[2]Sammons, G. D., "Study of the Thermal Behaviour of Solid-Propellants by Differential Scanning Calorimetry," *Analytical Chemistry*, Plenum Press, New York, 1968, pp. 305-311.

[3]Kishore, K., Pai Verneker, V. R., and Nair, M. N. R., "Condensed-Phase Reactions in Solid Propellant Combustion," *AIAA Journal*, Vol. 13, Sept. 1975, pp. 1,240-1,242.

[4]Pai Verneker, V. R., Kishore, K. and Nair, M. N. R., "Importance of Condensed-Phase Reactions in Solid-Propellant Combustion," Paper No. 75-1202, AIAA/SAE 11th Propulsion Conference, Anaheim, Calif., Sept. 29-Oct. 1, 1975.

[5]Pai Verneker, V. R., Kishore, K. and Mohan, V. K., "Correlation between Combustion and Decomposition of Solid-Propellants," *AIAA Journal*, Vol. 13, Oct. 1975, pp. 1415-1416.

[6]Rastogi, R. P., Kishore, K., and Singh, G., "Combustion of Polystyrene and Styrene-Oxygen Copolymer/NH_4ClO_4 Propellants," *AIAA Journal*, Vol. 12, Jan. 1974, pp. 9-10.

[7]Kishore, K., Pai Verenker, V. R., and Mohan, V. K., "Differential Scanning Calorimetric Studies on the Thermal Decomposition of Ammonium Perchlorate," *Thermochimica Acta*, Vol. 13, 1975, pp. 277-292.

[8]Kishore, K., Pai Verenker, V. R. and Nair, M. N. R., "Thermal Degradation of Polystyrene," *Journal of Applied Polymer Science*, (In press).

[9]Jacobs, P. W. M. and Kuveisky, A. R. T., "Kinetics of Thermal Decomposition of Podium Azide," *Journal of the Chemical Society*, 1964, pp. 4718-4723.

Compressible Laminar Boundary Layers with Large Acceleration and Cooling

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Nomenclature

a_{To} = sound speed at reservoir condition
c_D = mass flow coefficient
c_f = friction coefficient, $(c_f/2) = (\tau_w/\rho_e u_e^2)$
D = diameter
f' = dimensionless velocity, u/u_e
f''_w = gradient at surface in transformed coordinates
F = correlation function, Eq. (3)
g_w = surface to total gas enthalpy, H_w/H_{To}
G = dimensionless total enthalpy difference, Ref. 5
H = static enthalpy
H_T = total enthalpy, $H + u^2/2$
M = Mach number
r_w = body or channel radius
r_{th} = throat radius
r_c = throat radius of curvature
$Re_{\tilde\theta}$ = momentum thickness Reynolds number, $\rho_e u_e \tilde\theta/\mu_e$
Re_{Dth} = throat Reynolds number, $(\rho_e u_e D/\mu_e)_{th}$
T = temperature
u = velocity component parallel to surface
x = distance along surface
y = distance normal to wall
z = axial distance
$\bar\beta$ = acceleration parameter in transformed coordinates, Ref. 5
$\bar\beta\theta_t^2$ = acceleration parameter, Eq. (3)
γ = specific heat ratio
$\tilde\delta$ = boundary-layer thickness, $[1-(\rho u/\rho_e u_e)]$
$\tilde\delta^*$ = displacement thickness,

$$r_w^j\tilde\delta^* = \delta^*(r_w - \delta^*\cos\sigma/2)^j$$
$$= \int_0^\infty [(1-(\rho u/\rho_e u_e)]\,(r_w - y\cos\sigma)^j dy$$

δ_t^* = transformed displacement thickness, Eq. (5)
η = dimensionless transformed coordinate normal to surface
$\tilde\theta$ = momentum thickness,

$$r_w^j\tilde\theta = \theta(r_w - \theta\cos\sigma/2)^j$$
$$= \int_0^\infty (\rho u/\rho_e u_e)(1-u/u_e)(r_w - y\cos\sigma)^j dy$$

θ_t = transformed momentum thickness, Eq. (5)
μ = viscosity
υ = kinematic viscosity
ρ = density
σ = angle between wall and axis
τ_w = surface shear stress

Subscripts

e = condition at freestream edge of boundary layer
o = reservoir condition
T = stagnation condition
th = throat condition
w = surface condition

Introduction

THIS Note is concerned with extending an approximate prediction method involving the integral form of the momentum equation[1] to deduce the flow quantities of interest when compressibility effects become important and heat transfer may occur. The approximate method is applicable to a two-dimensional, laminar boundary layer on an im-

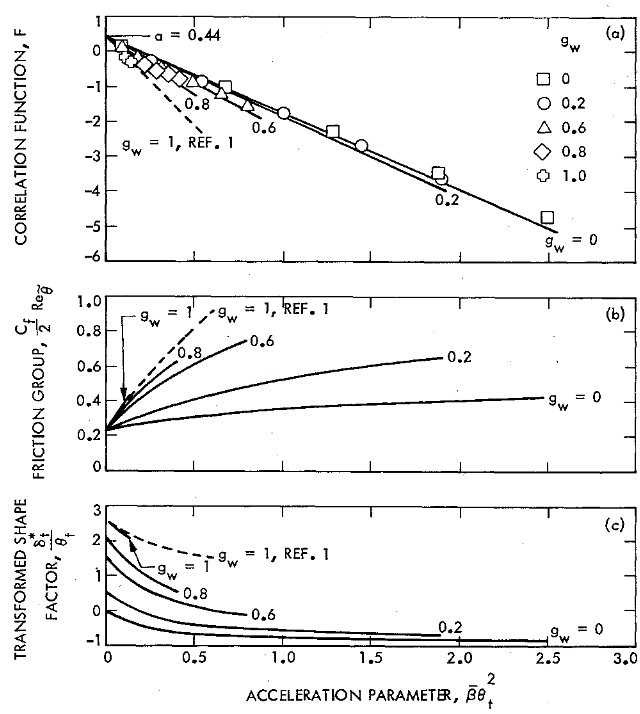

Fig. 1 Variation of the correlation function F, friction group $c_f/2\ Re_{\tilde\theta}$, and transformed shape factor δ_t^*/θ_t with acceleration parameter $\bar\beta\theta_t^2$ and surface-to-total gas enthalpy parameter g_w.

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permeable surface of negligible curvature for which the integral momentum equation is

$$\frac{d\tilde{\theta}}{dx}+\frac{\tilde{\theta}}{r_w^j\rho_e u_e^2}\frac{d}{dx}(r_w^j\rho_e u_e^2)+\frac{\tilde{\delta}^*}{u_e}\frac{du_e}{dx}=\frac{c_f}{2} \quad (1)$$

In this relation $j=1$ for an axisymmetric flow and $j=0$ for flow over a plane surface. The present investigation pertains to larger values of acceleration ($\bar{\beta}$ to 20 rather than 2) than previously considered[2,3] to account for rapidly accelerating flows such as in supersonic nozzles.

Approximate Method

The approximate method involves the use of similar solutions in conjunction with the integral momentum equation for isentropic, freestream flow of a perfect gas by assuming that $\mu \alpha T$, Prandtl number of unity, and $c_p=$const. The similar, boundary-layer velocity and total enthalpy profiles depend upon acceleration and cooling parameters when the combined Levy-Mangler transformation is applied to the differential form of the boundary-layer equations.[4] Equation (1) then can be written in a more convenient form as follows‡

$$u_e\frac{d}{dx}\left[\frac{\tilde{\theta}^2}{\nu_e}\right]=F(\bar{\beta}\theta_t^2,g_w)-2\frac{\tilde{\theta}^2}{\nu_e}\frac{u_e}{r_w^j}\frac{dr_w^j}{dx}$$

$$+\left[\frac{4\gamma-2}{\gamma-1}\right]\frac{\tilde{\theta}^2}{\nu_e}\frac{du_e}{dx}\left[\frac{T_{To}}{T_e}-1\right] \quad (2)$$

where

$$\bar{\beta}\theta^2{}_t=\frac{T_{To}}{T_e}\frac{\tilde{\theta}^2}{\nu_e}\frac{du_e}{dx};$$

$$F(\bar{\beta}\theta_t^2,g_w)=2\left[f_w''\theta_t-\left[2+\frac{\delta_t^*}{\theta_t}\right]\bar{\beta}\theta_t^2\right] \quad (3)$$

$$\frac{c_f}{2}Re_{\tilde{\theta}}=f_w''\theta_t;\quad \frac{\tilde{\delta}^*}{\tilde{\theta}}=\frac{T_{To}}{T_e}\left[1+\frac{\delta_t^*}{\theta_t}\right]-1;$$

$$\frac{\tilde{\delta}}{\tilde{\theta}}=\frac{\tilde{\delta}^*}{\tilde{\theta}}+\frac{\delta_t}{\theta_t} \quad (4)$$

In this formulation $\bar{\beta}\theta_t^2$ is the acceleration parameter, and the correlation function F depends only upon $\bar{\beta}\theta_t^2$ and g_w(the surface to total gas enthalpy or cooling parameter) from the similar solutions. The other quantities with a subscript t refer to the following expressions in the transformed coordinate η used in obtaining the similar solutions

$$\theta_t=\int_o^\infty f'(1-f')d\eta;\quad \delta_t^*=\int_o^\infty\left[G(1-g_w)+g_w-f'\right]d\eta;$$

$$\delta_t=\int_o^{\eta f'=0.99} f'\,d\eta \quad (5)$$

The similar solutions of Ref. 5 are used in particular because they extend to large values of $\bar{\beta}\theta_t^2$. Quantities of interest are given in Table 1 and values of F, the friction group $(c_f/2)Re_{\tilde{\theta}}$, and transformed shape factor δ_t^*/θ_t are shown in Fig. 1.

It appears that the linear relation

$$F=a-b[\bar{\beta}\theta_t^2]\quad\text{where } a=0.44 \text{ and } b=b(g_w) \quad (6)$$

‡In Ref. 3 the density-viscosity product $\rho_e\mu_e$ in the freestream was taken to be invariable along the flow, but this precludes letting the freestream pressure vary as it would in general. Consequently, the form of the momentum equation in Ref. 3 is different than Eq. (2).

though not exact, is a fair representation of the values shown in Fig. 1. The dependence of b on g_w is

g_w	0	0.2	0.6	0.8	1.0
b	2.2	2.3	2.7	3.4	5.1

Substitution of Eq. (6) into Eq. (2) then permits a simple integration for the variation of the momentum thickness along the surface

$$\frac{\tilde{\theta}^2}{\nu_e}=\left[\frac{2}{\gamma-1}\right]^{s/2}\frac{\left[1+\frac{\gamma-1}{2}M_e^2\right]^{s/2}}{r_w^{2j}M_e^b}$$

$$\left\{\frac{a}{a_{To}}\left[\frac{\gamma-1}{2}\right]^{s/2}\int_0^x\frac{r_w^{2j}M_e{}^{b-1}}{\left[1+\frac{\gamma-1}{2}M_e^2\right]^{(1/2)(s-1)}}dx+c \quad (7)$$

where c is a constant of integration to be evaluated at $x=0$, and $s=(4\gamma-2)/(\gamma-1)$. With the momentum thickness known, the friction coefficient is obtained from Fig. 1b and the displacement thickness from Eq. (4) via Fig. 1c. It is of note that in the low speed limit $M_e\to 0$, Eq. (7) reduces to Eqs. (4) and (6) in Ref. 1 for $j=0$ and 1, respectively; but when there is heat transfer, b is no longer equal to 5.15. The dependence of b on g_w reflects the influence of heat transfer on the boundary-layer quantities.

Applications

Confidence in the predictions was established by the relatively good agreement with the centerline temperature measurements by Rothe[6] in a nozzle with a divergent half angle of 20°, an expansion area ratio of $\epsilon_e=66$, a throat diam of $D_{th}=2.5$ mm, and at a throat Reynolds number of $Re_{Dth}=770$ ($B=1230$ in Rothe's nomenclature). These measurements shown in Fig. 2 were obtained with nitrogen at a

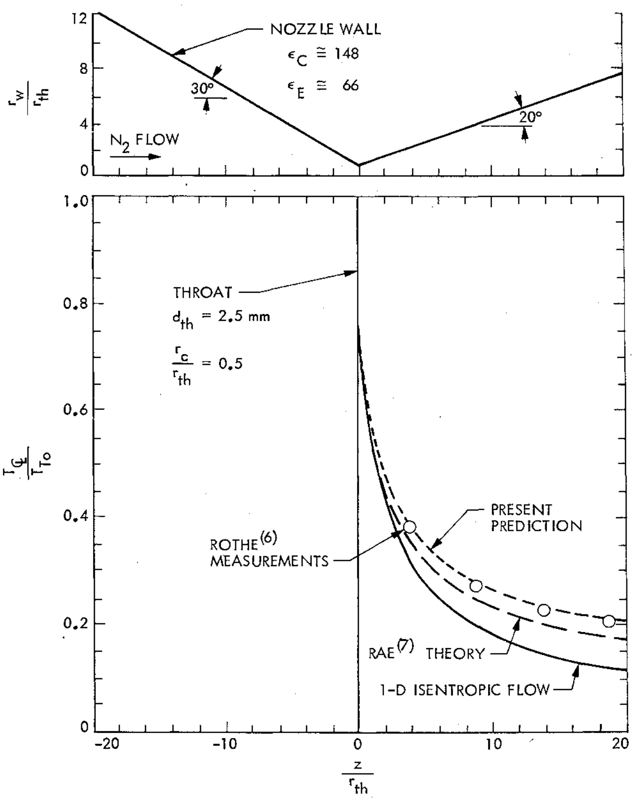

Fig. 2 Comparison between centerline temperature measurements and predictions.

Table 1 Quantities from similar solutions with wall cooling

g_w	$\bar{\beta}$	θ_t	$\bar{\beta}\theta_t^2$	δ_t^*/θ_t	δ_t/θ_t	f_w''	$f_w''\theta_t$	F
0	0	0.471	0	0	4.81	0.4696	0.221	0.442
	0.5	0.423	0.0896	−0.257	5.09	0.5812	0.246	0.180
	2	0.383	0.294	−0.539	5.47	0.7387	0.283	−0.292
	5	0.365	0.666	−0.711	5.75	0.8907	0.325	−1.066
	10	0.357	1.275	−0.810	5.91	1.0308	0.368	−2.297
	15	0.353	1.874	−0.856	5.97	1.1231	0.397	−3.494
	20	0.353	2.489	−0.880	5.98	1.1935	0.421	−4.732
0.2	0	0.471	0	0.517	4.80	0.4696	0.221	0.442
	0.5	0.409	0.0837	0.199	5.19	0.6550	0.268	0.168
	2	0.355	0.253	−0.166	5.75	0.9483	0.337	−0.253
	5	0.328	0.537	−0.419	6.22	1.2816	0.420	−0.858
	10	0.315	0.991	−0.579	6.51	1.6422	0.517	−1.782
	15	0.310	1.444	−0.656	6.64	1.9114	0.593	−2.694
	20	0.308	1.894	−0.703	6.72	2.1348	0.657	−3.600
0.6	0	0.471	0	1.551	4.80	0.4696	0.221	0.442
	0.5	0.380	0.0721	1.184	5.39	0.7952	0.302	0.145
	2	0.295	0.174	0.763	6.31	1.3334	0.393	−0.174
	5	0.246	0.302	0.414	7.38	1.9824	0.487	−0.483
	10	0.219	0.478	0.142	8.37	2.7162	0.594	−0.860
	15	0.207	0.641	−0.0092	8.91	3.2789	0.678	−1.198
	20	0.200	0.797	−0.110	9.26	3.7528	0.749	−1.514
0.8	0	0.471	0	2.067	4.80	0.4696	0.221	0.442
	0.5	0.365	0.0667	1.721	5.48	0.8623	0.315	0.133
	2	0.263	0.138	1.374	6.45	1.5134	0.398	−0.137
	5	0.202	0.204	1.081	7.69	2.3056	0.466	−0.327
	10	0.167	0.279	0.816	9.19	3.2066	0.536	−0.502
	15	0.152	0.345	0.649	10.23	3.8996	0.591	−0.643
	20	0.142	0.402	0.533	11.00	4.4843	0.636	−0.766
1.0	0	0.471	0	2.590	4.80	0.4696	0.221	0.442
	0.5	0.350	0.0614	2.297	5.56	0.9277	0.325	0.123
	2	0.231	0.106	2.156	6.29	1.6872	0.389	−0.106
	5	0.158	0.125	2.104	6.62	2.6158	0.414	−0.200
	10	0.115	0.132	2.095	6.74	3.6752	0.423	−0.239
	15	0.0951	0.136	2.083	6.80	4.4915	0.427	−0.253
	20	0.0828	0.137	2.075	6.78	5.1807	0.429	−0.260

stagnation temperature of 300°K, for a nearly adiabatic wall, and at a stagnation pressure of 0.020 bar. The present prediction method is in better agreement with the data than Rae's prediction,[7] which is for a wholly viscous flow through a slender nozzle. In the calculations for this relatively low Reynolds number flow, the displacement of the flow external to the boundary layer by the shear layer growth along the wall in the divergent section was taken into account in an iterative way, i.e., the appropriate external flow compatible with the boundary-layer flow is calculated. The external flow was taken to be one-dimensional in the divergent portion of the nozzle. Since the detailed nature of the upstream flow exerts little influence on the flow in the throat region, a displacement thickness correction was not made in the convergent portion of the nozzle, and the Mach number at the edge of the boundary layer was evaluated for one-dimensional flow. The boundary layer was presumed to be of zero thickness at the nozzle inlet. The displacement correction in the throat region determines the appropriate mass flow rate and the effective throat radius on which the calculations in the divergent region are dependent. There are limitations however on the present prediction method at even lower Reynolds numbers where the flow becomes wholly viscous in parts of the nozzle and resort must be made to Rae's prediction.

There is a good agreement between the predicted and measured mass flow rate[6,8] for nozzles with adiabatic walls as indicated in Fig. 3, where flow coefficients are shown. These predicted flow coefficients were obtained via the calculated displacement thickness and inviscid flow coefficient.[9]

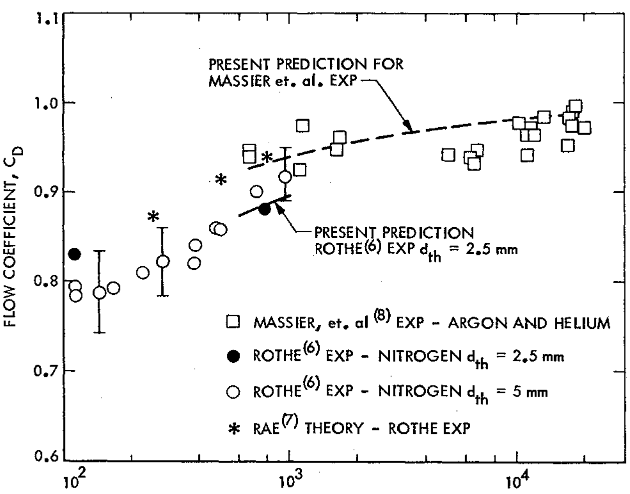

Fig. 3 Measured flow coefficients compared with predictions.

For supersonic nozzle flows with wall cooling,[10] good agreement was found between predicted displacement thicknesses using the procedure of Ref. 2 and values obtained from boundary-layer measurements ($M_e = 2$ and 10) for the case where selected values of b were similar in magnitude to those given herein.

Subsequent investigations, in particular of the heat transfer, would be useful in establishing the extent to which approximate methods such as the one considered herein agree with more exact solutions or experimental results. It is of note that the calculation of the heat transfer to the wall is less clear, there being numerous specifications, i.e., by being consistent with that obtained from the similarity solutions, by using the similarity solutions directly with $\bar{\beta}$ as the parameter,[4,5] by using the integral form of the energy equation,[11] or by other methods suggested for the one parameter method e.g., Hays and Probstein[12] and Chan,[13] but there is little heat transfer data to appraise the various methods in flows over a large range of speeds and accelerations such as in supersonic nozzles.

References

[1] Back, L.H., "Incompressible Laminar Boundary Layers with Large Acceleration," ASME *Journal of Applied Mechanics*, Vol. 36, Ser E, June 1969, pp. 336-338.

[2] Cohen, C. B. and Reshotko, E., "The Compressible Laminar Boundary Layer with Heat Transfer and Arbitrary Pressure Gradient," R-1294, 1956, NACA.

[3] Levy, S. "Effect of Large Temperature Changes (Including Viscous Heating) Upon Laminar Boundary Layers with Variable Free-Stream Velocity," *Journal of the Aeronautical Sciences*, Vol. 21, July 1954, pp. 459-474.

[4] Lees, L., "Laminar Heat Transfer Over Blunt-Nosed Bodies at Hypersonic Flight Speeds," *Jet Propulsion*, Vol. 26, April 1956, pp. 259-269.

[5] Back, L. H., "Acceleration and Cooling Effects in Laminar Boundary Layers—Subsonic, Transonic and Supersonic Speeds," *AIAA Journal*, Vol. 8, April 1970, pp. 794-802.

[6] Rothe, D. E., "Electron-Beam Studies of Viscous Flow in Supersonic Nozzles," *AIAA Journal*, Vol. 9, May 1971, pp. 804-811.

[7] Rae, W. J., "Some Numerical Results on Viscous Low-Density Nozzle Flows in the Slender-Channel Approximation," *AIAA Journal*, Vol. 9, May 1971, pp. 811-820.

[8] Massier, P. F., Back, L. H., Noel, M. B., and Saheli, F., "Viscous Effects on the Flow Coefficient for a Supersonic Nozzle," *AIAA Journal*, Vol. 8, March 1970, pp. 605-607.

[9] Back, L. H. and Cuffel, R. F., "Flow Coefficients for Supersonic Nozzles with Comparatively Small Radius of Curvature Throats," *Journal of Spacecraft and Rockets*, Vol. 8, Feb. 1971, pp. 196-198.

[10] Potter, J. L. and Carden, W. H., "Design of Axisymmetric Contoured Nozzles for Laminar Hypersonic Flow," *Journal of Spacecraft*, Vol. 5, Sept. 1968, pp. 1095-1100.

[11] Ambrok, G. S., "Approximate Solution of Equations for the Thermal Boundary Layer with Variations in Boundary Layer Structure," *Soviet Physics*, Technical Physics, Vol. 2, 1957, pp. 1979-1986.

[12] Hayes, W. F. and Probstein, R. F., "Hypersonic Flow Theory," Academic Press, Inc., New York and London, 1959, pp. 319.

[13] Chan, Y. Y., "Integral Method in Compressible Laminar Boundary Layers and Its Application," *Physics of Fluids*, Vol. 9, Feb. 1966, pp. 350-358.

Thermodynamics of Chemical Systems in External Fields

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RECENT experiments during space flight have accorded special importance to the thermodynamics of systems subjected to gravitational, electrical, and magnetic fields. There is considerable interest in preparing new types of materials or in processing materials in space, including regions of zero gravity in space.[1] Although formal thermodynamic treatment is available,[2,3] its application to chemical systems is obscure. It is the purpose of this paper to discuss explicitly the influence of external fields on phase equilibria, and the influence of external fields on chemical equilibria.

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Thermodynamics of Equilibrium Systems

The energy change dU for a multicomponent system in an external field X_j, because of an infinitesimal change in χ_j at temperature T and pressure P, is given by

$$dU = TdS - PdV + \Sigma\mu_i dn_i + \Sigma X_j d\chi_j \tag{1}$$

where χ_j represents the product of mass m and height z for a gravitational field, electric dipole moment for an electrical field, and magnetic dipole moment for a magnetic field. μ_i and n_i are the chemical potential and number of moles of component i, respectively. The Gibb's free energy change can be expressed in a similar manner, as follows

$$dG = -SdT + VdP + \Sigma\mu_i dn_i + \Sigma X_j d\chi_j \tag{2}$$

where the j summation is over different fields.

The thermodynamics of heterogeneous equilibria for a mixture having C components, and p phases in an external field, can be easily developed, in the usual manner using Eq. (2) as the basis. When T, P, and the χ_j associated with the other fields are kept constant

$$(dG)_{T,p,\chi j} = \Sigma\mu_i^I dn_i^I + \Sigma\mu_i^2 dn_i^2 + \text{----} + \Sigma\mu_i^p dn_i^p \tag{3}$$

where the superscripts refer to the corresponding phase. At equilibrium $(dG)_{T,P,\chi j} = 0$, and hence

$$\Sigma\mu_i^I dn_i^I + \Sigma\mu_i^2 dn_i^2 + \text{----} + \Sigma\mu_i^p dn_i^p = 0 \tag{4}$$

Because of conservation of mass, one would have

$$\sum_{j=I}^{p} dn_i^j = 0 \quad (\text{for } i = 1,2,3,\text{---}c) \tag{5}$$

Equation (5) combined with Eq. (4), using Lagrange's method of undetermined multipliers, yields the following $C(p-I)$ set of equations

$$\begin{array}{l}
\mu_I^I = \mu_I^2 = \mu_I^3 = \quad \text{--------} = \mu_I^p \\
\mu_2^I = \mu_2^2 = \mu_2^3 = \quad \text{--------} = \eta_2^p \\
\mu_3^I = \mu_3^2 \mu_3^3 = \quad \text{----------} = \mu_3^p \\
\text{--------------------------} \\
\text{--------------------------} \\
\mu_c^I = \mu_c^2 = \mu_c^3 = \quad \text{--------} = \mu_c^p
\end{array} \tag{6}$$

Since the number of variables in the system is $2 + (C - I)\,p$, and if f is the number of forces, the degree of freedom F would be given by

$$F = C - p + 2 + f \tag{7}$$

Considering only the gravitational field as a variable, it is obvious that in order that the degree of freedom may be zero for a one component system, we should have $p = 4$; i.e., there would exist an invariant point when four phases coexist in equilibrium. When the χ_j associated with the gravitational field is kept constant, the invariant point is called the triplepoint, and only three phases coexist in equilibrium at this temperature.

It is also obvious that

$$\left(\frac{dP}{dT}\right)_{\chi_j} = \frac{\Delta S}{\Delta V} \tag{8}$$