Ind. Eng. Chem. 44, 1269 - 1338 (1952).

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this theory, the rate of precipitation depends in a critical way upon the rate at which nuclei are formed, and the theory gives a detailed physical picture of the nucleus and a method for calculation of the nucleation rate. Apparently there has been no treatment of precipitation in a gas which is being chilled, but a straight-forward application of the theory yields the result

$$I = I_0 e^{\alpha t} \quad (1)$$

for the number of nuclei formed per unit time at the time t . I_0 and α are constants, dependent upon the properties of the precipitate, the temperature, and the rate of cooling; they will be discussed in more detail below.

A nucleus is supposed to be a spherical particle of solid matter. After its formation, it grows by the addition of single molecules of the material being precipitated. Thus its volume increases with time as:

$$\frac{d}{dt} \frac{4\pi}{3} R^3 = \pi R^2 v_1 n_1 V_1 \quad (2)$$

where R is the particle radius, v_1 the velocity of the monomer, n_1 the number of monomers per unit volume, and V_1 the volume of the monomer. Differentiation of (2) and cancellation of terms yields:

$$\frac{dR}{dt} = \frac{1}{4} n_1 v_1 V_1 = \beta \quad (3)$$

where β is defined by the equation. Under conditions of constant β the integration of (3) can be performed to give

$$R = \beta(t - t^1) \quad (4)$$

where t^1 is the time the nucleus of the particle was formed. (We are neglecting the volume of the original nucleus).

In a system in which equations (1) and (4) describe the precipitation

process, the total volume of precipitate formed at time t is

$$V(t) = \int_0^t I(t') \frac{4\pi}{3} [\beta(t-t')]^3 dt' \quad (5)$$

or

$$V(t) = \frac{4\pi}{3} I_0 \beta^3 \int_0^t e^{\alpha t'} (t - t')^3 dt' \quad (5a)$$

There is a natural zero time for this problem, since no nucleations can occur until supersaturation is attained. However, the form for the nucleation rate given in (1) is not actually valid, with constant α , until the nucleation rate is approaching its maximum value. Due to the exponential nature of this function, essentially all of the precipitation will take place at the same value of α . Thus we make a linear shift in the time coordinate and integrate from $-\infty$ to t . This gives for (5a)

$$\begin{aligned} V(t) &= \frac{4\pi}{3} I_0 \beta^3 \int_{-\infty}^t e^{\alpha t'} (t - t')^3 dt' \\ &= \frac{4\pi}{3} \beta^3 I_0 e^{\alpha t} \frac{6}{\alpha^4} \end{aligned} \quad (6)$$

According to this equation, at any time t , the fraction $(1 - e^{-1})$ of the precipitate was formed during the preceding time interval α^{-1} . Of course in this formulation we have neglected depletion of monomer (i.e. by using constant α and β) but it is clear that refinements of the theory will not alter the fact that most of the precipitation is expected in a time interval of approximately α^{-1} .

2. The particle size distribution

The number of particles which have radii between R and $R + dR$ at the time t are those which were formed at a time t' to $t' - dt'$ such that

$$R = \beta(t - t')$$

$$t' = t - R/\beta$$

$$dt' = -\frac{1}{\beta} dR$$

The distribution function is given by

$$N(R)dR = I(t')dt' = I_0 e^{\alpha(t - R/\beta)} \frac{dR}{\beta} = I_0 \frac{e^{\alpha t}}{\beta} e^{-\alpha/\beta R} dR \quad (7)$$

Thus

$$N(R) \propto e^{-\alpha/\beta R} \quad (7a)$$

at all times.

The average radius of this distribution is:

$$\bar{R} = \frac{\int_0^\infty R e^{-\alpha/\beta R} dR}{\int_0^\infty e^{-\alpha/\beta R} dR} = \beta/\alpha \quad (8)$$

The surface average and volume average radii are:

$$[\bar{R}^2]^{1/2} = \sqrt{2} \beta/\alpha = 1.41 \beta/\alpha \quad (9)$$

$$[\bar{R}^3]^{1/3} = \sqrt[3]{6} \beta/\alpha = 1.82 \beta/\alpha \quad (10)$$

One reason for believing that this mechanism may be the correct one is that empirically the distribution (7a) has been found from examination of many samples of bomb debris. At this time it remains something of a mystery that the value of β/α is almost independent of the composition or amount of condensable material. One possible interpretation of this result is given below in section II-6 of this report.

3. The constant α

The constant α must come from a detailed application of the Becker-Doring nucleation theory¹. The rate of nucleation can be given as²:

² Reiss, Ind. Eng. Chem. 44, 1284 (1952)

$$I = \sqrt{\frac{\Gamma}{\pi}} \beta^1 S(x^*) n(x^*) \quad (11)$$

where $n(x^*)$ is the number of clusters per unit volume which contain x^* monomer units. Clusters of various sizes are assumed to be in a statistical equilibrium and the nuclei are formed from those which reach a certain critical size containing x^* monomers.

$$n(x^*) = n_1 e^{-\frac{W(x^*)}{kT}} = n_1 \exp\left(-\frac{W(x^*)}{kT}\right) \quad (12)$$

$W(x^*)$ is the free energy difference between the cluster and the x^* gas molecules from which it was formed:

$$W(x^*) = (\mu_e - \mu_g)x^* + \gamma x^{*2/3} \quad (13)$$

$(\mu_e - \mu_g)$ is the free energy difference of a single molecule in a solid of infinite extent and in the gas phase; the second term $\gamma x^{*2/3}$ gives the surface free energy of the cluster.

β^1 is the number of molecules which strike unit surface in unit time (we are taking the so-called "accommodation coefficient" as unity in this discussion; i.e. all condensing molecules stay on the surface after they strike it).

$S(x^*)$ is the surface area of the critical cluster, and

$$\Gamma = \frac{\beta^1}{9} kT(x^*)^{4/3}$$

The reason for the existence of a critical cluster size is that the free energy for formation of clusters goes through a maximum with increase in cluster size. The position of the maximum determines x^* .

$$\frac{\partial W}{\partial x} = 0 = (\mu_e - \mu_g) + \frac{2}{3} \gamma (x^*)^{-1/3} \quad (14)$$

$$W(x^*) = \frac{4}{27} \left(\frac{\gamma}{\mu_g - \mu_e} \right)^2 \quad (15)$$

At the condition of saturation, $\mu_g - \mu_e = 0$; in super-saturation,

$\mu_g - \mu_e > 0$. An approximate expression which can be used for the temperature variation of the free energy difference is:

$$\mu_g - \mu_e = \Delta H_{\text{vap}} \left(1 - \frac{T}{T_s}\right) \quad (16)$$

Here ΔH_{vap} is the heat of vaporization (taken as constant) and T_s is the temperature at which the gas saturates.

The quantity ξ in the expression for the surface free energy is presumably slowly varying with temperature and may be taken as constant. It is related to the heat of vaporization, and so for convenience we shall write

$$\xi = c \Delta H_{\text{vap}} \quad (17)$$

where c is a constant multiplier.

As a further assumption, let us take a constant temperature drop with time:

$$T_s - T = a + bt \quad (18)$$

where a and b are constants; the value of a is fixed by the choice of zero time, as discussed below.

Substitution of those quantities into (15) gives:

$$\frac{W(x^*)}{kT} = \frac{4}{27} c^3 \frac{\Delta H_{\text{vap}}}{k(T_s - a - bt)} \left(\frac{T_s}{a + bt} \right)^2 \quad (19)$$

Expansion of this function of time into a power series with retention of the linear term gives:

$$\frac{W(x^*)}{kT} = \frac{4}{27} c^3 \frac{\Delta H_{\text{vap}}}{k(T_s - a)} \left(\frac{T_s}{a} \right)^2 \left\{ 1 - \frac{2b}{a} t + \frac{b}{T_s - a} t \right\} \quad (20)$$

This expansion allows us to identify α as:

$$\alpha = \frac{8}{27} c^3 \frac{\Delta H_{\text{vap}}}{k(T_s - a)} \left(\frac{T_s}{a} \right)^2 \frac{b}{a} \left\{ 1 - \frac{a}{2(T_s - a)} \right\} \quad (21)$$

The second term in the bracket will always be much smaller than unity and for our approximate consideration will be dropped. With this approximation we can write equation (20).

$$\frac{W(x^*)}{kT} = \frac{\alpha}{2b} - \alpha t \quad (22)$$

4. The rate of nucleation and choice of zero time.

A reasonable choice of zero time would appear to be that time at which all of the material would precipitate if the rate continued unaffected by depletion. With this usage, almost all precipitation will take place between $-\infty \leq t \leq 0$ and a good fraction of it will occur between $-\alpha^{-1} \leq t \leq 0$. For $0 \leq t$, depletion effects are dominant. The use of this definition and equation (6) gives:

$$V(0) = V_s = \frac{4\pi}{3} I_0 \frac{6\beta^3}{\alpha^4} \quad (23)$$

where V_s is the total volume of precipitate per unit volume. Substitution of the various quantities into equation (11) gives for I:

$$I = \frac{1}{12} \frac{6^{2/3}}{\pi^{5/6}} \sqrt{\frac{c \Delta H_{\text{vap}}}{k(T_s - a)}} \frac{\beta}{V_1^{1/3}} n_1 e^{-\frac{2a}{2b} + at} \quad (24)$$

so that we now have an explicit expression for I_0 . (Compare this with equation (1)).

Equation (23) becomes

$$V_s = \frac{2\pi^{1/6}}{3} 6^{2/3} \frac{c \Delta H_{\text{vap}}}{k(T_s - a)} \frac{\beta^4}{\alpha^4} \frac{n_1}{V_1^{1/3}} e^{-\frac{2a}{2b}} \quad (25)$$

The various quantities ΔH_{vap} , n_1 , V_1 , β , T_s , c are assumed known from physical properties and starting conditions. The single unknown quantity in this equation is $a = T_s - T$ and in a given case (25) can be solved for the unknown, a , by numerical methods. The value of a can then be calculated using equation (21).

5. The constant c .

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The extra surface energy of a small cluster of molecules is a difficult quantity to calculate, and the examples given here are at best very crude. Let us arbitrarily consider a definite cluster of 13 molecules in "close packing": one molecule is at the center and the other 12 are symmetrically arranged. Assume that there is a "bond" between nearest neighbors. In the

infinite solid, these 13 molecules would have

$$13 \times \frac{12}{2} = 78$$

bonds to hold them together. On the other hand, in the cluster, they only have

$$\frac{12}{2} + 12 \times \frac{5}{2} = 36$$

bonds. Thus the heat of surface formation is 42 bonds, or $7 \Delta H_{\text{vap}}$. There is an increase in entropy of the surface molecules due to their greater freedom of motion and this makes a contribution to the free energy of about half this amount.³

³ W. G. McMillan, Private communication.

Thus, for the cluster of 13 we would say

$$\frac{42}{3} (13)^{2/3} = 3.5 H_{\text{vap}} = c \Delta H_{\text{vap}} (13)^{2/3}$$

or

$$c = 0.63$$

This result must be considered as the correct order of magnitude. Another method was suggested to the author by McMillan³, who felt sure that at low temperatures the surface energy of most oxide surfaces would be around 10^3 ergs/cm². With the use of this value for the surface energy, we can write

$$W(x) = (-\Delta H_{\text{vap}} + T \Delta S)x + 1.43 \times 10^{19} S$$

for the free energy of formation, in cal/mole, for S given in cm² of surface of one cluster. If we take

$$V_1 = 2.5 \times 10^{-23} \text{ cm}^3$$

we get

$$S = 2.85 \times 10^{-15} x^{2/3}$$

and

$$W(x) = (-\Delta H_{\text{vap}} + T\Delta S) + 4.1 \times 10^4 \times 2/3$$

An estimate of the heat of vaporization can be obtained with the use of Troutons' rules as applied to solids. Say the solid vaporizes at 4500°K.

$$\Delta H_{\text{vap}} \approx 25 \times 4500 = 110,000 \text{ cal/mole}$$

The constant c is in this case $\frac{41,000}{110,000} = 0.37$.

This agrees in magnitude with the previous estimate.

6. Application to bomb clouds

Application of the above theory to the precipitation process in a bomb cloud is obviously somewhat arbitrary. The composition and temperature distribution at any time are not constant in space as in the theory. Furthermore the quantities which one must use are almost without exception very poorly known: properties of the various oxides, distribution of matter in the cloud, rate of cooling, etc. In the discussion of this section we have, therefore, merely tried to assign values to the various quantities which appear to be reasonable and which yield a correct overall picture, as it is presently known. Subsequent investigation may change details of this treatment considerably.

We have seen above that the ratio of the parameters β and α characterize the particle size distribution: β/α gives the average particle radius. Measurements on particles [REDACTED] have shown that the average particle size is remarkably insensitive to the composition of the debris. The total amount of material may vary a factor of one hundred or more for a particle size variation of only five or so. The ratios β/α for different pure materials, iron, aluminum, uranium, etc. would certainly vary by much greater factors.

One possible explanation of these facts is that the condensation is always dominated by uranium, which is always present. It would be expected that the parameter α would be more or less fixed by dominance of one material, but the parameter β which is given by the particle growth rate might be expected to vary more. If the largest component (iron or aluminum) which has a lower condensation temperature also has a low accommodation coefficient for sticking at the condensation temperatures, the independence of the parameter β on composition can also be understood.

Without detailed justification of our choices let us consider some numerical magnitudes. From (3)

$$\beta = \frac{1}{4} n_1 v_1 \bar{V}$$

Take: $n_1 = 10^{15}$

$$v_1 = 4 \times 10^4$$

$$V_1 = 2.5 \times 10^{-23}$$

and $\beta = 2.5 \times 10^{-4}$

If this is to be the "effective" value of β for the condensation, a particle requires 4 seconds to grow to a radius of 10 microns; so that if 10 particles are observed, condensation took place for at least such a period of time. On the other hand, if the average particle has a radius of about one micron, most of the condensation took place in about 0.4 second.

In order to obtain the value of α equation (25) must first be solved.

Take:

$$V_s = 10^{-8}$$

$$\frac{\Delta H_{\text{vap}}}{(T_s - a)} = 30$$

$$c = 1/3$$

$$(k = 2 \text{ cal/mole})$$

and equation (25) can be written:

$$e^{-\frac{a\alpha}{2b}} = 1.28 \times 10^{-17} \alpha^4$$

In this equation b is supposed to be known ($b = \frac{dT}{dt}$, the rate of cooling).

The simplest method for solution is to take various values of $2b/a$ and solve for α ; then the relations between b , a and α are all determined.

For $b/a = 0.1$, α turns out to be about 6 and $T_g/a = 9$. Thus if $T_s = 2800$, the temperature at which the condensation occurs is about 2500° , and the rate of cooling has been set at 30° per second.

For this assignment of constants⁴, $\beta/\alpha = 0.4 \times 10^{-4}$ cm which means that the average particle diameter is 0.8μ .

⁴ A further word concerning those highly tentative values may be said. If a bomb contains 60 kg of uranium, or 250 moles, a value of $n_1 = 10^{15}$ means that the pit materials has been spread into a spherical region of radius 33 meters.

If the vapor pressure is given by

$$p = e^{-\left(\frac{112,500}{2T} - \frac{112,500}{9,000}\right)}$$

(which means that the oxide (say UO_2) vaporizes at $4500^\circ K$ with a heat of 112,500 cal/mole). The saturation temperature is $2800^\circ K$.

A systematic study of the condensation process as a function of n_1 , would be interesting. Possibly a smaller value of n_1 with its corresponding lower saturation temperature would be in better agreement with the rate of cooling.

7. An alternative mechanism for condensation

The theory described above and applied to a bomb cloud has an essential part of its structure that the rate of nucleation is the limiting step in the precipitation. It will be recalled (see equation 14) that the size of the critical cluster depends upon the condition:

$$x^* = \frac{8}{27} \left(\frac{c^3 T_s}{T_s - T} \right)^3 \quad (14a)$$

where we have substituted quantities introduced subsequent to equation (14). From this equation it is clear that at some particular temperature the critical cluster size will decrease to 2, at which time all collisions start nuclei and there will be a rapid completion of the precipitate. It can be shown that this part of the precipitate will contain extremely small particles - of the order of 0.01 micron. This type of precipitate will result from very rapid cooling or very slow growth rate of particles.

The author of this report has been strongly influenced by evidence that most of the precipitates examined have been formed by the slow nucleation process. However, the possibility that some of the precipitate is formed by this second mechanism should not be overlooked.

A more thorough quantitative study of the equations presented here would lead to a better understanding of these possibilities.

III. Mechanisms contributing to fractionation

1. General picture regarding fractionation

It has generally been assumed that in the turbulent expansion of the pit material of a bomb there is complete mixing. Conceivably this is not true in an underground blast, but such cases are not considered here. At the early time of the maximum fire ball expansion, there is little reason to believe that fractionation of any active material exists. It is clear that any amount of re-mixing will not lead to fractionation: A separation mechanism is required. In the following events there is a turbulent rise and dispersion of the cloud, and the only kind of discrimination which can take place is on the basis of particle size. Furthermore, if all particles had the same chemical composition, particle size separation would not result in fractionation. Thus we are led

to the conclusion that a necessary condition for fractionation is the variation of chemical composition with particle size.

2. Variation of chemical composition with particle size

It is clear that the particles which are formed first will contain the most refractory material and will also be the largest. More volatile compounds will condense later and be preferentially incorporated in smaller particles.

If the mechanism elaborated in part II is approximately correct, the precipitate forms very fast, while the temperature is still rather high (2500° or so). Of course, it is the distribution of fission products which is present at the condensation which is important, i.e. 5 - 10 seconds. All of these volatile at 2500° will be excluded from the main precipitate and be deposited surface-wise on the precipitate as the cloud cools. During this time the cloud will be rising in very turbulent motion, increasing its volume all the time. There is the possibility that volatile components may fail to find the main precipitate before condensation of moisture presents another kind of deposition surface.

The most volatile components will be found preferentially on the smaller particles and the extent of deposition of volatile compounds will depend upon the total mass of precipitate.

3. Mechanisms for particle size separation

Separation of particles because of size difference is possible because the response of particles to forces depends on their size, since their viscous resistance to motion depends upon size. If a particle is subject to a force f in a medium which has a viscosity η , then its velocity will be given by:

$$v = \frac{2}{9} \int \frac{R^2}{\eta} f \quad (26)$$

where ρ is the particle density and R is its radius. Here we are neglecting a very short transient effect and only give the steady state velocity which is attained. For particles of density 2 in air:

$$v = 0.70 R^2 (f/g) \text{ ft/hour} \quad (27)$$

where g is the acceleration of gravity, and R is to be given in microns.

Fractionation by falling under the influence of gravity from a cloud which has reached its maximum height has long been recognized as a possible effect. Clearly it cannot be important for particles in the micron range at early times.

An effect which has not been investigated carefully is the possibility for separation in the rising cloud. Although there is mixing due to general turbulence, there is also motion which is effectively a centrifuge action, and values of f as great as 100 g may occur. However, such forces are rather short-lived and total particle displacements must be small. If $R = 10$, $f = 100 g$ and the duration is 1/10 hours, a particle could be displaced a total of 700 ft.

4. Loss of volatile components

Let us consider n molecules per unit volume which were too volatile to be incorporated into the main precipitate. At a later time the temperature is low enough so that they can condense, and at this time the volume is increasing as

$$V(t) = \frac{4\pi}{3} (R_0 + vt)^3 \quad (28)$$

the rate of condensation of the molecules is

$$-\frac{dn}{dt} = \frac{kn}{V(t)} \quad (29)$$

where k contains the surface area available. This equation integrates to give

$$\ln \frac{n_0}{n} = \frac{3k}{8\pi v} \left[\frac{1}{R_0^2} - \frac{1}{(R_0 + vt)^2} \right] \quad (30)$$

As $t \rightarrow \infty$, $\ln n_0/n$ approaches a constant value. This means, of course, that only a certain fraction of the molecules can ever be captured and the remainder will be lost. The fraction captured increases with the available surface area of precipitate.

$$\ln \frac{n_0}{n_\infty} = \frac{3k}{8\pi v R_0^2} = \frac{k}{\left(\frac{4\pi}{3} R_0^3\right)} \left(\frac{R_0}{2v} \right) \quad (31)$$

In this connection it is significant to note that beta-decay of atoms in surface layers may result in their being expelled into the gas phase, and from this treatment it is clear that they may not be deposited again with the precipitate.

JLM:el