The Energy Balance for a Bubble Column or a Gas Lift

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The energy balance for a system in which bubbles rise by gravity through a liquid takes on a surprising form, as will be shown. Before beginning with it, consider the case in which blocks of some perfectly rigid, low-density material rise by buoyancy through a liquid. Here it is assumed that there is no net liquid motion, that the blocks are introduced at a constant rate, and that they rise through the fluid at their terminal rise velocity.

The system boundaries are chosen well away from the top and bottom of the liquid to eliminate any entrance or exit effects, and a heating or cooling system is used to hold the temperature of the entire system constant. At steady state the energy balance for this system is

$$\frac{dQ}{dt} = \left[\Delta h + \frac{\Delta V^2}{2g_c J} + \frac{g\Delta z}{g_c J}\right]_B \dot{M}_B \qquad (1)$$

However, if the blocks are at their terminal rise velocity, then ΔV^2 is zero. Furthermore, if the blocks are perfectly rigid (more exactly, if their coefficient of thermal expansion is zero), then $\Delta h = \Delta P/\rho$; so

$$\frac{dQ}{dt} = \frac{1}{J}\left[\frac{\Delta P}{\rho_B} + \frac{g\Delta z}{g_c}\right]_B M_B \qquad (2)$$

Here ΔP is the change in pressure from bottom to top. If the column is wide enough and the flow rate slow enough, then this will equal the static pressure difference:

$$\Delta P = -\rho_L \frac{g\Delta z}{g_c} \qquad (3)$$

If the flow rate of the blocks is high, then this will not be correct; but, as the flow rate of the blocks is reduced toward zero, this value is approached as a limit. Inserting it into Equation (2), we obtain

$$\frac{dQ}{dt} = \left[\frac{-\rho_L}{\rho_B} + 1\right]\frac{g\Delta z}{g_c J}\dot{M}_B = \frac{-g\Delta z}{g_c J}[\rho_L - \rho_B]\frac{\dot{M}_B}{\rho_B} \qquad (4)$$

Here $\dot{M}_B/\rho_B$ is the volumetric flow rate of blocks.

Equation (4) is intuitively satisfying. It indicates that heat must be removed from the liquid (dQ/dt negative) and that the amount of heat to be removed is exactly equal to the amount of work which could have been extracted by letting the blocks rise reversibly, turning some kind of inverted waterwheel (that is, the buoyant force times distance per unit time).

Now consider the same system, replacing the blocks with bubbles of a perfect gas. To simplify the calculations, assume that the liquid has zero vapor pressure and that the gas is totally insoluble in the liquid so that there will be neither evaporation nor dissolution as the bubbles rise. The bubbles are assumed large enough that surface energy changes are negligible. Then Equation (1) still applies. It is also shown in most thermodynamics texts that the enthalpy of an ideal gas is unaffected by changes in pressure at constant temperature; so Δh is zero, and Equation (1) becomes

$$\frac{dQ}{dt} = \frac{1}{Jg_c}\left[\frac{\Delta V^2}{2} + g\Delta z\right]\dot{M}_G \qquad (5)$$

This equation is not as intuitively satisfying as Equation (4) because it indicates that heat must be added to make this flow isothermal. [The amount of heat added, as shown by Equation (5), is very small. For normal gravity, the $g\Delta z$ term amounts to 0.0013 B.t.u./(lb.$_m$)(ft.), or an amount of energy equivalent to that required to heat a gas like air 0.005°F./ft. of rise. In general, we may expect the bubbles to change their velocity because they will expand as they rise into a region of lower pressure. However, the kinetic energy associated with a velocity of 10 ft./sec., which is a high velocity for gas bubbles in a liquid, is only 0.002 B.t.u/lb.$_m$. Thus, the term in Equation (5), due to the change in kinetic energy, is likely to be much smaller than the gravity term. Therefore, to a very good approximation, Equation (5) could be rewritten $dQ/dt = 0$.] From Equation (5), we might conclude that there was no friction heating. However, this is obviously contradicted by direct observations of such systems; they are a mass of eddies and motions, which must cause friction heating.

The explanation of this peculiar energy balance is obtained by considering what would happen if we passed the gas through some kind of isothermal turbine or engine which extracted work from it. The energy balance for such an isothermal turbine is

$$\Delta h = \frac{dQ}{dm} - \frac{1}{J}\frac{dW}{dm} - \frac{g\Delta z}{g_c J} - \frac{\Delta V^2}{2g_c J} \qquad (6)$$

Thus, we see that, since the gas has no enthalpy change (because it has no temperature change), the heat absorbed from the surroundings must be exactly equal to the work done on the surroundings plus the increase in kinetic and potential energies of the stream passing through. In the case of the gas rising through the liquid, the cycle is: gas drives fluid circulation, doing work on fluid; fluid dissipates this work as heat; gas absorbs this heat from liquid, thereby emerging at same enthalpy and temperature as it entered if the amount of heat indicated by Equation (5) is supplied from an external source.

One may, however, see the consistency of Equations (4) and (5) by noting that the dQ/dt in Equation (4) is simply the amount of mechanical work done by the blocks on the fluid, which converts this work to heat by viscous dissipation. The same equation must also indicate the amount of work done by the gas rising through the liquid. However, for the gas it must be written in differential form because of the changing density of the gas; namely

$$d\left[\frac{dW}{dt}\right]_G = \frac{\dot{M}_G}{\rho_G}[\rho_L - \rho_G]\frac{gdz}{g_c} - \frac{\dot{M}_G}{g_c} d\left[\frac{V^2}{2}\right] \qquad (7)$$

(Here the change of kinetic energy term is added because the gas bubbles may increase in velocity due to their size changes.) Separating the first term into two parts and substituting for dz from the differential form of Equation (3) and for ρ_G from the ideal gas law, we obtain

$$d\left[\frac{dW}{dt}\right]_G = -\dot{M}_G\frac{RT\,dP}{P} - \dot{M}_G\frac{gdz}{g_c} - \frac{\dot{M}_G}{g_c} d\left[\frac{V^2}{2}\right] \qquad (8)$$

which may be integrated to

$$\left[\frac{dW}{dt}\right]_G = -\dot{M}_G\left[RT\ln\frac{P_2}{P_1}\right] - \dot{M}_G\frac{g\Delta z}{g_c} - \frac{\dot{M}_G}{g_c}\Delta\left[\frac{V^2}{2}\right] \qquad (9)$$

Here $(dW/dt)_G$ is the amount of work per unit time which is done by the gas on the liquid.

The foregoing has the built-in assumptions that all the irreversibilities are in the liquid phase [via the isothermal assumption and Equation (3)]. Thus, according to these assumptions, the gas is undergoing a reversible, isothermal process. From the entropy balance, we can calculate the rate of heat addition to the gas:

$$\left[\frac{dQ}{dt}\right]_G = \dot{M}_G\ RT\ \ln\frac{P_1}{P_2} \qquad (10)$$

The net heat added to the liquid per unit time is equal to the work done on it by the gas per unit time, so the heat which must be added externally is Equation (10) minus Equation (9), which is identical with Equation (5).

If all the processes going on in the gas are not reversible (that is, there are measurable temperature gradients or conversion of kinetic energy to internal energy), then the amount of heat added to the gas and, correspondingly, the amount of work done on the liquid will be less than that indicated by Equations (9) and (10) by exactly the same amount. It seems plausible to assume that any irreversibilities in the gas will be small compared with those in the liquid, so Equations (9) and (10) should be approximately correct.

If there is net liquid flow up or down, then there will be additional terms in the energy balance to account for the potential energy, kinetic energy, and enthalpy changes of the liquid. Assuming as before that the flow is steady and isothermal and that the liquid flow is upward, we find that Equation (5) becomes

$$\frac{dQ}{dt} = \frac{g\Delta z}{g_c J}\left[\dot{M}_G + \dot{M}_L\right] + \frac{1}{Jg_c}\left[\dot{M}_G\frac{\Delta V_G{}^2}{2} + \dot{M}_L\frac{\Delta V_L{}^2}{2}\right] + \dot{M}_L\ \Delta h_L \qquad (11)$$

[Although there is no term for the change of enthalpy in the isothermal flow of a gas, there is one for the liquid, as shown here. This is generally much smaller than the other terms. Similarly, the kinetic energy term in Equation (11) is generally much smaller than the potential-energy term.] As some of the work done by the gas is converted into increased potential energy of the liquid instead of being converted into internal energy by frictional heating, the amount of heat to be rejected by the liquid decreases; hence, the increase in heat which must be added from outside.

Several workers have prepared energy balances for this type of system, based on the mechanical energy balance. Govier et al. (*1*) and Hughmark and Pressburg (*2*) have given the following (here it is shown in the form given by Hughmark and Pressburg; Govier et al. give it in rearranged form):

$$\frac{[\dot{M}_L + \dot{M}_G]\Delta z}{\left[\dfrac{\dot{M}_L}{\rho_L} + \dfrac{\dot{M}_G}{\rho_G}\right]} + \frac{\dot{M}_L\,\Delta\left[\dfrac{V_L{}^2}{2}\right] + \dot{M}_G\,\Delta\left[\dfrac{V_G{}^2}{2}\right]}{g_c\left[\dfrac{\dot{M}_L}{\rho_L} + \dfrac{\dot{M}_G}{\rho_G}\right]} + \frac{\dot{M}_L\ F_L + \dot{M}_G\ F_G}{\left[\dfrac{\dot{M}_L}{\rho_L} + \dfrac{\dot{M}_G}{\rho_G}\right]} + \Delta P = 0 \qquad (12)$$

Hughmark and Pressburg explicitly and Govier et al. implicitly set g/g_c equal to 1, which results in the first term in Equation (12) having the dimensions lb.$_m$/sq.ft., and all the others having the dimension lb.$_f$/sq.ft. If one insists on dimensional consistency, he can obtain it by reinserting the g/g_c which these authors canceled out of the first term of Equation (12). Both sets of authors indicate that the second term in Equation (12) (the change of kinetic energy term) is much smaller than the others and can be ignored.

Both indicate that their balances apply to isothermal flow; neither indicates what amount of heat must be added or subtracted to maintain the isothermal condition. This quality of external heat addition is given by Equation (11). It is normally not a large heat quantity, but it is of the same order of magnitude as the terms in Equation (12). [For example, if one clears Equation (12) of fractions by multiplying through by the denominator of the first three terms, then the first two terms are the first two terms of Equation (11) and almost exactly the quantity of heat added.]

Nicklin (*3*) presents an analogous equation, which, converted to the notation used here, is

$$\frac{[\dot{M}_L + \dot{M}_G]g\Delta z}{\left[\dfrac{\dot{M}_L}{\rho_L} + \dfrac{\dot{M}_G}{\rho_G}\right]g_c} + \frac{\Delta z\,[H_L + H_G]}{Jg_c\left[\dfrac{\dot{M}_L}{\rho_L} + \dfrac{\dot{M}_G}{\rho_G}\right]} + \Delta P = 0 \qquad (13)$$

which is identical to Equation (12) if one drops the kinetic energy term and sets

$$\frac{H_L\,\Delta z}{J} = \dot{M}_L\ F_L,\ \text{etc.} \qquad (14)$$

Thus, although Nicklin criticizes the approach of Govier et al. and Hughmark et al., his only real change from their approach is to write the friction loss term as a heat production term.

Although Equations (12) and (13) are correct and useful, they can be misleading. The only heat term in them is the frictional heating term, which Nicklin shows specifically as a heat production term and which the others imply is a heat production term. These could certainly lead a reader to believe that, since heat is being produced by frictional dissipation, it must be rejected from the system, whereas, as shown above, this is not the case; heat must be added to the system in significant quantities.

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NOTATION

F = friction loss, (ft.) (lb.$_f$)/lb.$_m$
g = acceleration of gravity, ft./sec.^{2}
g_c = dimensional conversion constant, 32.2 (lb.$_m$)(ft.)/(lb.$_f$) (sec.^{2})
h = enthalpy per lb.$_m$, B.t.u./lb.$_m$
H = time rate of heat generation per unit length of tube, in one phase, B.t.u./(sec.) (ft.)
J = dimensional conversion constant, (778 ft.) (lb.$_f$)/B.t.u.
m = mass, lb.$_m$
$\dot{M}$ = mass flow rate, lb.$_m$/sec.

P = pressure, lb.$_f$/sq.ft.
Q = heat, B.t.u.
R = universal gas constant, B.t.u./(lb.-mole) (°R.) or equivalent
t = time, sec.
T = temperature, °R.
V = velocity, ft./sec.
W = work (excluding injection work), ft.lb.$_f$ or equivalent
z = elevation, ft.
ρ = density, lb.$_m$/cu.ft.

Subscripts

B = solid blocks
G = gas
L = liquid

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Discrimination Among Rival Hougen-Watson Models Through Intrinsic Parameters

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In attempting to describe rate data from a heterogeneous chemical reaction, the chemical engineer has frequently postulated a set of Hougen-Watson models (*1*, *2*), taken rate data, and analyzed them to specify a "best" model and to estimate the rate parameters in this model. In so doing, the techniques suggested by Yang and Hougen (*3*) of making appropriate linear plots of the initial rate data are among the most widely used procedures (*4*, *5*). Also, it is often necessary to test the ability of a model to fit high conversion data. This may be done by nonlinear least squares (*5*), by model building techniques at constant pressure (*6*), or by the use of nonintrinsic parameters (*7*). This communication presents an extension of an existing method (*8*) of preparing linear plots for high conversion data, which is entirely analogous to the method of initial rates. Hence, these plots provide a visual indication of the ability of a model to fit the high conversion data and thus allow a more complete test of a model than does the initial rate analysis alone; estimates of product adsorption constants are also obtained.

LINEAR ANALYSIS THROUGH INTRINSIC PARAMETERS

When any Hougen-Watson model is written in terms of fractional conversions instead of a partial pressures, two groupings of terms inherently arise within the denominator. These two groupings will be called the *intrinsic parameters* C_1 and C_2. It will first be shown how the linear initial rate analysis can be formalized through the specification of an intrinsic parameter C_1 and then how the high conversion analysis logically follows from a second intrinsic parameter C_2.

Consider for example, a single site model

$$r = \frac{kK_A\,(p_A - p_o p_W/K)}{(1 + K_A p_A + K_W p_W)} \tag{1}$$

When data are taken for the olefinic dehydration of a pure alcohol feed, Equation (1) may be rewritten in terms of fractional conversions:

$$r = \frac{k\,K_A\left(\dfrac{1-x}{1+x}\right)\pi}{\left[1 + K_A\left(\dfrac{1-x}{1+x}\right)\pi + K_W\left(\dfrac{x}{1+x}\right)\pi\right]} \tag{2}$$

In this formulation, the reaction is assumed to be essentially irreversible; the existence of product partial pressures in the numerator does not alter the method of analysis to be discussed here, however. Equation (2) may be written as

$$r = \frac{(1-x)\,\pi}{(C_1 + C_2 x)} \tag{3}$$

where

$$C_1 = \frac{1}{k\,K_A} + \frac{\pi}{k} \tag{4}$$

$$C_2 = \frac{1}{k\,K_A} + \frac{K_W - K_A}{k\,K_A}\,\pi \tag{5}$$

The C_1 parameter, then, is the collection of terms which is not multiplied by conversion, while C_2 is the collection which is multiplied by the conversion x.

The use of the parameter C_1 in Equation (3) has been discussed elsewhere (*3*), for Equation (3) can be utilized to estimate the parameter C_1 from zero conversion data ($C_1 = \pi/r_o$). Equation (4) requires that these observed values be linearly dependent upon total pressure if the model of Equation (2) is adequate. This constitutes a formalization of the conventional linear initial rate approach in terms of the intrinsic parameter C_1.

It can be seen from Equation (3) that rate data taken at zero conversion (initial rate data) can give little information concerning the magnitude and the pressure dependence of the parameter C_2. Equation (5) dictates that if values of the parameter C_2 can be estimated, they must be linearly dependent upon total pressure if the model of

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