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Theory of Droplet Growth in Clouds

I. The Transient Stage of the Boundary-Coupled Simultaneous Heat and Mass Transport in Cloud Formation¹

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Two solutions to the system of equations describing the simultaneous heat and mass transport involved in the condensational growth of a droplet in a supersaturated atmosphere are presented. The first, valid for very short times, describes the transient stage of such growth; the second, valid for longer times, presupposes the establishment of a steady-state condition. The two are shown to be complementary for the cases examined. The equations examined satisfy the usual boundary conditions imposed on a drop in a concentric sphere as required by the cellular model for cloud formation. Hence our results can be immediately extended to the treatment of the growth rate of drops in assemblage.

I. INTRODUCTION

The problem of condensational growth of cloud droplets has been the subject of extensive studies (1-5). Nevertheless, no general consensus has yet been reached and the various authors do not always agree with each other, and seldom with experimental observations. One of the reasons for the discrepancies is, as pointed out by Aleksandrov, Levin, and Sedunov (6), the fact that the *a priori* estimate of the effect of various factors on the droplet growth has not been sufficiently rigorous. In this series of papers, we shall not attempt to reformulate the theoretical problem of droplet growth in clouds in its entirety, but rather to limit our

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scrutiny to the more crucial and yet more subtle points, namely, the growth rate during the transient stage of the condensation process and its relationship with the customary quasi-steady-state approximation, the effect of droplet interaction on the diffusional process and heat transport (7), and the dynamical interaction between droplets and its influence on droplet velocities and coagulation rates.

In this paper, we shall examine the condensational growth process both in the transient stage and in the steady-state stage, with emphasis on the degree of accuracy of the solutions obtained and their relationship to each other and to the over-all growth rate.

So far, most of the treatments (1-5, 8, 9)of the diffusional growth of a liquid drop in a supersaturated atmosphere have generally avoided the transient stage of this growth on the grounds that it is too brief to warrant particular physical interest. However, certain cloud chamber experiments (10-13)dealing with the measurement of nucleation rates (as the number of drops formed per

second per unit volume) have justified a more detailed examination of this stage.

We shall limit outselves in this work to a treatment of the transient stage in the growth of a macroscopic drop (*i.e.*, one having dimensions greater than a mean free path). It is demonstrated that, for the cases presented, the usual quasi-steady-state situation is quite rapidly established, and the transient stage corresponds with the "quasi-steady-state" stage after a brief growth period.

II. THE TRANSIENT STAGE OF DROP GROWTH

Let us consider a drop immersed, at time zero, in an atmosphere composed of the vapor in dilute solution with some noncondensable gas. Physically, of course, there are always neighboring drops from which the drop under consideration must be isolated. This independence of one drop from another, constituting a basic assumption of the cellular model (14) that may be checked a posteriori, can be assured by describing a sphere around each drop, the diameter 2Rof which is roughly equal to the average distance between drops. The impermeability condition,

$$\nabla \rho(r, t) |_{r=R} = \nabla T(r, t) |_{r=R} = 0, \quad [1]$$

gives the drop "priority" over the vapor within the sphere. Here, ρ represents the vapor density in grams per cubic centimeter and T the temperature; r is the distance from the center of the drop. Were it not for the presence of other drops, the heat (and vapor) reservoir would extend out to large values of r. Clearly bulk depletion cannot be neglected if the annular region at the edge of a given cell is sensibly affected by events occurring at the drop.

Turning to that region of the R-sphere which is affected by the presence and growth of the drop, one expects to observe the double diffusion of vapor toward the drop, and heat, released by the condensing vapor, away from it. For constant diffusion coefficients D (mass diffusion) and k (thermal diffusion) the two governing equations can be written:

$$D\nabla^2 \rho = \partial \rho / \partial t + F_{\rho}(t), \qquad [2]$$

$$k\nabla^2 T = \frac{\partial T}{\partial t} + F_T(t), \qquad [3]$$

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where

$$abla^2 = \partial^2/\partial r^2 + 2r^{-1}\partial/\partial r$$

and $F_{\rho}(t)$ and $F_{T}(t)$ are sink terms which describe the course of the homogeneous, time-dependent supersaturation. In the preceding equations both the effect that heat diffusion has on mass diffusion and that of mass diffusion on heat diffusion are neglected. The last two assumptions are a consequence of the assumed degree of diluteness of the vapor in the gas phase.

The boundary conditions at the surface of the drop, r = a (a being the drop radius), representing a power balance and a linear vapor temperature equilibrium condition, are:

$$C_d dT(a, t)/dt = 4\pi a^2 \{LD\nabla\rho \mid_{r=a} + K\nabla T \mid_{r=a}\}$$
[4]

and

$$\rho(a, t) = bT(a, t) + c,$$
[5]

where K is the thermal conductivity of the gas,

$$C_d = (4/3)\pi a^3 \rho_l c_l$$

 ρ_l is the density, c_l is the heat capacity of the liquid, and L is its latent heat of condensation. Here b and c represent constants to be obtained from a linear approximation to the equilibrium vapor density curve in the region of interest. It should be pointed out that the modification of this equilibrium relationship, dictated by the Kelvin Thompson equation for a spherical interface, is negligible for drops larger than 0.1 μ in radius. The final steady-state temperature will be sufficiently close to the initial drop temperature that the above linearization will represent a fair approximation.

The growth rate of the drop is given by

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{D}{\rho_l} \frac{\partial \rho}{\partial r} \bigg|_{r=a(t)}.$$
 [6]

Now Eqs. [1]–[6] comprise a fairly general description of macroscopic growth provided some initial condition is specified. A closed form solution is possible if, in Eq. [6], da/dt = 0. Such a fixed boundary solution, valid only for extremely short times during which radial growth is negligible, may lend itself

to a stepwise extension to longer times wherein the final solution for any given step constitutes the initial condition for the next. This solution should provide a criterion to determine the advent of steady state.

Solutions to Eqs. [2] and [3] by perturbation methods have been attempted by several authors (15) for the case of a spherical drop in an infinite medium. The non-steady-state solution obtained by perturbation techniques takes the form of an integral equation to be computed numerically. Perturbation methods have also been used by Acrivos and Taylor (16) to estimate the rates of

heat and mass transfer from a moving sphere in Stokes' region, and by Soo and Ihrig (17) to study the evaporation rate of a liquid droplet in the absence of macroscopic convection. Their non-steady-state solutions are similar in form to that given by Plesset and Zwick. Here, we present a more straightforward method based on the Laplace transform theory for handling both diffusion equations with their attendant boundary conditions (Eqs. [1]-[5].) Detailed analysis of the problem is given in the Appendix. We obtain the following expressions for $\rho(r, t)$ and T(r, t), valid for the transient stage:

$$T(r,t) = (T_{a} - T_{o}) \sum_{l} \Xi_{k}(r, p_{l}) \exp(p_{l}t) - \sum_{l} \Xi_{k}(r, p_{l})F_{T}(t)^{*} \exp(p_{l}t) + \alpha_{o}Q \sum_{m,l} mA_{m}\Xi_{k}(r, p_{l}) E_{D} + \beta_{o}Q \sum_{n,l} nA_{n}'\Xi_{k}(r, p_{l}) E_{k} + \left(\frac{\alpha_{o}}{a}\right) \sum_{m,j,l} \left(\frac{p_{j}}{D}\right)^{1/2} \left(\frac{A_{m}c_{D}(p_{j})}{p_{j} + D_{m}}\right) \Xi_{k}(r, p_{l}) [E_{p} - E_{D}] + \left(\frac{\beta_{o}}{a}\right) \sum_{n,j,l} \left(\frac{p_{j}}{k}\right)^{1/2} \left(\frac{A_{n}'c_{k}(p_{j})}{p_{j} + k_{n}}\right) \Xi_{k}(r, p_{l}) [E_{p} - E_{k}] - \Xi_{k}(r, 0)X_{D}(0)\alpha_{o} \int_{0}^{t} (bF_{T} - F_{p}) dt - L^{-1}(bF_{T} - F_{p}) * \sum_{l} \Xi_{k}(r, p_{l})X_{D} \frac{\exp(p_{l}t)}{p_{l}} - \alpha_{o}c'\Xi_{k}(r, 0)X_{D}(0) - \alpha_{o}c' \sum_{l} \Xi_{k}(r, p_{l})X_{D} \frac{\exp(p_{l}t)}{p_{l}} + T_{o} + \int_{0}^{t}F_{T}(t) dt + r^{-1} \sum_{n} A_{n}' \exp(-k_{n}t) \sin\left[\frac{n\pi(r-a)}{(R-a)}\right] + r^{-1} \sum_{n,j} A_{n}'c_{k}(p_{j})E_{k} \sin\sqrt{\frac{p_{j}}{k}} (r-a).$$

$$\rho(r,t) = c' \sum_{l} \Xi_{D}(r,t) \exp(p_{l}t) + L^{-1}(bf_{T} - f_{\rho}) * \sum_{l} \Xi_{D}(r,p_{l}) \exp(p_{l}t) + \beta_{\rho}L^{-1}(bf_{T} - f_{\rho}) * M + \beta_{\rho}c'M + b(T_{a} - T_{o}) \sum_{l} \Xi_{D}(r,p_{l}) \exp(p_{l}t) - b \sum_{l} \Xi_{D}(r,p_{l})F_{T}(t) * \exp(p_{l}t) + \alpha_{\rho}bQ \sum_{m,l} mA_{m}\Xi_{D}(r,p_{l})E_{D} + \beta_{\rho}bQ \sum_{n,l} nA_{n}'\Xi_{D}(r,p)E_{k} + \rho_{\rho} + \left(\frac{\alpha_{\rho}b}{a}\right) \sum_{m,j,l} \left(\frac{p_{j}}{D_{m}}\right)^{1/2} \left(\frac{A_{m}c_{D}(p_{j})}{p_{j} + D_{m}}\right) \Xi_{D}(r,p_{l}) [E_{p} - E_{D}] + \left(\frac{\beta_{\rho}b}{a}\right) \sum_{n,j,l} \left(\frac{p_{j}}{k_{n}}\right)^{1/2} \left(\frac{A_{n}'c_{k}(p_{j})}{p_{j} + k_{n}}\right) \Xi_{D}(r,p_{l}) [E_{p} - E_{k}]$$
[8]

$$+ \int_{0}^{t} F_{\rho}(t) dt + r^{-1} \sum_{m} A_{m} \sin \left[\frac{m\pi(r-a)}{(R-a)} \right] \\ + \sum_{m} r^{-1} A_{m} c_{D}(p_{j}) \sinh \left[\left(\frac{p_{j}}{D} \right)^{1/2} (r-a) \right].$$

Here,

$$Q = \pi/a(R - a); \qquad X_k = \chi_b(p_l);$$

$$E_p = (p_j - p_l)^{-1}[\exp(p_j t) - \exp(p_l t)];$$

$$E_D = (p_l + D_m)^{-1}[\exp(p_l t) - \exp(-D_m t)];$$

$$E_k = (p_l + k_n)^{-1}[\exp(p_l t) - \exp(-k_n t)];$$

and

$$M = \Xi_{k}(r, 0)X_{k}(0) + \sum_{l} \Xi_{D}(r, p_{l})X_{k} \exp((p_{l}t)/p_{l}).$$

Other symbols are defined in the Appendix.

In order to evaluate the above solutions, even for very simple initial conditions, it is perhaps worth while to discuss a couple of preliminary steps.

First, the transcendental equation g(p) = 0 in the Appendix must be solved since any choice of initial conditions leads to solutions requiring at least one sum over these roots. These roots are expected to be real and negative, and the smallest of them represents the quasi-steady-state solution.

Second, the computation procedure can be facilitated if the expressions Ξ_D , Ξ_k , X_D , and X_k are put in forms into which one can explicitly substitute $|p_l|$.

Third, in order to calculate the mass influx, use will be made of the following equation:

$$\Delta m(t) = 4\pi a^2 D \int_0^t \frac{\partial \rho}{\partial r} (r, t) \bigg|_{r=a} dt, \quad [9]$$

where $\Delta m(t)$ is the mass increment in a time t. The calculation of $\Delta m(t)$ is simplified by the identity

$$\frac{\mathrm{d}}{\mathrm{d}r} \Xi_D(r, p_l) = -X_D(r, p_l) \Xi_D(r, p_l). \quad [10]$$

III. QUASI-STEADY-STATE STAGE OF DROP GROWTH

The equations for this stage are, in the notation already established,

$$\nabla^2 \rho = \nabla^2 T = 0; \qquad [11]$$

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$$a(a) = bT(a) + c$$
: [12]

$$\partial T$$
 ∂a ∂a

$$\beta_o \left. \frac{\partial T}{\partial r} \right|_{r=a} = - \alpha_o \left. \frac{\partial \rho}{\partial r} \right|_{r=a}.$$
 [13]

For the outer boundary conditions:

$$\rho(R, t) = \rho_R , \qquad [14]$$

and

$$T(R, t) = T_R, \qquad [15]$$

where ρ_R and T_R are constants for comparatively long periods of time.

The solutions to Eq. [11] with boundary conditions, Eqs. [12]-[15], are

$$\rho(r,a) = \frac{a}{r} \frac{R-r}{R-a} \qquad [16]$$
$$\cdot [\rho(a) - \rho_R] + \rho_R;$$

$$T(r,a) = \frac{a}{r} \frac{R-r}{R-a}$$

$$\cdot [T(a) - T_R] + T_R.$$
[17]

Here, from Eqs. [12], [13],

$$T(a) = \frac{\alpha_o T_R + \beta_o [\rho_R - c]}{\alpha_o + b\beta_o}; \qquad [18]$$

$$\rho(a) = \frac{b}{\alpha_o + \beta_o b}$$

$$\cdot [\alpha_o T_R + \beta_o (\rho_R - c)] + c.$$
[19]

Now the growth equation gives for a(t)

$$a(t) = (a_0^2 + 2D[\rho(a) - \rho_R]t)^{1/2},$$

which, when substituted into Eqs. [16] and [17], yields the quasi-steady-state solutions. These will be valid until the time when the mass influx expression,

$$\mathrm{d}m/\mathrm{d}t = 4\pi a^2 D \nabla \rho \mid_{r=a}$$

indicates a perceptible decrease in bulk vapor density, at which time the conditions [14] and [15] must be adjusted appropriately.

IV. COMPARISON BETWEEN THE QUASI-STEADY-STATE AND TRANSIENT SOLUTIONS

The quasi-steady-state approximation can be analyzed according to the following argument. The fixed boundary solution permits the calculation of a virtual mass influx, that is, the influx which occurs when the drop radius does not grow into the surrounding atmosphere. The difference between this and the true mass influx will have to be considered small compared with either influx term. Also the mass of the drop, throughout its brief "growth" period, is considered constant, so that its contribution to the specific heat of the drop is necessarily neglected. However, an averaged mass, somewhere between the initial and final masses for a given growth period t, could be introduced as an approximation. The radial change is given by

 $\Delta a/a_0 = (1/3)(\Delta m/m_0),$

where subscript zero denotes initial values. The validity of the quasi-steady-state approximation will then depend on the condition that the variation of the steady-state solution with respect to the above change in radius be negligible and on the magnitude of its departure from the fixed radius solution.

In order to gain some insight into the validity of these solutions, let us consider the simplest nontrivial problem often encountered in cloud formation: that of a drop suddenly inserted into an atmosphere of constant supersaturation, where the drop is initially at the same temperature as the atmosphere. This gives simply

$$h_1(p) = c'/p_1$$

 $h_2(p) = 0,$

where

$$c'=bT_0-\rho_0+c,$$

and where T_0 and ρ_0 are the initial temperature and vapor density, respectively. In this case the transformed solutions reduce to

$$\begin{split} \bar{T} &= -(\alpha_0 c'/p)\xi_k(r,\,p)\chi_D(a)\,+\,T_0/p;\\ \bar{\rho} &= (c'/p)[p\,+\,\beta_0\chi_k(a)]\xi_D(r,\,p)\,+\,\rho_0/p. \end{split}$$

These have the inversions

. .

$$T(r, t) = -\alpha_{o} c' \Xi_{k}(r, 0) \chi_{D}(0)$$

- $\alpha_{o} c' \sum_{l} \frac{p_{l}^{l} + \beta_{0} X_{k}(p_{l})}{p_{l}}$
 $\cdot \Xi_{D}(r, p_{l}) \exp(-|p_{l}|t + T_{o},$
 $p(r, t) = c' \lim_{p \to 0} [p + \chi_{k}(a)]\xi_{D}(r, p)$
+ $c' \sum_{l} \frac{p_{l} + \beta_{o} X_{k}(p_{l})}{p_{l}}$
 $\cdot \Xi_{D}(r, p_{l}) \exp(-|p_{l}|t + \rho_{o},$

where, if $a \ll R$, as is usually the case,

$$X_D(0)\Xi_k(r,0)\cong rac{lpha_o\,c^{'}/D}{eta_o/k+blpha_o/D}$$

and

$$\lim_{p \to 0} [p + \chi_k(a)] \xi_D(r, p) \cong \frac{\beta_o/k}{\beta_o/k + b\alpha_o/D}$$

As a numerical example, typical cloud chamber data may be used. The following were obtained by Grayson (18): $T_0 =$ 3.6°C; $\rho_0 = 17.76 \times 10^{-6} \text{ gm/cm}^3$; Average supersaturation S = 5.89; R = 0.3 cm; number of drops formed during brief ($\simeq 0.01$ sec) supersaturation pulse = 8 cm⁻³. The cloud chamber gas is composed of helium as a solvent and water vapor as a solute. Experimental values for D, the vapor diffusion coefficient, were obtained from Schwertz and Brow (19) and extrapolated down to the temperature of interest. The diffusivity k, along with the temperaturevapor equilibrium parameters c and b, was calculated for helium alone from data available (20).

Solutions to the problem for a 10 μ drop are displayed in Figs. 1–4 for two times, $t = 10^{-4}$ sec and $t = 10^{-3}$ sec. Evidently by 10^{-3} sec the quasi-steady-state solution is nearly concurrent with that of the fixedradius, time-dependent solution. Mass influx calculations give, after 10^{-3} sec, $(\Delta m/m_o) =$ 0.047, which leads to less than 2% change in radius, showing no detectable change in steady-state solutions. The present analysis appears to indicate that the growth of a 10- μ drop is entirely described by the fixed-radius theory in conjunction with the quasi-steady-

state theory, and in addition, that the quasisteady-state theory holds for a large part of the growth time. data, are shown in Figs. 5 and 6 for a $1.0-\mu$ drop, but now with an initial temperature of -0.1° C (where $T_0 = -3.6^{\circ}$ C). The temperature -0.1° C is obtained from an analy-

Additional solutions, along with pertinent



FIG. 1. Vapor density vs. radius for $a = 10 \mu$, $t = 10^{-4}$ sec. ---- transient; ---- quasi steady state.



FIG. 2. Vapor density vs. radius for $a = 10 \mu$, $t = 10^{-3}$ sec. —— transient; - - - - quasi steady state. Journal of Colloid and Interface Science, Vol. 33, No. 2, June 1970

sis of the growth up to 1 μ according to Buecher (24). Here quasi steady state represents a good approximation in less than 10^{-4} sec. At this time, $(\Delta m/m_0) = 0.18$ and $(\Delta a/a_0) = 0.06$. Now, whereas a 6 % change in radius yields again an undetectable change in the quasi-steady-state solution, an 18% change in mass should lead to a prolongation of the time it takes the fixed-radius solution to concur with the quasi-steady-state solution. If the drop is endowed with a slightly greater mass, say about midway between



FIG. 3. Temperature vs. radius for $a = 10 \mu$, $t = 10^{-4}$ sec. ---- transient; ---- quasi steady state.



FIG. 4. Temperature vs. radius for $a = 10 \mu$, $t = 10^{-3}$ sec. — transient; - - - - quasi steady state. Journal of Colloid and Interface Science, Vol. 33, No. 2, June 1970

initial and final masses for $t = 10^{-4}$ sec, a certain sluggishness should be observed. Despite this, analysis with the augmented mass shows that the quasi-steady-state solution is still reached before 10^{-4} sec. It is

mentioned again that below 1 μ the usual macroscopic theory begins to lose significance, since the mean free path λ is of the order of 10⁻⁵ cm for present conditions.

On the other hand, it may be argued that



FIG. 5. Vapor density vs. radius for $a = 1.0 \mu$, $t = 10^{-5}$ sec. — transient; - - - - quasi steady state.



FIG. 6. Temperature vs. radius for $a = 1.0 \mu$, $t = 10^{-5}$ sec. — transient; - - - - quasi steady state. Journal of Colloid and Interface Science, Vol. 33, No. 2, June 1970

the validity of the fixed-radius solutions should become suspect at higher supersaturation since these would lead to greater radial increments in any given time. The increase in mass influx is primarily attributable to the increase in initial vapor density, which gives rise to an increase in c'. Since c'can be factored out of the equation for mass influx, one can write

$$\frac{(\mathrm{d}m/\mathrm{d}t)_1}{(\mathrm{d}m/\mathrm{d}t)_2} = \frac{c_1'}{c_2'},$$

which represents a rough criterion, in terms of any known influx, for the influx at some different ρ_o .

In conclusion, from our analysis of solutions of the transient stage and the quasisteady-state stage, we have found that the fixed-radius solution in conjunction with the quasi-steady-state approximation can provide an adequate description of macroscopic drop growth for most cloud chamber experiments and the transient stage solution corresponds to that of the quasi steady stage after a very brief growth period.

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LIST OF SYMBOLS

- *a*—radius of the drop.
- a_o —initial drop radius.
- b, c—empirical constants in the (linear) equilibrium vapor density approximation
- C_d —heat capacity (constant pressure) of drop.
- C_{r} —specific heat capacity of drop liquid.
- D-diffusion coefficient of vapor in noncondensable gas.
- $F\rho(t)$ —vapor density sink function.
- $F_T(t)$ —heat sink function.
- k—thermal diffusivity of noncondensable gas.
- K—thermal conductivity of noncondensable gas.
- L—latent heat of condensation of drop liquid.
- m—mass of drop of radius a at time t.

 m_o —initial mass of drop.

- p—complex variable in transform space.
- *r*—distance from center of drop (independent variable).
- R—radius of outer sphere or "cell."
- S—supersaturation.
- *t*—time (independent variable).
- T—temperature as a function of r and t.
- T_o —initial temperature.
- T_R —bulk temperature (at r = R).
- ρ —vapor density as a function of r and t.
- ρ_o —initial vapor density.
- ρ_R —bulk vapor density (at r = R).

REFERENCES

- 1. HOWELL, W. E., J. Meteorol. 6, 134 (1949).
- 2. MORDY, W., Tellus 11, 16 (1959).
- NEIBURGER, M., AND CHIEN, C. W., Geophys. Monograph No. 5, Physics of Precipitation, NAS-NRC No. 746, American Geophys. Union, p. 191 (1960).
- ALEKSANDROV, E. L., LEVIN, L. M., AND SEDUNOV, YU. S., Trans. (Trudy) Inst. Appl. Geophys. 9, pp. 47–55 (1967).
- VASILJEVA, K. I., AND SEDUNOV, YU. S., Proc. 7th Intern. Conf. Condensation Ice Nuclei, Sept. 18-24, 1969, Prague-Vienna, pp 342-346.
- ALEKSANDROV, E. L., LEVIN, L. M., AND SEDUNOV, YU. S., Izv. Atmospheric Oceanic Phys. 3, 872–880 (1967).
- 7. CARSTENS, J. C., WILLIAMS, A., AND ZUNG, J. T., submitted to J. Atmospheric Sci.
- FRANK, F. C., Proc. Roy. Soc. Ser. A 201, 586 (1950).
- 9. MASON, B. J., Proc. Phys. Soc. B64, 773 (1951).
- KASSNER, J. L., AND SCHMIDT, R. J., J. Chem. Phys. 44, 4166 (1966).
- ALLARD, E. F., AND KASSNER, J. L., J. Chem. Phys. 42, 1401 (1965).
- ALLEN, L. B., Ph. D. Dissertation, University of Missouri-Rolla, Rolla, Missouri, 1968.
- ALLEN, L. B., AND KASSNER, J. L., J. Colloid and Interface. Sci. 30, 81 (1969).
- 14. ZUNG, J. T., J. Chem. Phys. 46, 2064 (1967).
- PLESSET, M. S., AND SWICK, S. A., J. Appl. Phys. 23, 95 (1952); SCRIVEN, L. E., Chem. Eng. Sci. 10, 1 (1959); GOODRICH, F. C., J. Phys. Chem. 70, 3660 (1966); CABLE, M., AND EVANS, D., J. Appl. Phys. 38, 2899 (1967); PHILIP, J. R., J. Atmospheric Sci. 22, 196 (1965).
- ACRIVOS, A., AND TAYLOR, T. D., Phys. Fluids 5, 387 (1962).
- Soo, S. L., AND IHRIG, H. K., JR. Proc. Gas Dyn. Symp. Aerothermochem. Evanston 1955, p. 35 (1956).

- GRAYSON, M., Private communication. Department of Physics, University of Missouri-Rolla, Rolla, Missouri, March 15, 1965.
- SCHWERTZ, F. A., AND BROW, J. E., J. Chem. Phys. 19, 644 (1951).
- International Critical Tables of Numerical Data, Physics, Chemistry, and Technology, p. 5. McGraw-Hill, New York, 1926.
- SCOTT, F. J., Transform Calculus with an Introduction to Complex Variables, p. 56. Harper and Brothers, New York, 1955.
- SCOTT, F. J., "Transform Calculus with an Introduction to Complex Variables," p. 57. Harper and Brothers, New York, 1955.
- Scorr, F. J., "Transform Calculus with an Introduction to Complex Variables," p. 56 Harper and Brothers, New York, 1955.

APPENDIX

Laplace transform theory provides a straightforward way of solving both diffusion equations (Eqs. [2] and [3]) with their appropriate boundary conditions (Eqs. [4] and [5]) for the *transient stage*.

The Laplace transform of a function will be denoted in one of the following ways:

$$LH(t) = h(p) = \bar{H}(p)$$

= $\int_0^\infty H(t) \exp(-pt) dt$, [A.1]

where p is the transform variable, p = x + iy. The transformed problem can now be written as:

$$D\nabla^2 \overline{\rho}(r, p) = p \overline{\rho}(r, p) - \rho(r, 0) + f_{\rho}(p),$$
[A.2]

$$k\nabla^2 \bar{T}(r, p) = p\bar{T}(r, p) - T(r, 0) + f_T(p),$$
[A.3]

$$\nabla \bar{\rho}(R, p) = \nabla \bar{T}(R, p) = 0,$$
 [A.4]

$$\bar{\rho}(a, p) = b\bar{T}(a, p) + c/p,$$
 [A.5]

and

$$p\bar{T}(a, p) - T(a, 0) = \alpha_0 \nabla \bar{\rho}(a, p) + \beta_0 \nabla \bar{T}(a, p),$$
 [A.6]

where

$$lpha_0 = rac{3LD}{a
ho_1 c_l} \quad ext{and} \quad eta_0 = rac{3k}{a
ho_1 c_l}.$$

For initial conditions, T(r, 0) and $\rho(r, 0)$ Journal of Colloid and Interface Science, Vol. 33, No. 2, June 1970 take the modified form:

$$T(r, 0) = T_0 + T'(r, 0),$$

where

$$T_0 = \lim_{r \to a} T(r, 0)$$

and similarly for $\rho(r, 0)$.

Introduction of T_0 and ρ_0 will put the solution in a form that will reduce unequivocally to the initial conditions,

$$ho(r, 0) =
ho_R, \qquad a < r < R, \ T(r, 0) = T_R, \qquad a < r < R,$$

and $T(r, 0) = T_a$, r < a,

which are to be used later.

The heat diffusion equation with $\overline{T} = \overline{\Psi}_T r^{-1}$ becomes

$$(k/r) d^2 \bar{\Psi}_T / dr^2 - p \bar{\Psi}_T / r$$

= $-r^{-1} \Psi_T (r, 0) - f_T (p).$

Now we let

$$ar{\Psi}_T=ar{\Psi}_h+ar{\Psi}_1+ar{\Psi}_2\,,$$

where $\overline{\Psi}_{\hbar}$ is the homogeneous solution and $\overline{\Psi}_1$ and $\overline{\Psi}_2$ are particular solutions. With the boundary condition, Eq. [A.4], one obtains for the homogeneous solution,

$$ar{\Psi}_h = A'(p) \sinh \{ (p/k)^{1/2} (R-r) - \tanh^{-1} R (p/k)^{1/2} \}.$$

For $\overline{\Psi}_2$ one takes

$$\overline{\Psi}_2 = \Psi_2^0 + f$$
$$= \sum_n a_n'(p) \sin\left[\frac{n\pi}{R-a}(r-a)\right] + f,$$

where Ψ_2^0 is imagined to be extended as an odd function, and f is a solution to

$$(\mathrm{d}^2/\mathrm{d}r^2 - p/k)f = 0.$$

Substitution of $\overline{\Psi}_2^0$ into

$${\rm d}^2 {ar \Psi}/{{\rm d}} r^2 \;-\; (p/k) {ar \Psi} \;=\; -k^{-1} \Psi'(r,\;0)$$

gives

$$a_n'(p) = 2(R-a)^{-1} \left[k \left(\frac{n}{R-a} \right)^2 + p \right]^{-1}$$
$$\cdot \int_a^R rT'(r,0) \sin\left(\frac{n\pi(r-a)}{R-a} \right) \mathrm{d}r.$$

The condition of Eq. [A.4] is satisfied if

$$\frac{\mathrm{d}}{\mathrm{d}r} \left[r^{-1} \sum_{n} a_n'(p) \sin \frac{n(r-a)}{R-a} \right]_{r=R} + \left[\mathrm{d}(fr^{-1})/\mathrm{d}r \right]_{r=R} = 0.$$

A satisfactory expression for f is

$$f = \frac{\pi}{(R-a)} \\ \cdot \left\{ \frac{\sum_{k=1}^{n} (p)n(-1)^{n} \sinh\left\{(p/k)^{1/2}(r-a)\right\}}{\left\{R^{-1} - (p/k)^{1/2} \coth\left[(p/k)^{1/2}(R-a)\right]\right\}} \cdot \sinh\left\{(p/k)^{1/2}(R-a)\right\} \right\}.$$

A similar analysis holds for $\bar{\rho}(r, p)$.

Collecting results, we can write the transformed solutions as

$$\begin{split} \bar{T} &= r^{-1}A'(p) \sinh \left\{ (p/k)^{1/2}(R-r) \\ &- \tanh^{-1}R(p/k)^{1/2} \right\} + f_r/p + T_0/p \\ &+ \sum_n r^{-1}a_n'(p) \sin \left\{ n\pi(r-a)/(R-a) \right\} \\ &+ r^{-1}c_k(p)\alpha'(p) \sinh \left[(p/k)^{1/2}(r-a) \right], \\ \end{split}$$
[A.7]

and

$$\bar{\rho} = r^{-1}A(p) \sinh \left[(p/D)^{1/2}(R - r) - \tanh^{-1}R(p/D)^{1/2} \right] + f_{\rho}/p + \rho_0/p + \sum_m r^{-1}a_m(p) \sin \left[m\pi(r - a) / (R - a) \right] + r^{-1}c_D(p)\alpha(p) + r^{-1}c_D(p)\alpha(p) + (p/D)^{1/2}(r - a)].$$
(A.8)

where

$$\begin{aligned} \alpha' &= \pi (R - a)^{-1} \sum a_n'(p) n (-1)^n, \\ \alpha &= \pi (R - a)^{-1} \sum_m a^m(p) m (-1)^m, \end{aligned}$$

$$c_{k} = \{R^{-1} \sinh [(p/k)^{1/2}(R - a)] - (p/k)^{1/2} \cosh [(p/k)^{1/2}(R - a)]\}^{-1},$$

$$c_{D} = \{R^{-1} \sinh [(p/D)^{1/2}(R - a)] - (p/D)^{1/2} \cosh [(p/D)^{1/2}(R - a)]\}^{-1}.$$

Equations [A.7] and [A.8] can now be substituted into the boundary conditions as given by Eqs. [A.5] and [A.6] in order to determine A(p) and A'(p). Direct substitution yields

$$\bar{T}(r,p) = \frac{a}{r} \frac{h_2(p) - \alpha_0 h_1(p) \chi_D(a)}{[p + \beta_0 \chi_k(a) + b\alpha_0 \chi_D(a)]}$$
$$\cdot \frac{\sinh \eta_k(r)}{\sinh \eta_k(a)} + \frac{f_T(p)}{p} + \frac{T_0}{p}$$
$$+ r^{-1} \sum_n a_n'(p) \sin\left\{\frac{n\pi(r-a)}{(R-a)}\right\}$$
$$+ r^{-1} \alpha' c_k \sinh\left[\left(\frac{p}{\bar{k}}\right)^{1/2}(r-a)\right],$$
and

and

$$\overline{p}(r, p) = \frac{a}{r} \frac{h_1(p)[p + \beta_0 \chi_k(a)] + bh_2(p)}{[p + \beta_0 \chi_k(a) + b\alpha_0 \chi_D(a)]}$$
$$\cdot \frac{\sinh \eta_D(r)}{\sinh \eta_D(a)} + \frac{f_p(p)}{p} + \frac{\rho_0}{p}$$
$$+ r^{-1} \sum_m a_m(p) \sin \left[m\pi \left(\frac{r-a}{R-a} \right) \right]$$
$$+ r^{-1} \alpha(p) c_D(p) \sinh \left[\left(\frac{p}{D} \right)^{1/2} (r-a) \right],$$

where

$$\begin{split} \eta_k(r) &= (p/k)^{1/2}(R-r) - \tanh^{-1}R(p/k)^{1/2};\\ \eta_D(r) &= (p/D)^{1/2}(R-r) - \tanh^{-1}R(p/D)^{1/2};\\ h_1(p) &= p^{-1}[bf_T(p) - f_\rho(p)] + c'/p;\\ c' &= bT_0 + c - \rho_0;\\ h_2(p) &= (T_a - T_0) \end{split}$$

$$-f_{T}(p) + \frac{\alpha_{0}\pi}{a(R-a)} \sum_{m} a_{m}(p)m \\ + (p/D)^{1/2}a^{-1}[\alpha_{0}\alpha(p)c_{D}(p)] \\ + \frac{\beta_{0}\pi}{a(R-a)} \sum_{n} a_{n}'(p)n(-1)^{n} \\ + \beta_{0}(p/k)^{1/2}a^{-1}[c_{k}(p)\alpha'(p)]; \\ \chi_{D}(r) = (p/D)^{1/2} \operatorname{coth}\eta_{D}(r) + 1/r; \\ \chi_{k}(r) = (p/k)^{1/2} \operatorname{coth}\eta_{k}(r) + 1/r.$$

The problem is now reduced to one of inverting \overline{T} and $\overline{\rho}$, which is to be attempted by using the inversion integral (21):

$$L^{-1}f(p) = \frac{1}{2\pi i} \lim_{R \to \infty} \int_{\gamma_{-iR}}^{\gamma_{+iR}} f(p) \exp(pt) dp.$$



FIG. 7. Inversion contour

Here, γ divides the complex plane into a right-hand region which is free of poles and a left-hand region which is not. The existence of γ is due to a theorem quoted by Scott (22). The usual closed contour is obtained by completing the semicircle as shown in Fig. 7. It may be shown that the contribution to the integral from the contour around ABCD vanishes as $R \to \infty$, where $p = R \exp(i\theta)$.

Further abbreviated functions to be used are

$$g(p) = p + \beta_0 \chi_k(a) + b\alpha_0 \chi_D(a);$$

$$\xi_D(r) = r^{-1} a g^{-1}(p) \frac{\sinh \eta_D(r)}{\sinh \eta_D(a)};$$

$$\xi_k(r) = r^{-1} a g^{-1}(p) \frac{\sinh \eta_k(r)}{\sinh \eta_k(a)};$$

$$D_m = D \left(\frac{m\pi}{R-a}\right)^2; \qquad k_n = k \left(\frac{n\pi}{R-a}\right)^2$$

Since convolution techniques are to be enlisted in the inversions of $\bar{\rho}$ and \bar{T} , some important individual transforms will here be collected. To do this, straightforward summation of residues will be employed following the techniques outlined by Scott (23). The poles are assumed single.

$$L^{-1}\xi_D(r) = \sum_l \Xi_D(r, p_l) \exp(p_l t),$$

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where

$$\Xi_D(r, p_l) = \left(\frac{a}{r}\right) \left(\frac{\mathrm{d}g}{\mathrm{d}p}\right) \Big|_{p=p_l}^{-1} \left.\frac{\sinh \eta_D(r)}{\sinh \eta_D(a)}\Big|_{p=p_l}.$$

In order to determine $L^{-1}h_2(p)$ it is necessary to find

$$L^{-1}\alpha'(p)c_{k}(p)(p/k)^{1/2} = \frac{\pi}{R-a}L^{-1}\sum_{n}a_{n}'(p)n(-1)^{n} * L^{-1} \\ \cdot \frac{(p/k)^{1/2}}{\frac{1}{R}\sinh\sqrt{\frac{p}{k}(R-a)}} - \sqrt{\frac{p}{k}\cosh\sqrt{\frac{p}{k}(R-a)}}$$

where the symbol * represents convolution. The transform

$$L^{-1} \frac{(p/k)^{1/2}}{\frac{1}{R} \sinh \sqrt{\frac{\bar{p}}{\bar{k}}} (R-a)} - \sqrt{\frac{\bar{p}}{\bar{k}}} \cosh \sqrt{\frac{\bar{p}}{\bar{k}}} (R-a)$$

can be performed by summation of residues around the contour ABCD (*Fig.* 7). The other inversion is:

$$L^{-1}a_n'(p) = \exp\left(-k_n t\right) \frac{2}{R-a}$$
$$\cdot \int_a^R T'(r,0)r \sin\left[\frac{n\pi(r-a)}{R-a}\right] dr.$$

Performing the convolution gives:

$$L^{-1}\alpha'(p)c_k(p)\left(\frac{p}{\bar{k}}\right)^{1/2} = \sum_{j,n} A'_n c_k (p_j)$$
$$\cdot \left(\frac{p_j}{\bar{k}}\right)^{1/2} \left[\frac{\exp(p_j t) - \exp(-k_n t)}{p_j + k_n}\right],$$
where

where

$$A'_{n} = \frac{2}{R-a} \int_{a}^{R} T'(r, 0)r$$
$$\cdot \sin\left[\frac{n\pi(r-a)}{R-a}\right] dr,$$

and the p_j 's represent solutions to

sinh
$$(p/k)^{1/2}(R - a)$$

= $R(p/k)^{1/2} \cosh (p/k)^{1/2}(R - a)$.
This gives for $L^{-1}h_2(p)$:

. .

$$L^{-1}h_{2}(p) = (T_{a} - T_{0})\delta(t) - F_{T}(t) + \frac{\alpha_{0} \pi}{a(R-a)} \sum_{m} A_{m} m \exp(-D_{m} t) + \frac{\beta_{0} \pi}{a(R-a)} \sum_{n} A_{n}' n \exp(-k_{n} t) + \frac{\alpha_{0}}{a} \sum_{m,j} A_{m} c_{D}(p_{j}) \left(\frac{p_{j}}{D}\right)^{1/2} \cdot \left[\frac{\exp(p_{j} t) - \exp(-D_{m} t)}{p_{j} + D_{m}}\right]$$

$$+ \frac{\beta_0}{a} \sum_{n,j} A_n' c_k (p_j) \left(\frac{p_j}{k}\right)^{1/2} \cdot \left[\frac{\exp(p_j t) - \exp(-k_n t)}{p_j + k_n}\right],$$

where $\delta(t)$ is the Dirac Delta function.

The inversion of $\overline{T}(r, p)$ and $\overline{\rho}(r, p)$ give Eqs. [7] and [8] of the text, as written in terms of convolutions of the inverses calculated above.