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

[1] Wales, R. D. and Leubben, M. G., "Evaporation of electroplated cadmium in high vacuum," J. Spacecraft Rockets **2,** 467–469 (1965).

[2] Jaffe, L. D. and Rittenhouse, J. B., "Behavior of materials in space environments," Jet Propulsion Lab. TR 32-150, p. 73 (1961).

[3] van de Hulst, H. C., "Empty space," Sci. Amer. **193,** 5, 73–78 and 80 (1955).

[4] Fonda, G. R., "Evaporation of tungsten under various pressures of argon," Phys. Rev. **31,** 260–266 (1928).

[5] Gloria, H. R., Stewart, W. J., and Savin, R. C., "Initial weight loss of plastics in a vacuum at temperatures from 80° to 500°F," NASA TN D-1329 (1962).

[6] Greenbank, J. C. and Argent, B. B., "Vapor pressures of magnesium, zinc and cadmium," Trans. Faraday Soc. **61,** 655–664 (1965).

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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 pressure materials used in the systems. Vaporization and backdiffusion 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

$$dP/dT = \Delta H/T\Delta V \tag{1}$$

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

$$d \ln P/dT = L/RT^2 \tag{2}$$

where $L$, the molar heat of sublimation, replaces $\Delta H$. 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,

$$\ln P = L/RT + C \tag{3}$$

or

$$\ln P = -A/T + B \tag{4}$$

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

$$dL/dT = \Delta C \tag{5}$$

where $\Delta C$ is the difference between the heat capacity of the gaseous and condensed phase, respectively. Thus,

$$L = Lo + \int_0^T \Delta C dT \tag{6}$$

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

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

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

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

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Of course, if Eq. (6) is written

$$L = \int_0^T \Delta\, c dT \tag{9}$$

then Eqs. (7) and (8) may be written as

$$\ln P = \int_0^T \frac{\Delta C}{RT}\, dT + \text{const} \tag{10}$$

and

$$\ln P = (\Delta\, C/R) \ln T + \text{const} \tag{11}$$

Equation (11) may be written

$$\ln P = a \ln T + b \tag{12}$$

which is the equation proposed by Davis. The pressure $P$ in all the previous equations is the partial pressure and not the total or system pressure. It follows that, in most experiments, the actual partial pressure of the material under study is lower than the equilibrium value.

We might also point out that any number of equations can be chosen to represent a given set of experimental data and be true over the range represented. However, extrapolation of the effects outside the particular range of data can be extremely hazardous, particularly at extremely low temperatures where only the most fundamental degrees of freedom are generally considered to be extant.

We would suggest, in conclusion, that Davis give more theoretical and experimental justification for his equation, our derived Eq. (12), with comments relative to the various simplifying assumptions. Since the equations presently utilized are admittedly semiempirical and useful over only short temperature ranges, a more general equation useful over longer temperature ranges would be of interest to all.

### References

[1] Greenbank, J. C. and Argent, B. B., "Vapor pressures of magnesium, zinc, and cadmium," Trans. Faraday Soc. **61**, 655–664 (1965).

[2] Wales, R. D. and Leubben, M. G., "Evaporation of electroplated cadmium in high vacuum," J. Spacecraft Rockets **2**, 467–469 (1965).

[3] Fonda, G. R., "Evaporation of tungsten under various pressures of argon," Phys. Rev. **31**, 260–266 (1928).

[4] Gloria, H. R., Stewart, W. J., and Savin, R. C., "Initial weight loss of plastics in a vacuum at temperatures from 80° to 500°F," NASA TN D-1329 (1962).