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AN EQUATION THAT DESCRIBES MATERIAL OUTGASSING FOR CONTAMINATION MODELING

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On page 12 following equation (A-8), the page should read:

Solving equation A-8 for P and substituting into equation A-1 and then solving for dx/dt gives:

$$\frac{dx}{dt} = 4.39 \times 10^{-4} \sqrt{M/T} \left[\frac{(P_v - P_w) A_1 RT\sqrt{M/T} + (P_v - P_b) 2278\,MF}{2278\,MF + (A_1 + A) RT\sqrt{M/T}} \right] \tag{A-9}$$

The room temperature collection term, S, is

$$S = 4.39 \times 10^{-4} A_1 \sqrt{M/T} \left[\frac{(P_v - P_w) ART\sqrt{M/T} - (P_w - P_b) 2278\,MF}{2278\,MF + (A_1 + A) RT\sqrt{M/T}} \right]$$

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16. Abstract

A generalization of the Clausius-Claperon equation for vapor pressure is made for an outgassing material. The expression is derived using Langmuir's equation for the outgassing rate of a material and using an empirical equation based on D. F. Wilcock's work for the vapor pressure of a material as a function of its molecular weight and temperature. Also, outgassing rate equations are derived in terms of the vapor pressure of the outgassing material for three general geometries.

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CONTENTS

AN EQUATION THAT DESCRIBES MATERIAL OUTGASSING FOR CONTAMINATION MODELING

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INTRODUCTION

For many years, molecular contamination from material outgassants has been a continuing problem in the construction of spacecraft. Instruments with cooled detectors and optical instruments that operate in the ultraviolet light region are particularly susceptible. In many cases, contamination sources are at or near room temperature, while condensing surfaces are at a lower temperature.

Prediction of the time- and temperature-dependence of room temperature outgassing rates is complicated because rates are usually so low as to make direct measurement impractical,* and also, the lack of molecular homogeneity in most materials complicates application of the Langmuir equation. The Langmuir equation relates the outgassing rate and the vapor pressure of a homogeneous monomolecular weight material during exposure to high vacuum. These two difficulties were encountered in a contamination problem on a series of very high resolution radiometers (VHRR's) that were flown on weather satellites (ITOS D through G) for the National Oceanic and Atmospheric Administration (NOAA). Efforts to solve the contamination problem resulted in the derivation of an equation for a material's vapor pressure that can be used in contamination modeling. Three examples of this type of application are given in the Appendix.

DERIVATION

Langmuir's equation for the outgassing rate of a material exposed to high vacuum is

$$\frac{dW}{dt} = 0.439A\sqrt{M/T}\ P_v,^{\dagger} \tag{1}$$

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*Direct measurements are impractical either because of the length of time involved or because the room temperature vapor pressures of outgassants are close to or less than the pressures obtained in outgassing test equipment.

†Refer to the Appendix, Case 1, for application of Langmuir's equation to a vacuum microbalance system and for the conditions under which use of equation 1 is justified.

where

$\frac{dW}{dt}$ = Weight loss rate, mg/sec

A = Surface area, cm^2, of sample

M = Molecular weight, g/mole

T = Absolute temperature, K

P_v = Vapor pressure, Pascal, at T

P_v, according to the Clausius - Claperyron equation is

$$P_v = P_o e^{-(E/R)(1/T - 1/T_o)}.$$

where

P_o = Vapor pressure, Pascal, at T_o

E = Heat of vaporization, cal/gmole

R = gas constant, 1.98 cal/gmole K

Thus,

$$\frac{dW}{dt} = 0.439A\sqrt{M/T}\, P_o e^{-(E/R)(1/T - 1/T_o)} \qquad (2)$$

For an outgassing plastic or adhesive, E and P_o are functions of molecular weight M, which, in turn, is a function of time and temperature. D. F. Wilcock (Reference 1) experimentally determined vapor pressure as a function of molecular weight and temperature for mono-molecular weight factions of methylpolysiloxanes. Generalizing from Wilcock's work, a relation between molecular weight, temperature, and vapor pressure was presumed to be

$$P_v = c_1 e^{c_2 M} e^{-c_3 M/RT} \qquad (3)$$

where c_1, c_2, c_3 are material constants.

Substituting the right side of equation 3 for P_v in equation 1 and defining three new constants y, E_o, and M_o such that $e^{M(c_2 - c_3/RT_o)} = y^M$, $c_3 = E_o/M_o$, and $c_1 = P_o/y^{M_o}$, results in the generalization of equation 2, which is

$$\frac{dW}{dt} = 0.439A\sqrt{M/T}\ P_o y^{M - M_o} e^{-(E_o M/RM_o)(1/T - 1/T_o)} \tag{4}$$

Extending this generalization to the Clausius-Claperyron equation gives

$$P_v = P_o y^{M - M_o} e^{-(E_o M/RM_o)(1/T - 1/T_o)} \tag{5}$$

DISCUSSION

M_o is taken to be the molecular weight of the lightest faction of a given species and E_o is its heat of vaporization. The factor $P_o\ y^{M - M_o}$ gives the variation of vapor pressure with molecular weight at T_o and the expression $E_o\ M/M_o$ gives the variation of the heat of vaporization with molecular weight. The constant y must be less than 1 in order for vapor pressure to decrease with increasing molecular weight at T_o.

If a material were actually composed of a single generic species such as Wilcock's methylpolysiloxanes and its molecular weight distribution were given by Ω, then there would be one expression such as equation 5 for each molecular weight, M, represented in Ω. The total vapor pressure of the outgassants would be the sum of these individual partial pressures defined by equation 5 and the composition of Ω would determine how long the various partial pressures would exist. The problem becomes complicated at this point because the composition of Ω would have to be time-dependent. This is because some molecular weight factions would be exhausted before others as a function of the original amounts which were present and their rates of depletion. Also, if reaction or polymerization occur that change the distribution of molecular weights, these would have to be represented in Ω as a time-temperature function.

In the outgassing of a real material, a number of generic species are usually evolved simultaneously; therefore, the system becomes even more complex and makes the problem extremely unwieldy analytically unless some simplifying assumptions are made.

It has been found that an equivalent (from an outgassing point of view) material can be defined that allows the problem to be dealt with on a phenomenological basis. Using this approach a functional form of M is defined that makes equation 4 fit observed outgassing data with the values of E_o and P_o equal to the constants for water at T_o. The most successful attempt at defining M in this manner has been with equations of the form

$$M = M_o \times f(W/W_o), \quad M_o = 18 \tag{6}$$

where W_o is conceptually equivalent to the "active mass" referred to in Papazin's work (Reference 2) and $f(W/W_o)$, is a continuous function that increases with increasing fractional weight loss, W/W_o. The "active mass" W_o is an increasing function of increasing temperature. An equation of this type describes an equivalent material whose outgassing initially consists mainly of water. It assumes a material that predominantly outgasses vapor with a single molecular weight after a given weight loss at a particular temperature and it assumes that the molecular weight of the outgassed vapor continuously increases as sample weight decreases. Time is not explicit in equation 6 and there are no time-temperature, cross-product terms; therefore, the equation does not account for polymerization or reaction in time to form a different molecular weight distribution in the material. The extent to which the outgassing of a material cannot be described by an equivalent material such as described in equation 6 is measured by the extent of the variation in the constants in the equation for $f(W/W_o)$ when it is fitted to observed outgassing data.

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APPENDIX

APPLICATION OF EQUATION 5 TO THREE COMMON OUTGASSING SYSTEMS

Let x be the net weight of material lost from an outgassing sample per unit area. The rate of this weight loss is equal to the difference between the rate of evaporation, G (g/cm_2 sec) and the rate of condensation, C.

$$\frac{dx}{dt} = G - C$$

The rate of evaporation from the material, according to the Langmuir equation (Reference 1, p. 18), is

$$G = 4.39 \times 10^{-4} \sqrt{M/T}\ P_v$$

where P_v is the vapor pressure (Pascal) of the material with molecular weight M (g/mole) being evaporated at temperature T (K).

The rate (g/cm_2 sec) at which molecules of molecular weight, M, strike the surface of the outgassing material is equal to $4.39 \times 10^{-4} \sqrt{M/T}\ P$; where P is the material's partial pressure in the vicinity of the sample (Reference 1, p. 14). Assuming a sticking coefficient of 1, which is justified for most room temperature outgassants* (Reference 1, p. 18), then

$$C = 4.39 \times 10^{-4} \sqrt{M/T}\ P$$

Thus

$$\frac{dx}{dt} = 4.39 \times 10^{-4} \sqrt{M/T}\ (P_v - P) \qquad \text{(A-1)}$$

Having established this, most outgassing contamination problems consist of determining P in terms of P_v from constitutive equations based on the conservation of mass, and determining P_v experimentally.

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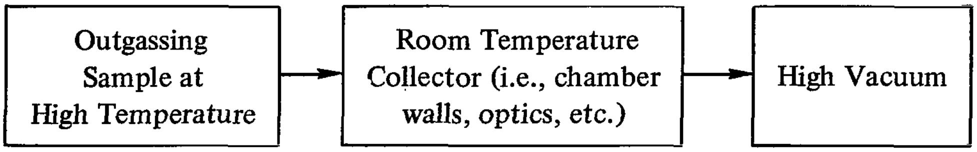
*The sticking coefficient referred to here is not the same as the sticking factor discussed in Reference 2. The sticking coefficient referred to here is the probability that a molecule will strike the surface and stay there long enough to accomodate thermally to that surface rather than rebound specularly from the surface. The sticking factor defined in Reference 2 is a relative deposition rate normalized to the rate of 253 K (-20° C).

Case I. Condensing Surface in Series with a Pump

This problem is outlined in the following flow diagram:



The meaning of the flow diagram is that all the molecules outgassed from the sample must first condense on the room temperature collector and then be reemitted before being lost from the system. An example of this system is an Ainsworth balance often used to conduct outgassing measurements. Material outgassed from the sample goes to one of three places. It either returns to the sample and condenses as indicated by the P term in equation A-1, or it strikes the relatively cold chamber walls and condenses, or else it is reemitted from the walls and finds its way to the diffusion pump with its liquid nitrogen (LN_2) cold trap, and leaves the system. The latter two possibilities are expressed as follows:

$$\underbrace{A \frac{dx}{dt}}_{\substack{\text{material}\\ \text{lost from}\\ \text{sample}}} = \underbrace{4.39 \times 10^{-4} A_1 \sqrt{M/T}\,(P - P_w)}_{\substack{\text{material condensed}\\ \text{on room temperature}\\ \text{chamber walls}}} + \underbrace{\frac{MF}{RT}(P_w - P_b)}_{\substack{\text{material lost to}\\ \text{vacuum pump}}} \qquad \text{(A-2)}$$

where

A = the sample area (cm^2)

A_1 = the area where material condenses at room temperature (cm^2)

P_w = the vapor pressure (Pascal) of material with molecular weight M at the wall temperature

P_b = the vapor pressure of material with molecular weight M, in the diffusion pump cold trap

F = the conductance (liter/sec) between the point where vapor pressure is P_w and where it is P_b

R = Gas Constant = 8.294×10^3 Pascal - liter/mole K

Solving equation A-2 for P and substituting into equation A-1 and solving for dx/dt gives:

$$\frac{dx}{dt} = \frac{4.39 \times 10^{-4} A_1 \sqrt{M/T}}{(A_1 + A)} (P_v - P_w) + \frac{MF}{RT(A_1 + A)} (P_w - P_b) \qquad \text{(A-3)}$$

Equation A-3 expresses the same thing that equation A-2 does and interpretation of the two terms involved is the same except now the equation is expressed in terms of the vapor pressure of the material.

Equation A-3 can be applied to an Ainsworth balance system used at the Goddard Space Flight Center (GSFC). A schematic of the system is shown in figure A-1.

Material is observed to condense on the inside of the quartz chamber wall along a 5- to 10-cm long area immediately adjacent to the heater. Thus, if the length of a condensation area is taken as 10 cm

$$A_1 = 2 \times 2\pi \left(\frac{7.62}{2}\right) (10) = 479 \text{ cm}^2$$

The conductance between a point just outside the furnace and the diffusion pump is complex. Davis (Reference 3) has calculated F for cylindrical elbows and other geometrics that prevent line-of-sight transmission. However, this is not needed because the mass flow for material that did not condense at room temperature just outside the furnace is the same at any point along the line to the diffusion pump, or else an accumulation would be observed. Therefore its value can be determined at any point along the line. A measure of this flow is given by the expression:

$$\frac{MF_1 (P_w - P_{b_1})}{RT \quad (A_1 + A)} \qquad \text{(A - 4)}$$

where P_{b_1} is the material's vapor pressure at some point between the area where its vapor pressure is P_w and the diffusion pump cold trap where its vapor pressure is P_b. The constant F_1 is the conductance in the area between the points where the vapor pressure is P_w and where it is P_{b_1}. Expression A- 4 can therefore be substituted for the second term in equation A-3. A pressure measurement is determined at the base of the first elbow in the system by an ionization gage that is calibrated for air. It typically reads in the 1.33×10^{-4} Pascal range

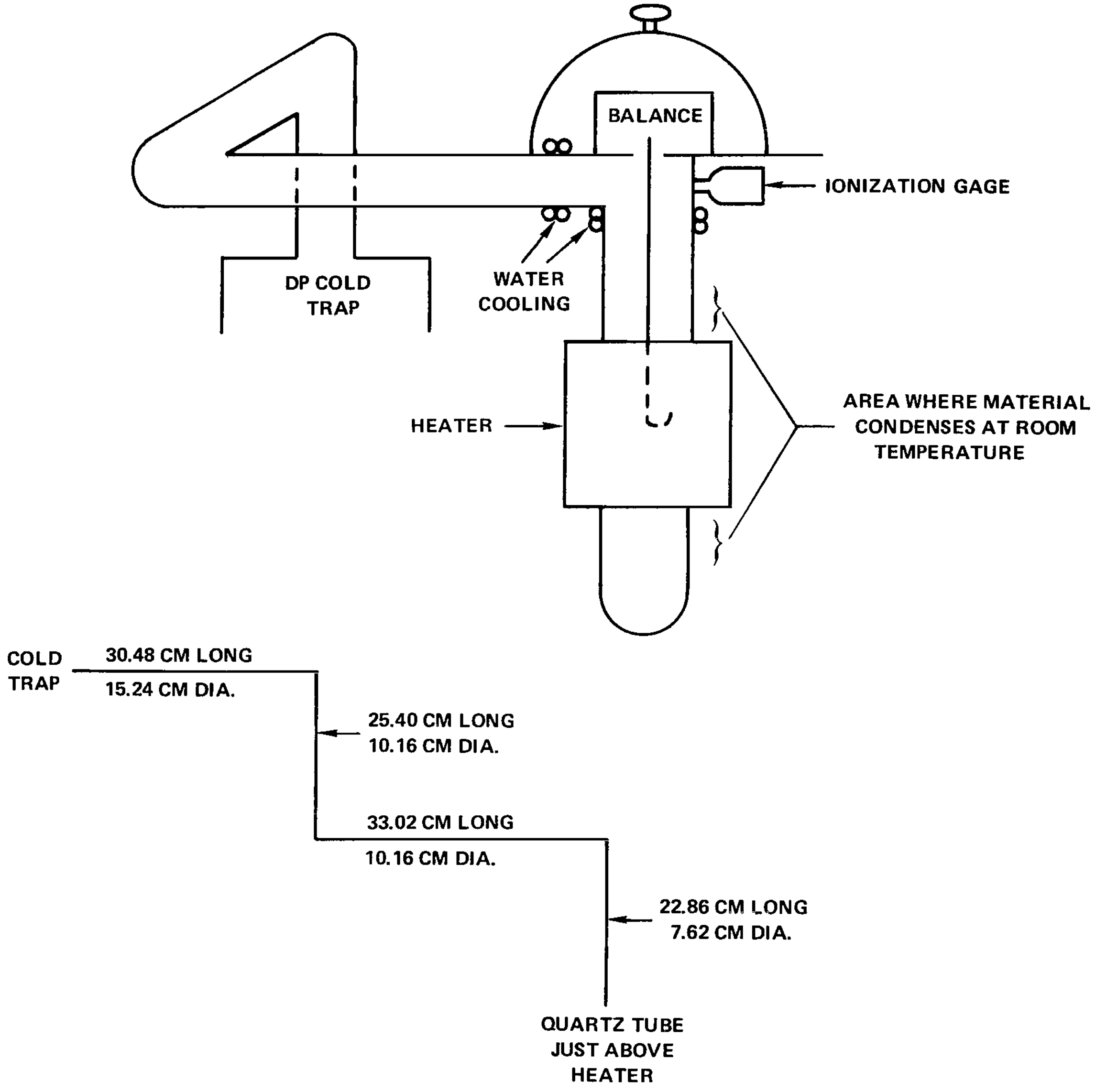


Figure A-1. Schematic diagram of an Ainsworth balance.

soon after evacuation has started (figure A-1). The conductance from just above the furnace to this point is relatively simple and is given by (Reference 1, p. 88)

$$F_1 = 30.48 \frac{d^3}{L} \left(\frac{T}{M}\right)^{1/2} \text{ liter/sec}$$

where d = the diameter of the tube (cm) and L is its length in cm. For a material with molecular weight 18 at 300 K in the Ainsworth balance

$$F_1 = 30.48 \frac{(7.62)^3}{(22.86)} \left(\frac{300}{18}\right)^{1/2} = 2408 \text{ liter/sec}$$

The sample area is typically 20 cm^2. Substituting expression A-4 in equation A-3 and using 6.65×10^{-4} Pascal for P_{b_1} gives

$$\frac{dx}{dt} = 1.05 \times 10^{-4} (P_v - P_w) + 3.49 \times 10^{-5} (P_w - 6.65 \times 10^{-4}) \qquad \text{(A-5)}$$

for T = 300 K.

Ordinarily $A \ll A_1$ and at temperatures greater than room temperature $P_v \gg P_w$ and 6.65×10^{-4} Pascal, therefore equation A-3 reduces to

$$\frac{dx}{dt} = 4.39 \times 10^{-4} \sqrt{M/T}\ P_v \text{ g/cm}^2 \text{ sec or } \sim 1.05 \times 10^{-4} P_v \text{ (M = 18 g/mole, T > 300 K)}$$

which is subtantively equation 1 in the main text.

However, at room temperature $P_v = P_w$ and equation A-5 points up a caution that must be exercised in applying equation 1 once the equation for P_v is determined. Equation 1, which adequately describes high temperature outgassing rates, cannot be used to give room temperature rates for this type of system. As room temperature (300 K) is approached, the outgassing rate for M = 18 is approximated more closely by

$$\frac{dx}{dt} = \frac{MF_1 (P_w - P_{b_1})}{RT \ (A_1 + A)} - \sim 3.49 \times 10^{-5} (P_w - 6.65 \times 10^{-4}) \text{ g/cm}^2 \text{ sec} . \qquad \text{(A-6)}$$

Equation A-6 also indicates that materials with a room temperature vapor pressure less than $P_{b_1} \sim 6.65 \times 10^{-4}$ Pascal do not appear to lose weight in this system and can even appear to gain weight slightly once very volatile materials have been removed and backstreaming pump oil starts to condense on a material that has a large surface area. This phenomeon has been observed with aluminum anodize, for example.

For Case I systems, the room temperature collection term is generally of the most interest since in practical applications, other than the Ainsworth balance system, the room temperature collector surface usually represents an optic of some sort. If S represents this term then

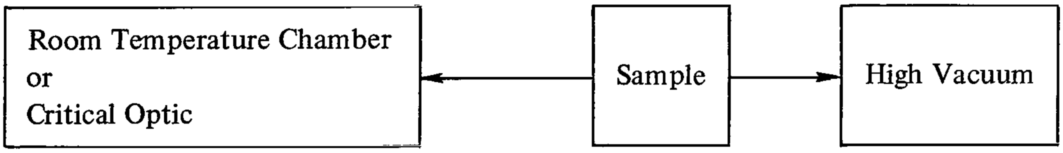
$$S = 4.39 \times 10^{-4} A_1 \sqrt{M/T}\ (P - P_w) \tag{A-7}$$

Solving equation A-1 for P and substituting into equation A-7 and substituting equation A-3 for dx/dt gives, on rationalizing

$$S = \frac{4.39 \times 10^{-4} AA_1 \sqrt{M/T}}{(A_1 + A)} (P_v - P_w) - \frac{A_1 MF}{(A_1 + A)} (P_w - P_b)$$

Case II. Condensing Surface in Parallel with Pump

This problem is illustrated in the following flow diagram:



In this case the constitutive equation resulting from the conservation of mass is

$$A \frac{dx}{dt} = 4.39 \times 10^{-4} A_1 \sqrt{M/T}\ (P - P_w) + \frac{MF}{RT} (P - P_b) \tag{A-8}$$

Solving equation A-8 for P and substituting into equation A-1 and then solving for dx/dt gives:

$$\frac{dx}{dt} = 4.39 \times 10^{-4} \sqrt{M/T} \left[\frac{(P_v - P_w) A_1 RT \sqrt{M/T} + (P_v - P_b) \overset{2278}{\cancel{4.39 \times 10^{-4}}} MF}{\underset{2278\ MF\ +}{\cancel{4.39 \times 10^{-4} MF}} + (A_1 + A) RT \sqrt{M/T}} \right] \tag{A-9}$$

The room temperature collection term, S, is

$$S = 4.39 \times 10^{-4} A_1 \sqrt{M/T} \left[\frac{(P_v - P_w) ART \sqrt{M/T} - (P_w - P_b) \overset{2278\ MF}{\cancel{4.39 \times 10^{-4} MF}}}{\underset{2278\ MF}{\cancel{4.39 \times 10^{-4} MF}} + (A_1 + A) RT \sqrt{M/T}} \right]$$

Case III. No Return Flux due to Container

In this case there is no interaction of the evolved gas with anything but itself. To approximate this situation the outgassant is imagined to evolve into an expanding volume, V, whose radius, r, is given by the mean free path. The constitutive equation is therefore

$$P = \frac{nRT}{V} = \frac{Ax}{M}\frac{RT}{V},\ V = \frac{4}{3}\pi r^3 \qquad \text{(A-10)}$$

$$r = L_o + v_r t$$

where

L_o = initial mean free path

v_r = mean molecular velocity = $\left(\frac{3RT}{M}\right)^{½}$

Substituting equation A-10 into equation A-1 gives

$$\frac{dx}{dt} = 4.39 \times 10^{-4}\sqrt{M/T}\left(P_v - \frac{x3ART}{4\pi M(L_o + v_r t)^3}\right)$$

In this case if a small room temperature collector is introduced which returns relatively little material to the sample, then the room temperature collection term, S, is simply the product of the outgassing rate times a view factor assuming a sticking coefficient of one. The view factor is determined in the same way as for a radiative heat transfer problem.

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