τ = dimensionless time ≡ ωt
ω = oscillation frequency
ω_{res} = resonant value of ω

Symbols

$< >$ = cross-sectional average
$-$ = peripheral average
$\sim$ = time average

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Error in the Propagation of Error Formula

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To predict the mean and variance of a dependent variable from the ensemble (or sample) means of the independent variables in a process model, engineers frequently use the "propagation of error" relation, shown in Equation (2) below. For linear models, no difficulty arises in using this relationship. However, we wish to point out that it can yield quite misleading results if the dependent variable in the process model is a nonlinear function of the independent variables.

To avoid complexity in what follows, we assume that the independent variables in the process model are also statistically independent so that crossproduct terms in the propagation of error relation can be deleted.

Let us express the process model as a function of several random variables $X_1, X_2, \ldots, X_n$ with $Y = f(\mathbf{X})$ representing the dependent variable. The usual procedure is to linearize $f(\mathbf{X})$ by a Taylor series

$$Y \simeq f(\mathbf{x}_0) + \sum_{i=1}^{n} \frac{\delta f(\mathbf{x}_0)}{\delta x_i}(X_i - x_{i0}) \tag{1}$$

and thereafter compute the Var $\{Y\} \equiv \sigma^2{}_Y$ by

$$\mathrm{Var}\,\{Y\} \simeq \sum_{i=1}^{n} \left[\frac{\delta f(\mathbf{x}_0)}{\delta x_i}\right]^2 \mathrm{Var}\,\{X_i\} \tag{2}$$

where x_{i0} is a deterministic reference value, such as the value of the ensemble or sample mean of X_i.

If the ensemble means μ_{X_i}, and the ensemble variances $\sigma^2{}_{X_i} \equiv \mathrm{Var}\{X_i\}$ are substituted into (1) and (2) to approximate μ_Y and $\sigma^2{}_Y$, we can show by a simple example how distorted the approximations can be. As an example, we calculate the equilibrium constant from data for the standard free energies at a temperature T

$$K = \exp\left(-\frac{\Delta F^\circ}{RT}\right) \tag{3}$$

Let us assume the random variable ΔF° can be represented by a normal distribution with a known ensemble mean $\mu_{\Delta F^\circ}$ and variance $\sigma^2{}_{\Delta F^\circ}$. Then

$$\mu_K \equiv \mathcal{E}\{K\} = \mathcal{E}\left\{\exp\left(-\frac{\Delta F^\circ}{RT}\right)\right\}$$

$$= \int_{-\infty}^{\infty} \exp\left(-\frac{\Delta F^\circ}{RT}\right) p(\Delta F^\circ) d(\Delta F^\circ)$$

where

$$p(\Delta F^\circ) = \frac{1}{\sqrt{2\pi}\,\sigma_{\Delta F^\circ}} \exp\left[-\tfrac{1}{2}\left(\frac{\Delta F^\circ - \mu_{\Delta F^\circ}}{\sigma_{\Delta F^\circ}}\right)^2\right]$$

After integration we find

$$\mu_K = \exp\left[-\frac{\mu_{\Delta F^\circ}}{RT} + \tfrac{1}{2}\left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2\right] \tag{4}$$

Similarly,

$$\sigma_K{}^2 \equiv \mathrm{Var}\,\{K\} = \int_{-\infty}^{\infty} (K - \mu_K)^2 p(K) dK$$

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$$= \mathcal{E}\{K^2\} - \mu^2{}_K$$

$$\mathcal{E}\{K^2\} = \int_{-\infty}^{\infty} \exp\left(-\frac{2\Delta F^\circ}{RT}\right) p(\Delta F^\circ) d(\Delta F^\circ)$$

$$= \exp\left[-\frac{2\mu_{\Delta F^\circ}}{RT} + 2\left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2\right]$$

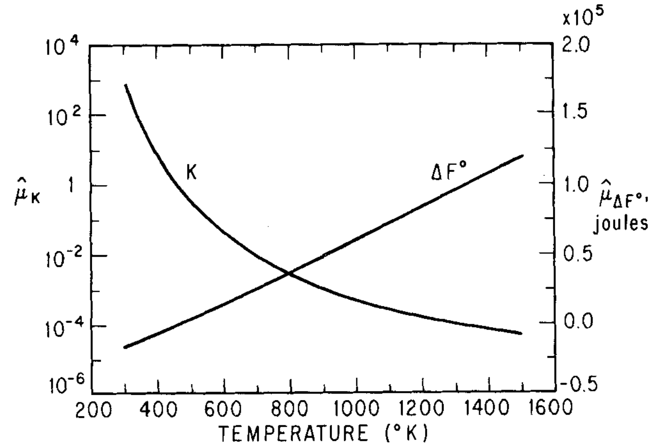

Figure 1. Correct values of the equilibrium constant, *K*, and free energy, Δ*F*°, as a function of temperature.

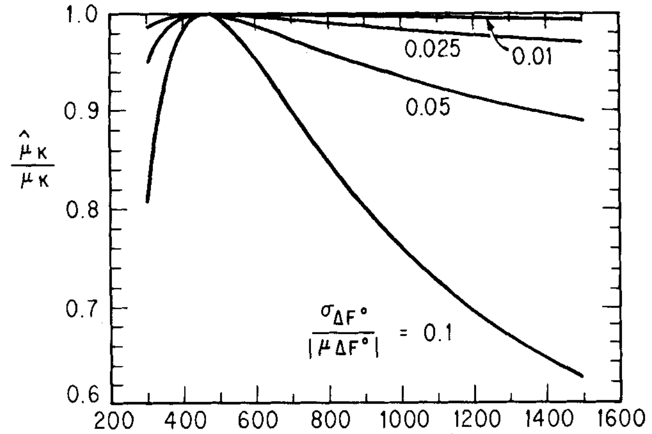

Figure 2. Divergence of the mean value of *K* estimated by direct substitution from the correct value as a function of the correct coefficient of variation (the relative error) in ΔF°.

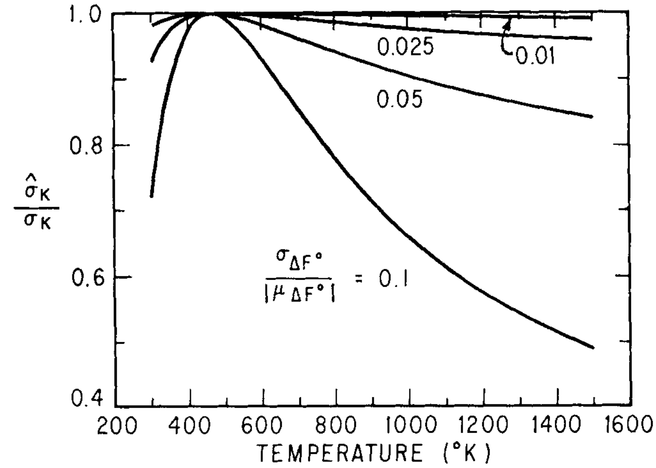

Figure 3. Divergence of the standard deviation of *K* estimated from the propagation of error formula from the correct value as a function of the coefficient of variation (the relative error) in ΔF°.

so that

$$\sigma_K{}^2 = \exp\left[-\frac{2\mu_{\Delta F^\circ}}{RT} + \left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2\right]\left[\exp\left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2 - 1\right] \tag{5}$$

By way of contrast, direct substitution would give

$$\hat{\mu}_K = \exp\left[-\frac{\mu_{\Delta F^\circ}}{RT}\right] \tag{6}$$

and the propagation of error relation would give

$$\hat{\sigma}_K = \frac{\sigma_{\Delta F^\circ}}{RT} \exp\left[-\frac{\mu_{\Delta F^\circ}}{RT}\right] \tag{7}$$

where the superscript caret (^) designates estimate of the mean and variance, respectively.

One means of showing the distortion mentioned above is to plot the ratio of means and the ratio of standard deviations

$$\frac{\hat{\mu}_K}{\mu_K} = \exp\left[-\tfrac{1}{2}\left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2\right] \tag{8}$$

$$\frac{\hat{\sigma}_K}{\sigma_K} = \frac{\sigma_{\Delta F^\circ}}{RT} \frac{\exp\left[-\tfrac{1}{2}\left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2\right]}{\left[\exp\left(\frac{\sigma_{\Delta F^\circ}}{RT}\right)^2 - 1\right]^{1/2}} \tag{9}$$

As a specific example look at the well known reaction

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftarrows NH_3(g)$$

For this reaction (Hougen et al. 1959)

$$\begin{aligned}\Delta F^\circ = &-38409.3 + 30.5423T \ln T \\ &- (1.46521)(10^{-2})T^2 \\ &+ (0.0023132)(10^{-5})T^3 + (0.32908)(10^{-9})T^4 \\ &- 96.6816T\end{aligned}$$

where ΔF° is in J/(g mole)(°K).

Figure 1 shows the values of K and ΔF° as a function of temperature for the ammonia reaction. Curves of $\hat{\mu}_K/\mu_K$ and $\hat{\sigma}_K/\sigma_K$ vs. temperature are shown in Figures 2 and 3, respectively. As can be seen, departures from the correct values can be quite substantial at the lower temperatures, and at higher temperatures—if the relative error in ΔF° gets as high as 10% ($\sigma_{\Delta F^\circ}/\mu_{\Delta F^\circ} = 0.10$). For this particular example, the improperly estimated values of $\hat{\mu}_K$ and $\hat{\sigma}_K$ are all low, but for other examples, the opposite may be true. On the other hand, as expected, the deviation in K is quite small (usually insignificant) for relatively small errors in ΔF°, the region in which the linearization by the Taylor series represents the variance of K well.

NOTATION

$\mathcal{E}\{\ \}$ = expected value (ensemble value)
$f(X)$ = function of X
ΔF° = standard free energy
K = thermodynamic equilibrium constant
R = ideal gas constant
T = absolute temperature
Var $\{X\}$ = variance of X
x_{i0} = deterministic reference value for X_i
$\mathbf{x}_0$ = deterministic reference value for $\mathbf{x}$
X_i = random variable
$\mathbf{X}$ = vector of random variables

$p(\Delta F^\circ)$ = probability density of ΔF°
Y = dependent variable (random)
μ_X, μ_Y = ensemble mean of X, Y
σ_X, σ_Y = ensemble standard deviation of X, Y
σ_X^2, σ_Y^2 = ensemble variance of X, Y

Overlays

$\wedge$ = estimated improperly

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A Theoretical Criterion of Transition in the Free Motion of Single Bubbles and Drops

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Quantitative description of the behavior of bubble and drop dispersions in continuous fluids is often based on the description of free motion of a single bubble or drop, whose size is usually defined by the diameter D of the volume equivalent sphere; that is

$$D = (6V/\pi)^{1/3} \tag{1}$$

A coarse classification of the free motion of single bubbles and drops distinguishes between two main regimes (Figure 1). In regime 1, terminal velocity U is influenced by viscosity. In regime 2, terminal velocity U is predicted by equations that are independent of viscosity.

In a given combination of clean fluids, there is a critical diameter D_c such that particle motion is in regime 1 when $D < D_c$ and in regime 2 when $D > D_c$; the terminal velocity U_c of a bubble or drop of size D_c is a peak velocity (Figure 1).

A calculable criterion for transition from regime 1 to regime 2 is of interest. In a given combination of fluids, particle size is the independent variable; the problem is the prediction of D_c. Implicit and explicit empirical predictions of D_c have been made in conjunction with observation of liquid-liquid systems, for example, Hu and Kintner (1955), Klee and Treybal (1956), Krishna et al. (1959), Yamaguchi et al. (1975). There are empirical predictions for onset of bubble path oscillation (Tsuge and Hibino, 1977). In conjunction with other aspects, an ad hoc equation was formulated that predicts D_c in both bubble and drop systems (Lehrer, 1977). One form of this equation is

$$D_c = \frac{4.67\,\{(2\mu_d + \mu_c)/2\}^{1/3}}{\rho_c^{1/6}} \quad \frac{\sigma^{1/4}}{(\Delta\rho\, g)^{5/12}} \tag{2}$$

While the predictive ability of Equation (2) compares favorably with that of others, it still lacks an analytical basis.

The basic equation for terminal velocity of a single particle is derived from the force balance

$$\pi D^3 \Delta\rho\, g/6 = C_D(\pi D^2/4)(\rho_c\, U^2/2) \tag{3}$$

A new transition criterion is based on the following considerations.

In regime 1, particle shape is almost spherical, and with increasing D, terminal velocity U becomes greater than that of rigid spheres of equal D that are subject to the same force $\Delta\rho V g$. The drag reduction has been ascribed to orderly internal circulation which, near the interface, moves parallel to the external flow. The wake is only narrow. Such flows have been observed in drop experiments (Kintner, 1963), with external streamlines resembling those of potential flow. In evaluation of the drag of spherical gas bubbles in liquids, Haas et al. (1972) showed that due to the assumption of a mobile interface, streamlines in the continuous phase almost coincide with those for potential flow.

In regime 2, particle shape is nonspherical and may oscillate strongly; motion may be irregular also. Periodic wakes follow air bubbles whose *Re* is of order 10^3 (Lindt, 1971), and drops move with vortex shedding (Davies, 1972).

In view of the foregoing, it is postulated here that at the transition from regime 1 to regime 2 in clean systems, the interface moves with the velocity v_θ of the tangential component of potential flow around a sphere. In regime 2, irregular and oscillating motion of the interface eliminates viscosity as a significant calculable factor.

Related to discussion of drag reduction, Ackeret (1952) derived an equation that states the power required to move a curved surface that is in contact with viscous fluid, the surface moving at the velocity v_θ of the tangential component of potential flow. The power is

$$P = -\int \tau_0 v_\theta\, dA \tag{4}$$

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