

CONDENSATION AND EVAPORATION FOR THERMALLY UNEQUILIBRATED PHASES

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Introduction: The Hertz-Knudsen (H-K) equation for the rate of condensation of a gas or evaporation of a solid or liquid is used for systems in thermal equilibrium [1,2,3]. In astrophysical settings, both processes may occur when the gas temperature, T_g , differs from that of the condensed phase, T_s . Here, we modify the H-K equation for this case, and apply it to shock wave-induced evaporation and condensation of a chondrule precursor.

Theory: The number of molecules of gas colliding with unit area of a surface per unit time at temperature T is $\nu(T)C/4$, where $\nu(T)$ is the mean velocity of the gas molecules at T and C is the gas concentration [4]. If $\alpha_c(T)$ is the sticking probability, the condensation flux, J_c , is $\alpha_c(T)\nu(T)C/4$ (Eq 1). For a condensed phase in thermodynamic equilibrium with vapor, the evaporation flux, J_e , at T equals the condensation rate and is written $\alpha_e(T)\nu(T)C^e(T)/4$ (Eq 2), where $C^e(T)$ is the concentration of the vapor in thermodynamic equilibrium with the condensed phase at T , $\alpha_e(T)$ is the evaporation coefficient, and $\alpha_e = \alpha_c$.

For evaporation where $T_s \neq T_g$, T_s is the temperature of the condensed phase within an atomic layer or so of the surface. If an evaporating molecule thermally equilibrated with the condensed phase passes through a transition state, TS (a point of no return), to the gas, it does so with a velocity distribution given by T_s , so the T in Eq 2 is T_s and $C^e(T) = C^e(T_s)$, the concentration of vapor in thermodynamic equilibrium with the condensed phase at T_s .

In the condensation flux of Eq 1, there are two limiting cases when $T_s \neq T_g$. One occurs when a molecule lands on a solid, thermally equilibrates with it but has only a small probability of settling into some site, so re-evaporation dominates. In this several step process, the rate-controlling step is the final settling in, the point of no return is a TS thermally equilibrated with the solid, and T for $\alpha_c(T)$ in the condensation flux is T_s , not T_g . In the other limiting case, landing of the molecule on the surface, perhaps in a specific orientation, is the rate-limiting step, there is no prior thermalization with the condensed phase, and settling into a site eventually always occurs. Since thermalization of the colliding molecule with the condensed phase occurs after the rate-limiting step, $\alpha_c(T) = \alpha_c(T_g)$. For liquids, no diffusion along the surface to an appropriate site is needed, so $\alpha_c(T_g)$ is used, not $\alpha_c(T_s)$. Using $\nu = \sqrt{8kT/\pi m}$ and $C = p/kT$ [4], the net evaporation flux for the latter thermally non-equilibrated system is

$$J = \frac{\alpha_e(T_s)P^e(T_s)}{\sqrt{2\pi mkT_s}} - \frac{\alpha_c(T_g)P(T_g)}{\sqrt{2\pi mkT_g}} \quad (\text{Eq 3}).$$

Application: Eq 3 was used to study evaporation and recondensation in partially molten chondrule precursors subjected to a 6 km/sec shock wave in a complementary gas enriched in dust and water but otherwise of solar composition. Evaporation curves for $T_s = T_g$ are compared to those for $T_s \neq T_g$. The thermal disequilibrium effect is significant but relatively small.

References: [1] Hirth J. P. & Pound G. M. 1963. *Condensation and Evaporation, Nucleation and Growth Kinetics*, Pergamon, 192 pp. [2] Hertz H. 1882. *Ann. d. Phys. Chem.* 17:177. [3] Knudsen M. 1915. *Ann. Phys.* 47:697. [4] Loeb L. B. 1934. In *Kinetic Theory of Gases*, McGraw-Hill, Chaps. 2 and 3.