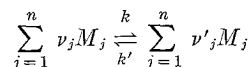


Consider the following reversible reaction for species M_j ($j = 1, \dots, n$)



where the ν_j are the stoichiometric coefficients for the reactants as are the ν'_j for the products (ν_j and ν'_j have no common factor). If the species represented by M_i does not occur as a reactant, then $\nu_i = 0$, etc. The reaction-rate constants k and k' are considered to be functions of temperature only. If we suppose that the rate equation

$$\frac{d[M_i]}{dt} = (\nu'_i - \nu_i) \left\{ k(T) \prod_{j=1}^n [M_j]^{\nu_j} - k'(T) \prod_{j=1}^n [M_j]^{\nu'_j} \right\} \quad (2)$$

in which k and k' are functions of temperature only is valid for all processes and for the full range of species concentrations,[†] it then follows that $K_e(T) = k(T)/k'(T)$ where $K_e(T)$ is the equilibrium constant.

To prove this statement, we define $K(T) = k(T)/k'(T)$ and show that $K(T) \equiv K_e(T)$. Let us consider a process in which constant temperature is maintained at $T = T_0$ by heat sources or by sinks, whichever is needed; in the beginning of the process, let the species be either all reactants or all products. Since (2) is valid for all processes and for the full range of species concentrations, the rate of change of species M_i is dictated by (2), and all chemical species will eventually approach their equilibrium values. Throughout the process, the function $K(T)$ remains constant $K(T) = K(T_0)$. At equilibrium, we have $d[M_i]/dt = 0$ or

$$K(T_0) = \frac{k(T_0)}{k'(T_0)} = \frac{\prod_{j=1}^n [M_j^*]^{\nu'_j}}{\prod_{j=1}^n [M_j^*]^{\nu_j}} \quad (3)$$

where $[M_j^*]$ denotes concentrations of M_j at equilibrium. The right-hand side of (3), however, is precisely the equilibrium constant $K_e(T_0)$; hence, we obtain $K(T_0) = K_e(T_0)$. We now let T_0 take every value of temperature in the range of interest and show that $K(T) \equiv K_e(T)$. Note that it suffices to consider the isothermal process to prove (1) deductively. Besides, other processes can be considered to be isothermal in a short time interval, and the rate constants depend only on the temperature, not on the rate of change of temperature. Since in a short time interval any given process cannot be distinguished from an isothermal process so far as the rate constants are concerned, if (1) is valid for the isothermal process, it is valid for all other processes.

Experiments to determine $k(T)$ are often carried out behind a shock wave in a region where dissociation predominates, whereas experiments to determine $k'(T)$ are often carried out behind an expansion wave in a region where recombination predominates. At present, the available experimental data differ rather widely from one another.^{6,7} Suppose that such measurements can be made highly accurate and that (1) is repeatedly disproved by accurate measurements; then the rate equation (2) must be modified since (2) implies (1).

In some cases, the relation (1) is not valid. We may mention the following simple example.⁸ Consider the reaction $A \rightleftharpoons B$ for which two mechanisms are possible: $2A \rightleftharpoons A + B$ and $2A \rightleftharpoons 2B$. If the first mechanism dominated, the backward rate would be $(k/K_e)[A][B]$; however, if the second reaction dominated, the backward rate would be $(k/K_e^2)[B]^2$. From the latter, we find $k/k' = K_e^2$. We may also note that, when the system is not in vibrational equilibrium, the reaction-rate constants depend on some variables besides temperature, and (1) is not valid.⁹ Nevertheless, with the introduction of a coupling factor and a modified-rate equation, the simple relation (1) can still be used when dissociation is coupled to vibrational relaxation.²

In sum, the use of (1) to relate the equilibrium constant to the reaction-rate constants is consistent with the use of (2) to express the rate of change of species, so long as the rate constants depend on temperature only. If the relation (1) is disproved by experiments or, in some cases, when the rate constants also depend on variables characterizing the deviation from equilibrium, the rate equation (2) must be modified.

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A Simple Relationship between the Drag Near Zero Lift and the Initial Normal-Force-Curve Slope Obtained from Newtonian Theory

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FROM the integrals of pressure distribution used for obtaining the forces acting on a body, it can be shown that a simple relationship exists between C_{D0} , the drag coefficient and $C_{N\alpha_i}$, the initial slope of the normal-force-coefficient curve when the pressures are given by Newtonian impact theory. The analysis to follow is for axially symmetric bodies, although a parallel argument can be made for two-dimensional symmetric bodies. The axial- and normal-force coefficients are given, respectively, by

$$C_x = \frac{1}{A_r} \int_A C_p \sin \theta \, dA \quad (1)$$

and

$$C_N = \frac{1}{A_r} \int_A C_p \cos \theta \cos \Phi \, dA \quad (2)$$

where θ is the angle between the local tangent and the body axis, C_p is the local pressure coefficient, Φ is the angle of revolution about the body axis, A is the surface area, and A_r is a reference area.

From modified Newtonian theory

$$C_p = C_{p_{\max}} \cos^2 \beta \quad (3)$$

where $C_{p_{\max}}$ is the stagnation-point (or maximum) pressure

[†] This requirement must be met if (2) is to be used for various nonequilibrium flow computations.

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coefficient, and β is the angle between the local normal and the freestream velocity. From geometric consideration, it is found that

$$\cos^2\beta = \cos^2\alpha \sin^2\theta + \frac{1}{2} \sin 2\alpha \sin 2\theta \cos\Phi + \sin^2\alpha \cos^2\theta \cos^2\Phi \quad (4)$$

where α is the angle of attack.

The drag of the body at zero lift can be expressed by substituting Eqs. (3) and (4) into Eq. (1) and imposing $\alpha = 0$, as

$$C_{D_0} = C_{x_{\alpha=0}} = \frac{C_{P_{\max}}}{A_r} \int_A \sin^3\theta dA \quad (5)$$

We note from geometry that

$$dA = r ds d\Phi \quad (6)$$

where r is the cylindrical radius and ds is an element of arc length along a body meridian. Substitution into Eq. (5) and integration with respect to Φ yields

$$C_{D_0} = \frac{2\pi C_{P_{\max}}}{A_r} \int_0^S \sin^3\theta r ds \quad (7)$$

Considering now the normal-force-curve slope, differentiations of Eq. (2) with respect to the angle of attack α , after substitution of Eq. (3), gives

$$\frac{dC_N}{d\alpha} = C_{N_\alpha} = \frac{C_{P_{\max}}}{A_r} \int_A \frac{d(\cos^2\beta)}{d\alpha} \cos\theta \cos\Phi dA \quad (8)$$

and differentiation of Eq. (4) with respect to angle of attack gives

$$[d(\cos^2\beta)/d\alpha] = -2 \sin\alpha \cos\alpha \sin^2\theta + \cos 2\alpha \sin 2\theta \cos\Phi + 2 \sin\alpha \cos\alpha \cos^2\beta \cos^2\Phi \quad (9)$$

which, at $\alpha = 0$, reduces to

$$(d \cos^2\beta/d\alpha)_{\alpha=0} = \sin 2\theta \cos\Phi = 2 \sin\theta \cos\theta \cos\Phi \quad (10)$$

Substituting Eqs. (6) and (10) into Eq. (8) and integrating with respect to Φ results in

$$C_{N_{\alpha_i}} = \frac{2\pi C_{P_{\max}}}{A_r} \int_0^S (\sin\theta - \sin^3\theta) r ds \quad (11)$$

If we now substitute Eq. (5) and note that $\sin\theta ds = dr$, we get

$$C_{N_{\alpha_i}} = (\pi R^2/A_r) C_{P_{\max}} - C_{D_0} \quad (12)$$

where R is the maximum cylindrical radius.

In most cases the reference area A_r is equal to πR^2 , so that

$$C_{N_{\alpha_i}} = C_{P_{\max}} - C_{D_0} \quad (13)$$

Similarly, for the initial-lift-curve slope,

$$C_{L_{\alpha_i}} = C_{P_{\max}} - 2C_{D_0} \quad (14)$$

Equations (13) and (14) can be considered as simple rules of thumb for estimating $C_{N_{\alpha_i}}$ or $C_{L_{\alpha_i}}$, because C_{D_0} is usually easier to estimate or calculate. The surprising feature about these relationships is that they are independent of geometry within the limitations of the Newtonian theory for axisymmetric bodies. These relationships are most applicable to noses only because Newtonian theory gives no contribution to $C_{N_{\alpha_i}}$ or $C_{L_{\alpha_i}}$ from cylindrical or convergent afterbodies. However, there is experimental evidence¹ that the derivative of Eq. (14)

$$dC_{L_{\alpha_i}}/dC_{D_0} = -2 \quad (15)$$

is a reasonable rule of thumb, even for noses with cylindrical afterbodies.

The corresponding expressions for $C_{N_{\alpha_i}}$ and $C_{L_{\alpha_i}}$ for symmetric two-dimensional configurations are

$$C_{N_{\alpha_i}} = 2C_{P_{\max}}(A_f/A_r) - 2C_{D_0} \quad (16)$$

$$C_{L_{\alpha_i}} = 2C_{P_{\max}}(A_f/A_r) - 3C_{D_0} \quad (17)$$

where A_f is the frontal area. The discussion of Eqs. (13) and (14) for axially symmetric flow applies in an analogous fashion to Eqs. (16) and (17).

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Unsteady Reacting Boundary Layer on a Vaporizing Flat Plate

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Nomenclature

B_∞	= $c_p^* T_\infty^*/\Delta t^*$
c_p	= specific heat at constant pressure
D_{12}	= binary diffusion coefficient
F	= boundary-layer stream-function variable
g	= low-frequency expansion functions of P
h	= low-frequency expansion coefficients of σ
H, S, V_k	= high-frequency expansion functions for P, σ , and \mathcal{Y}_k
R, U, W_k	
h, s, v_k	= high-frequency expansion functions for H, S , V_k, R, U , and W_k
r, u, w_k	
i	= complex variable $(-1)^{1/2}$
j	= stoichiometric mass ratio, oxidizer to fuel
k_k	= low-frequency expansion coefficients of \mathcal{Y}_k
Δl	= latent heat of vaporization
\mathcal{L}	= linear operator
$m = \frac{m^* Re^{1/2}}{\rho_\infty^* u_\infty^*}$	= mass flow rate per unit area
M	= Mach number
\mathfrak{M}	= space dependent part of m perturbation
$\mathcal{O}[\quad]$	= the order of $[\quad]$
p	= pressure
P	= space dependent part of ψ perturbation
q	= stoichiometric heat of reaction
Re	= Reynolds number
$s = L$	= axial distance from leading edge
t	= time
T	= temperature
u	= velocity in s direction
v	= velocity in y direction
y	= boundary-layer variable in normal direction
Y_k	= mass fraction of k th species
\mathcal{Y}_k	= space dependent part of Y_k perturbation
α	= high-frequency variable
β, β_2	= high-frequency boundary-layer variables
γ	= ratio of specific heats
ϵ	= small perturbation parameter
η	= boundary-layer variable
μ	= viscosity
$\hat{\mu}$	= boundary-layer variable
ξ	= low-frequency boundary-layer variable
ρ	= density
σ	= space dependent part of T perturbation
τ	= liquid temperature

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