

A. Nelson Dingle
 Professor Emeritus of Atmospheric Science
 The University of Michigan
 Ann Arbor, MI 48109

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Abstract

Analysis of droplet nucleation upon Al_2O_3 nuclei in typical SRM exhaust clouds is presented. The free energy released in the phase transition is evaluated as a function of HCl molefraction and nucleating particle radius for the conditions found in the exhaust cloud from a Titan III launch 90 seconds after ignition. The surface thus derived is saddle shaped with a unique equilibrium at the saddle point, and a narrow and sharply defined droplet growth region. For this environment, specified at 298K, $p_{H_2O} = 23582$ dynes cm^{-2} , $p_{HCl} = 104.5$ dynes cm^{-2} , the saddle point occurs at $x_{HCl} = 8.8 \times 10^{-2}$, $r = 1.3 \times 10^{-6}$ cm, and the most efficient droplet growth proceeds at nearly constant HCl molefraction. This is equivalent to a molality of 5.355. The free energy surface for these conditions is shown for a range of HCl molefractions up to 0.2 and particle sizes of 10^{-7} cm $\leq r_p \leq 10^{-4}$ cm.

1. The Free Energy Equation

The free energy change, ΔF , of a system is a measure of the tendency of that system to progress from one thermodynamic state to another. For the case of condensation/evaporation of i different vapors on wettable particles, the general expression is

$$\Delta F = 4\pi\sigma'(a^2 - r_p^2) - \sum_i (\dot{n}_i kT \ln S_i') \quad (1)$$

where

ΔF is the Helmholtz free energy
 σ' is the surface energy per unit area of the droplet surface
 a is the radius of the droplet
 r_p is the radius of the nucleating particle
 \dot{n}_i is the number of i -molecules condensed on the drop
 k is Boltzmann's constant
 T is the absolute temperature of the droplet surface
 S_i' is the saturation ratio of vapor i with respect to a flat surface of bulk solution at the same concentration as the droplet

2. Analysis

The present purpose is to explore the application of this basic thermodynamic statement to the case of the co-condensation/evaporation of H_2O and HCl vapors on wettable particles in the open air. For this case, let $i = 1$ specify H_2O and $i = 2$ HCl, and let the HCl molefraction, x_2 , express the solution concentration. By definition, then, the molality, $M = 55.5 x_2 / (1 - x_2) = 55.5 f(x_2)$.

The drop radius is

$$a = \left[\frac{3}{4\pi} \frac{\dot{n}_1 \dot{m}_1}{\rho'} (1 + f(x_2)\beta) + r_p^3 \right]^{1/3} \quad (2)$$

where

\dot{m}_1 is the mass of a molecule of H_2O
 ρ' is the solution density
 β is M_2/M_1 and M_1 is the molecular weight of i .

Empirical expressions are used for the solution surface energy,

$$\sigma' = 75.728 - 0.1535(T-273.16) - 10.575f(x_2) \quad (3)$$

and the solution density

$$\rho' = 1.0 - 0.72158 f(x_2) \quad (4)$$

The saturation ratio for each vapor with respect to a flat surface of the solution is given by

$$S_i' = P_i / P_i^{sat}(x_2, T) \quad (5)$$

where

P_i is the environmental partial pressure of i and
 $P_i^{sat}(x_2, T)$ is the equilibrium vapor pressure of i over a flat surface of solution of concentration x_2 and temperature T .

For $T = 288^\circ$ K, the values of S_1' and S_2' as functions of x_2 are shown in Fig. 1. Note that $S_2' > 1$ only for $x_2 < 8.85 \times 10^{-2}$, whereas $S_1' > 1$ only for $x_2 > 8.15 \times 10^{-2}$, hence at 288 K, the vapors are both supersaturated with respect to the bulk solution only in the narrow HCl molefraction range of $8.15 \times 10^{-2} \leq x_2 \leq 8.85 \times 10^{-2}$.

By means of (2), (3), (4) and (5), ΔF may now be expressed in terms of the six variables P_1 , P_2 , T , n_1 , r_p , and x_2 . For any particular case, the environmental values of P_1 , P_2 and T must be specified, thus ΔF may be expressed for such a case in terms of r_p , \dot{n}_1 and x_2 .

The total number of molecules, \dot{n}_s , required to form a monolayer of solution on a particle may be estimated as a function of r_p and x_2 as follows. If the particle and its coating of solution is spherical, then \dot{n}_s is given by

$$\dot{n}_s = \dot{n}_1 + \dot{n}_2 = 4 \left(1 + \frac{r_p}{\dot{r}_s} \right)^2 \quad (6a)$$

also

$$\dot{n}_1 = 4 \left(1 + \frac{r_p}{\dot{r}_s} \right)^2 / (1 + f(x_2)) \quad (6b)$$

where \dot{r}_s is the mean molecular radius of a "molecule" of solution,

defined by

$$\dot{r}_s \equiv \left\{ \frac{3}{4\pi} [(1 - x_2) \dot{v}_1 + x_2 \dot{v}_2] \right\}^{1/3}$$

where \hat{v}_1 and \hat{v}_2 are respectively the molecular volumes of H_2O and HCl in solution. In general, the molecular volume of species i may be written

$$\hat{v}_i = M_i / \rho' \eta_0$$

where η_0 is Avogadro's number giving

$$\hat{v}_1 = 2.9914 \times 10^{-23} \left(\frac{1}{\rho'} \right)$$

and $\hat{v}_2 = \beta \hat{v}_1$.

Values of \hat{r}_s for the concentration range $1.8 \times 10^{-5} \leq x_2 \leq 6.4306 \times 10^{-1}$ are given in Table 1.

Table 1. Values of \hat{r}_s for HCl_{aq} in the concentration range $10^{-3} < M < 10^2$

x_2	M	x_1	$10^8 \cdot \hat{r}_s \text{ cm}$
1.8×10^{-5}	10^{-3}	0.999982	1.9256
1.8×10^{-4}	10^{-2}	0.99982	1.9259
1.8×10^{-3}	10^{-1}	0.9982	1.9269
1.77×10^{-2}	10^0	0.9823	1.9373
1.5266×10^{-1}	10^1	0.84734	2.0212
6.4306×10^{-1}	10^2	0.35694	2.2794

A reasonable value for \hat{r}_s in the concentration range of $8 \times 10^{-2} < x_2 < 9 \times 10^{-2}$ is 2×10^{-8} cm. Using this value in (6b), \hat{n}_1 may be calculated, and ΔF may be determined as a function of r_p and x_2 for specified environmental conditions.

Taking environmental conditions as found in the stabilized ground cloud generated by a Titan III launch: $T = 298.16^\circ K$, $P_1 = 23582$ dynes/cm², $P_2 = 104.5$ dynes/cm² at time $t = 90$ sec., the map of ΔF in (x_2, r) coordinates (Fig. 2) is constructed.

3. Features of the $\Delta F(x_2, r_p)$ Surface

The contours of the ΔF surface in the r_p, x_2 coordinates show a definite "saddle point", which for the specified environmental conditions, occurs at $r_p = 1.3 \times 10^{-6}$ cm, $x_2 = 8.8 \times 10^{-2}$. This point is analogous to the critical point defined for single vapor heterogeneous nucleation (see, e.g., Byers, 1965, Chap. 2). The surface thus defined is equivalent to the free energy surface $\Delta F(n_A, n_B)$ for the $H_2O - H_2SO_4$ system that has been discussed by Reiss (1950)², Kiang and Stouffer (1973)⁴, Hamill (1975)⁵ and Hamill, et al (1977)³. Reiss (1950)⁵ showed that, when the surface energy term is included in the free energy expression, the free energy surface $\Delta F(n_A, n_B)$ is saddle-shaped with a

saddle point defined by $\frac{\delta}{\delta n_A} (\Delta F) = 0$ and $\frac{\delta}{\delta n_B} (\Delta F) = 0$.

The saddle shape was also found to be present under stratospheric conditions for the $H_2O - H_2SO_4$ system by Hamill, et al (1977).³

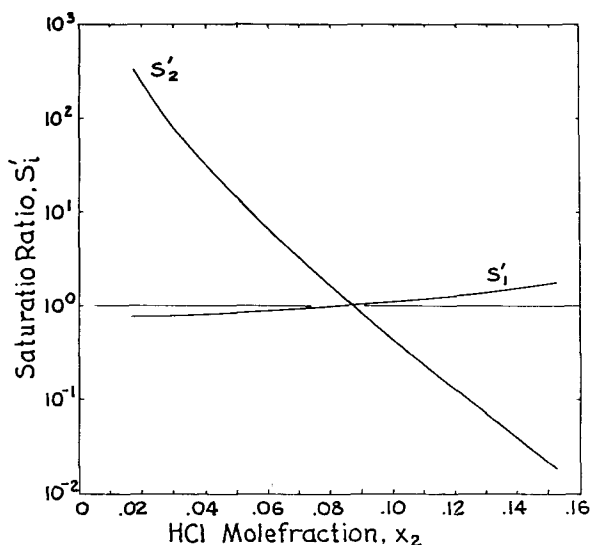


Fig. 1

Several features of the $\Delta F(x_2, r_p)$ surface (Figure 2) merit discussion. At constant $x_2 = 8.8 \times 10^{-2}$, ($M = 5.355$), the ΔF values rise gradually with increasing particle size in the range 10^{-8} cm $\leq r_p \leq 1.3 \times 10^{-6}$ cm, reaching a maximum of 25×10^{-11} erg at the latter size (saddle point). ΔF then decreases to 0 at $r_p = 2.67 \times 10^{-6}$ cm and decreases sharply to large negative values for larger sizes.

At higher and lower concentrations, e.g., $x_2 \geq 13 \times 10^{-2}$ and $x_2 \leq 4 \times 10^{-2}$, the ΔF surface rises sharply as r_p increases above 10^{-6} cm. Thus, the growth region for HCl_{aq} droplets lies between nearly vertical "canyon" walls at $x_2 \sim 5.8 \times 10^{-2}$ and $x_2 \sim 11.7 \times 10^{-2}$ for nuclei of size $r_p \sim 2 \times 10^{-6}$ cm and larger. The bottom of the "canyon" is relatively broad and flat with the locus of minima lying near $x_2 = 8.8 \times 10^{-2}$.

The profile of the $\Delta F(x_2, r_p)$ surface taken at $r_p = 10^{-6}$ cm (Figure 3) shows the shape of the "canyon." In addition the values of the respective components of ΔF are shown for $r_p = 10^{-6}$ cm as a matter of interest. This diagram necessarily is discontinuous at $\Delta F = 0$. The terms represented are:

$$\Delta F_\sigma = 4\pi\sigma' (a^2 - r^2) - \text{constant}$$

$$\Delta F_1 = \hat{n}_1 k T \ln S_1'$$

$$\Delta F_2 = \hat{n}_2 k T \ln S_2'$$

$$\Delta F' = \Delta F_1 + \Delta F_2$$

$$\Delta F = \Delta F' + \Delta F_r$$

ΔF_2 is affected by two factors: (a) as x_2 increases, \hat{n}_2 also must increase, and (b) as x_2 increases S_2' must decrease causing $\ln S_2'$ to go from positive to negative values as S_2' decreases through 1.0. The result of this is a minimum in ΔF_2 near $x_2 = 4.5 \times 10^{-2}$, and a sign reversal near $x_2 = 8.8 \times 10^{-2}$. No minimum is found for ΔF_1 because both \hat{n}_1 and S_1' decrease as x_2 increases for the given r_p value. Inasmuch as droplet growth cannot proceed unless both vapors are saturated, the curves ΔF_1 and ΔF_2 indicate that the region for droplet growth is in fact much narrower than the

ΔF "canyon." This is true because, if either vapor is undersaturated, a droplet in that vapor must yield the undersaturated species by evaporation because the mass diffusion is proportional to $P_1(S_1'-1)$. The approximate range for nucleation to occur is $8.5 \times 10^{-2} \leq x_2 \leq 8.85 \times 10^{-2}$. The minimum value of ΔF occurs at $x_2 = 8.82 \times 10^{-2}$, thus this is the most probable HCl concentration for a particle size $r = 10^{-5}$ cm under the specified conditions.

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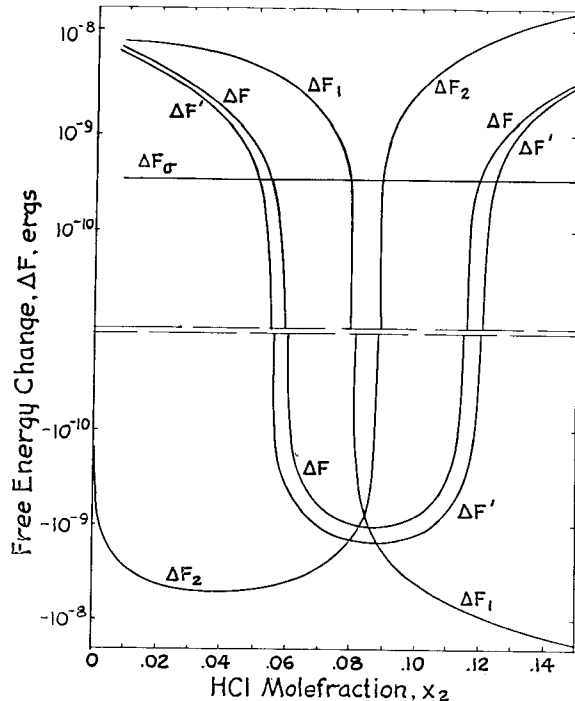


Figure 3

4. Conclusion

It is clear that $\Delta F(x_2, r)$ varies with T , P_1 and P_2 . For the purposes of NASA, the maps of $\Delta F(x_2, r)$ for the various environmental conditions that may be encountered at different launch sites and in all seasons should be computed. Particularly the changes imposed upon the system by the increase of solid rocket booster capacity required for the Space Shuttle should be more completely evaluated.

Acknowledgments

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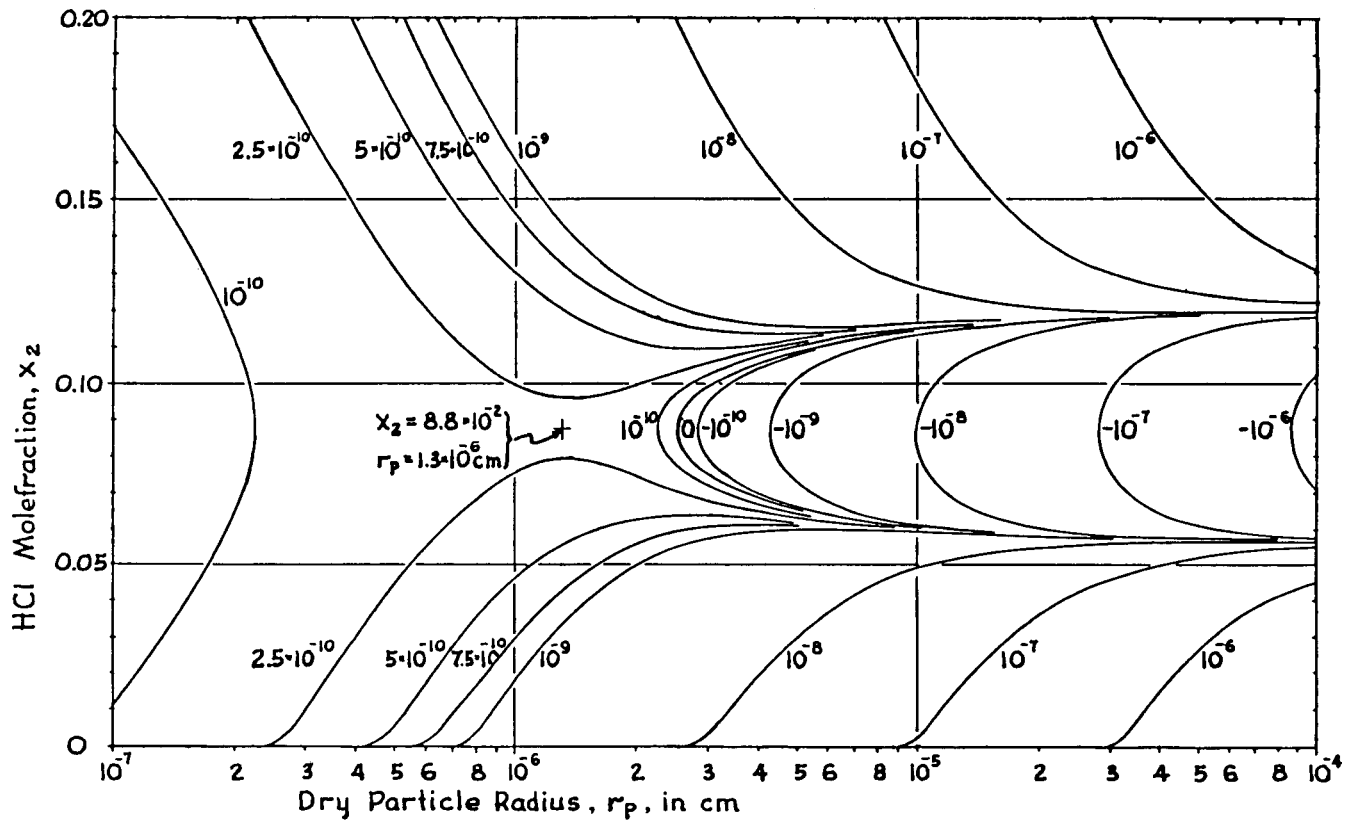


Figure 2