Comment on "Evaporation of Electroplated Cadmium in High Vacuum"

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WALES and Leubben[1] stated: "The question has arisen concerning the desirability and feasibility of using cadmium in the space environment." However, they neglected to define any general or specific space zone by corresponding pressure and temperature values. Some measured or estimated ambient pressures and temperatures for various space environments, presented in rounded numbers, are as follows. For earth orbit at altitude of 125 miles, Jaffe and Rittenhouse[2] give the pressure as 10^{-6} mm Hg, and the GT-4 spacesuits provided protection against temperatures from $-150°$ to $+250°$F (equivalent to 10^{-9} atm and $172°$ to $394°$K). The immediate moon environment is represented by a pressure of 10^{-13} mm Hg and a temperature range of $-250°$ to $450°$F (equivalent to 10^{-16} atm and $117°$ to $505°$K). For interplanetary space, Jaffe and Rittenhouse[2] indicate in their Table 1 that the pressures are of the order of 10^{-16} to 10^{-15} mm Hg, and the temperatures range from 10^3 to 10^5°F and/or °C (equivalent to 10^{-19} to 10^{-18} atm and $811°$ to $100,000°$K). For interstellar space, van de Hulst[3] estimated the atomic population as about one atom per cubic centimeter, which corresponds to 10^{-17} mm Hg (equivalent to 10^{-20} atm).

In laboratory apparatus, evaporation rate and vapor pressure measurements for cadmium have been made at pressures from 10^{-6} to 10^3 mm Hg and at temperatures of from $260°$ to $1409°$F (equivalent to 10^{-9} to 1 atm and $400°$ to $1038°$K, the latter value being for the boiling point of cadmium).

Wales and Leubben[1] also stated: "This study was undertaken to determine a few of the properties of electroplated cadmium in a simulated space environment." However, their pressure of 10^{-6} mm Hg corresponds only to the space environment at an altitude of 125 miles above the earth, whereas the condensation-evaporation range of $23°$ to $400°$F covers only about 56% of the corresponding temperature range of $-150°$ to $+250°$F. Thus any significant projection of the properties of cadmium in environments such as the moon and interplanetary space must include most careful derivations from the excellent data obtained in the authors' laboratory. It is unfortunate that they did not make their data available directly in tabular form.

Projection from Laboratory to Space Environment

In making such projections one must not only recognize that there is a significant increase in evaporation rates at the much lower ambient pressures but also recognize the necessity for a more accurate projection to temperature ranges far below those used in laboratory studies. No data are available on the increased evaporation rate for cadmium with a decrease in pressure which would permit projection to 10^{-13} mm Hg. However, an analogous situation has long been known for tungsten. Fonda[4] found that decreasing pressure by eight orders of magnitude resulted in a 100-fold increase in the evaporation rate at $4707°$F ($2870°$K) and an even greater increase at $4437°$F ($2720°$K). These observations suggest that an increase in the rate of evaporation of cadmium with reduction in pressure from 10^{-6} to 10^{-13} mm Hg might well be 100 times, and probably considerably more. The same effect has been observed for the complete vaporization of silicone "grease" in space, even though it had been evaluated as sufficiently nonvolatile from evaporation rates under laboratory "high vacuum."

Wales and Leubben use the vapor pressure equation derived by Gloria, Stewart, and Savin[5] as $\log P$, mm Hg $= -5693.1/T + 8.564$, or

$$\log P_{atm} = -5693.1/T + 5.68 \qquad (1)$$

Greenbank and Argent[6] have recently reported the vapor pressures of cadmium, zinc, and magnesium in connection with their study of the extent to which evaporation is inhibited by material adsorbed at the surface.

The conventional reciprocal temperature dependence required by $\log P = -A/T + B$ is based on an esoteric deduction evolved solely by mathematical necessity with no warranty of any reality for derived values for temperatures significantly removed from the data range, particularly in low-temperature ranges.

In retrospect, the requirement for reciprocal temperature dependence for the vapor pressure of cadmium is even more incongruous when it may be noted that the natural habit of atomic aggregates of cadmium are reflected in many measured physical properties, such as electrical resistivity, heat capacity, and coefficient of thermal expansion, which all show a substantially linear temperature dependence.

Development of a more realistic vapor pressure equation

The superb data on the vapor pressures of the solid elements from helium to carbon (graphite) have been re-examined for a $7200°$F ($4000°$K) temperature range. It has been observed that the temperature dependence of the vapor pressure of solids is uniformly and more accurately expressed by

$$\log P = a \log T + b \qquad (2)$$

with such relationship applying over any temperature range wherein the heat capacity has a substantially linear temperature dependence. This relationship is fully consistent with the second law of thermodynamics relating to the degradation and dissipation of energy in any thermal process. Differentiation of Eq. (2) leads to a term common to the Clausius-Clapeyron equation in its usual differential form. Equating and clearing give the temperature dependence of the heat of sublimation L expressed by

$$L = aRT \qquad (3)$$

Determinations of the vapor pressure of cadmium which have been made in the temperature range of $280°$ to $532°$F ($411°$ to $551°$K) yield

$$\log P_{atm} = 24.0 \log T - 70.55 \pm 0.15 \qquad (4)$$

Comparison of linear and reciprocal temperature dependent equations

The literature on the vapor pressures of solids has been generously illustrated over the last 50 yr with $\log P$ vs $1/T$ plots showing the data points reposing in a concave lens section traversed by the required rectilinear least squares derivation. The same type of curvature for data points is shown by Wales and Leubben in their Fig. 2 on the rate of evaporation of cadmium ($\log G$ vs $1/T$).

It is important to note that the choice of vapor pressure equation to be used is of little importance in the temperature range of original data. Thus, for the upper moon temperature of $450°$F ($505°$K), the $\log P = -5.68$ [Eq. (4)] whereas $\log P = -5.59$ [Eq. (1)], thus being essentially identical.

The significance of the choice of derivation used is particularly significant at low temperatures during the study of condensation rates and evaporation rates using vapor pressure derivations for reference. At the low temperature of $-150°$F ($172°$K) in orbit of the earth at the 125-mile elevation, $\log P = -16.90$ [Eq. (4)] as compared to $\log P = -27.41$ [Eq. (1)], thus being 10 powers higher than the conventional derivation.

Likewise, for the low temperature of the moon environment, $-250°$F ($117°$K), $\log P = -20.92$ [Eq. (4)] as com-

pared to $\log P = -42.98$ [Eq. (1)], thus being 22 powers higher than the conventional derivation.

The conventional derivation for the vapor pressure of cadmium at 1°K gives $\log P = -5688$ [Eq. (1)], or $P = 10^{-5688}$ atm, which is so obviously devoid of any remote resemblance to physical reality as to warrant any further comment.

The use of a more realistic form of vapor pressure equation that reflects the linear temperature dependent natural habit of solid atomic aggregates is urged for reference with newly acquired condensation rate and evaporation rate data. This should lead to more reliable conclusions for the design and construction of a wide variety of space components in order that more successful operation will include greater safety for the space explorers.

References

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Reply by Authors to A. L. Davis

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WE feel that it is unnecessary to define a particular pressure zone since we are concerned primarily with nonequilibrium conditions.

The temperature of a vehicle in space is primarily dependent upon the radiant energy striking it (from, e.g., the sun, the moon, the earth), the energy generated in the vehicle (from, e.g., the engine and other power sources, and passengers), and the energy radiated by the vehicle. Proper thermal control maintains the vehicle at any desired average temperature, which probably varies from $-50°$ to $+150°$F depending upon many factors, e.g., the thermal inertia of the part, the orbit of the vehicle, and the thermal requirements of the payload. The higher temperatures are more critical in terms of the rate of evaporation of cadmium. The temperatures quoted by Davis for interplanetary space (and interstellar space) are kinetic temperatures (of, e.g., hydrogen) and not ambient temperatures.

Various problems have arisen in long-time studies in high vacuum technology, and many of these problems have been attributed to the silicone "grease" and other low vapor pres-

sure materials used in the systems. Vaporization and back-diffusion of most of the "oils" and "greases" used in short-time studies create many problems in long-time studies, even with the use of extensive and complex baffles and traps.

The work of Greenbank and Argent[1] verifies our conclusions[2] that the purity of the material, and/or its surface, are definite factors affecting the rate of evaporation.

Fonda[3] performed his studies at pressures between 10 cm Hg and 2 atm. Furthermore, he stated, that at lower pressures, the evaporation rate follows more classical lines, and his equations and findings are not applicable. Thus, Davis' statement, based upon this work, that the rate of evaporation at a pressure of 10^{-13} mm Hg is over 100 times the rate at 10^{-6} mm Hg, is improper.

Furthermore, since the vaporized material is leaving the surface and can return only by changing its direction of travel (e.g., by collision), and since the gas diffusion sheath ceases to be a factor as the pressure is lowered (cf. Ref. 3), little or no material returns to the surface. The mean free path in air at 10^{-6} mm Hg pressure is about 5000 cm. Also, since the conditions of our study and, indeed, most such studies, are not equilibrium conditions, it can be postulated that the rate of evaporation will not be affected drastically by changing the pressure from 10^{-6} to 10^{-13} mm Hg.

The Clapeyron-Clausius equation was derived (using thermodynamic principles) assuming that the phases were in equilibrium, and if vaporization takes place isothermally and reversibly at a temperature T, then

$$dP/dT = \Delta H/T \Delta V \qquad (1)$$

Furthermore, if the temperature is not near the critical value and if the ideal gas laws may be assumed to be applicable, Eq. (1) may be written as

$$d \ln P/dT = L/RT^2 \qquad (2)$$

where L, the molar heat of sublimation, replaces ΔH. Equation (2) is presumably the differential form referred to by Davis. Note that assumptions have already been made, most of which are not in agreement with the usual experimental conditions. Now, if L is assumed to be constant,

$$\ln P = L/RT + C \qquad (3)$$

or

$$\ln P = -A/T + B \qquad (4)$$

which is the form generally used and which, incidentally, was not derived by Gloria, Stewart, and Savin.[4] The values of A and B are determined experimentally and probably have no theoretical significance because of the nonequilibrium nature of most experiments and because of the various assumptions made.

It is recognized that there is a variation in the latent heat, so that an equation has been presented utilizing a form of the Kirchhoff equation

$$dL/dT = \Delta C \qquad (5)$$

where ΔC is the difference between the heat capacity of the gaseous and condensed phase, respectively. Thus,

$$L = Lo + \int_0^T \Delta C dT \qquad (6)$$

and Eq. (3) can be written in the form

$$\ln P = -\frac{Lo}{RT} + \int_0^T \frac{\Delta C}{RT} dT + \text{const} \qquad (7)$$

Application of this equation requires a knowledge of the effect of temperature upon ΔC. A simplifying assumption that has been made is that ΔC is independent of temperature, which results in

$$\ln P = -Lo/RT + (DC/R) \ln T + \text{const} \qquad (8)$$