

original  
14

# The Gibbs-Duhem Equation of Process Design and Control

Sigurd Skogestad

Chemical Engineering  
Norwegian Institute of Technology (NTH)  
N-7034 Trondheim  
Norway

July 21, 1989

Presented at AIChE Annual Meeting, San Francisco, Nov. 5-10, 1989.

Session: Modelling issues in process control. Paper 142e.

UNPUBLISHED.

©Author

## Abstract

Fundamental consistency relationships exist between the effect of changes in extensive variables under steady-state conditions. These relationships are not directly related to the Gibbs-Duhem equation of thermodynamics but their derivation is very similar. The relationships may be used to obtain data for or to check consistency of linear steady-state models used for process control or for sensitivity analysis in process design.

# 1 Introduction

The results in this paper originated from some consistency relations the author derived for distillation columns (Skogestad,1988). A more careful analysis revealed a close relationship between the derivation of these relations and the derivation of the Gibbs-Duhem equation of thermodynamics. This again led to the realization that there is a close similarity between thermodynamics and steady-state models for process design and control, and that the latter field might benefit from applying methods development within thermodynamics. Surprisingly, no one seems to have pointed out this explicitly before.

In both thermodynamics and steady-state modelling the first step is to identify some set of independent variables. The effect of small changes in these independent variables on the dependent variables is then sought. In thermodynamics this effect is the “partial derivative”, in process control it is the “gain”, and in process design it is the “sensitivity”. An example of a steady-state model used for process control is

$$dy = g_{yu_1} du_1 + g_{yu_2} du_2 \quad (1)$$

where  $u_1$  and  $u_2$  are the independent variables,  $y$  is some dependent variable and the  $g$ 's denote gains.  $dy$  is the differential of  $y$ , that is, a small change in  $y$ . In process control it is often implicitly assumed that Eq.1 is in terms of deviation variables and that only small deviations are allowed. To simplify notation one then often replaces the differential  $dy$  by  $y$  and similar for the independent variables. In order to avoid confusion this simplification is not used in this paper.

Models such as Eq.1 are also used in steady-state sensitivity analysis of processes. In this case the gain  $g_{yu}$  might express the sensitivity of  $y$  (eg., equipment size or investment) with respect to some design variable  $u$  (such as flow rate or product specification). Although it is often referred to process control in this paper, it is implicitly understood that the results apply to any steady-state model of the form in Eq.1.

*Gibbs-Duhem consistency relationships.* Most engineers have a most respectful relationship to the Gibbs-Duhem equation. In some strange way one is able to obtain out of nothing an equation which expresses something about the change in the mystical chemical potential. Looking closer at how the Gibbs-Duhem equation is derived it is realized that the key idea is to use physical insight about the difference between extensive and intensive variables. Intensive variables, such as pressure and temperature, are point values independent of the size of the system. Extensive variables, such as volume and mass, depend on the size of the system in an additive way. This means that if two equal subsystems are combined to form a new system then the intensive variables are unchanged while the extensive variables are doubled. Using this kind of insight to steady-state models one is also out of “nothing” able to derive some quite interesting relationships. Surprisingly, these fundamental relationships have not been reported previously in the literature, and one can easily find models in the literature which do not satisfy them.

*An introductory example.* Consider the flash tank with heater in Fig.1 in which a feed stream  $F$  with composition  $z$  is supplied the amount of heat  $Q$ , and is then separated into a vapor stream  $F_V$  with composition  $y$  and a liquid stream  $F_L$  with

composition  $x$  (extensive variables are here shown with capital letters; intensive variables with lower case letters). There is no chemical reaction. Make the following physical assumptions:

- 1) The independent variables are  $F, z$  and  $Q$ .
- 2) Increasing  $F$  and  $Q$  by a factor  $k$  keeps all intensive variables constant ( $F_V$  and  $F_L$  also increase by a factor  $k$ , but the compositions  $x$  and  $y$  remain constant).

Using assumption 1) a linear steady-state model for  $y$  may be formulated as a total differential of all the independent variables:

$$dy = \left( \frac{\partial y}{\partial F} \right)_{Q,z} dF + \left( \frac{\partial y}{\partial Q} \right)_{F,z} dQ + \left( \frac{\partial y}{\partial z} \right)_{F,Q} dz \quad (2)$$

or in terms of process control notation

$$dy = g_{yF}dF + g_{yQ}dQ + g_{yz}dz \quad (3)$$

Integrating Eq. 3 by increasing  $F$  and  $Q$  from 0 to their steady-state values  $F$  and  $Q$  while keeping  $z$  and  $y$  constant yields

$$0 = \left( \frac{\partial y}{\partial F} \right)_{Q,z} F + \left( \frac{\partial y}{\partial Q} \right)_{F,z} Q \quad (4)$$

or

$$g_{yF}F = -g_{yQ}Q \quad (5)$$

Thus, there is an exact consistency relationship between the steady-state gains  $g_{yF}$  and  $g_{yQ}$ . It may be used to compute one gain given the other (thereby reducing the need for performing simulations or experiments), or to check a derived model for consistency. Actually,  $y$  in Eq.4 may represent any independent intensive variable, for example, composition, temperature, density, etc. For example, if  $y$  represents temperature, then Eq.4 tells us that a 1% increase in heat input  $Q$  has the same effect on temperature as a 1% decrease in feed flow  $F$ . The basis for this statement is of course our physical assumption that a 1% increase in feed rate may be compensated by increasing the heat input 1%.

In the paper a more rigorous treatment is given and it is shown that similar, but less trivial relationships may be derived for other examples such as distillation columns. The main limitation is that they are restricted to steady-state and to small perturbations from this steady-state (linearity).

## 2 Similarities between thermodynamics and process control

### 2.1 Thermodynamics

A basic postulate of equilibrium thermodynamics is that specifying temperature ( $T$ ), pressure ( $p$ ) and the number of moles ( $n_i$ ) of each species uniquely determines the

state of the system. Any other property of the system, for example, the Gibbs energy ( $G$ ) is then a function of these variables, that is

$$G = f(T, P, \{n_i\}) \quad (6)$$

where  $\{n_i\}$  represents the set of mole numbers  $n_1, n_2, \dots, n_c$  where  $c$  is the number of components. Differentiating yields the total differential of  $G$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p, \{n_i\}} dT + \left(\frac{\partial G}{\partial p}\right)_{T, \{n_i\}} dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, p, \{n_j, j \neq i\}} dn_i \quad (7)$$

## 2.2 Process Control

In process control the independent variables  $u_i$  are usually divided into two classes, manipulated inputs and disturbances, but this distinction is not needed here. Assume that at steady state the value of these variables uniquely determine the state of the system. Let  $y$  denote any dependent variable. Then

$$y = f(u_1, u_2, \dots, u_i, \dots) \quad (8)$$

Differentiating yields the total differential of  $y$

$$dy = \left(\frac{\partial y}{\partial u_1}\right)_{u_j, j \neq 1} du_1 + \left(\frac{\partial y}{\partial u_2}\right)_{u_j, j \neq 2} du_2 + \dots \quad (9)$$

In process control, the terms “gains” is usually used to denote the partial derivatives in this equation and we write

$$dy = g_{yu_1} du_1 + g_{yu_2} du_2 + \dots \quad (10)$$

With this notation it may not be clear what independent variables were used when evaluating the gain. In some cases we shall use a superscript on the gain to show explicitly the independent variables, that is, in Eq.10 above

$$g_{yu_1}^{u_1 u_2} \equiv g_{yu_1} \quad (11)$$

## 2.3 Similarities

In both the above cases we assume equilibrium or steady-state conditions and postulate a set of independent variables. A small change in the independent variables yield a new steady-state, and the change in any dependent variable,  $dy$ , may be obtained from the total differential of  $y$  with respect to the independent variables.

*Variable transformations.* There are also other similarities. One is that we may want to use another set of independent variables. In thermodynamics entropy ( $S$ ) and volume ( $V$ ) are dependent variables when  $p, T$  and  $n_i$  are specified. However, we may want to use  $S$  and  $V$  as independent variables instead of  $p$  and  $T$ . Similarly, in distillation column control, we may know the gains when  $L$  and  $V$  are independent

variables and seek the gains when we instead use  $D$  and  $V$  as independent variables (see Fig. 2). In both these cases the variable transformation problem arises: How do we evaluate the partial derivatives (“gains”) for one set of independent variables in terms of the partial derivatives of another set? Students trying to learn thermodynamics usually get very confused about these transformations.

To be more specific, let  $u_1$  and  $u_2$  be the independent variables and assume that their effect (that is, the partial derivatives in the equation below) on the dependent variables  $y_1$  and  $y_2$  is known

$$dy_1 = \left( \frac{\partial y_1}{\partial u_1} \right)_{u_2} du_1 + \left( \frac{\partial y_1}{\partial u_2} \right)_{u_1} du_2 \quad (12)$$

$$dy_2 = \left( \frac{\partial y_2}{\partial u_1} \right)_{u_2} du_1 + \left( \frac{\partial y_2}{\partial u_2} \right)_{u_1} du_2 \quad (13)$$

or in process control notation

$$dy_1 = g_{11} du_1 + g_{12} du_2 \quad (14)$$

$$dy_2 = g_{21} du_1 + g_{22} du_2 \quad (15)$$

Next, choose the independent variables to be  $u_1$  and  $y_2$ . We then seek to find

$$dy_1 = \left( \frac{\partial y_1}{\partial u_1} \right)_{y_2} du_1 + \left( \frac{\partial y_1}{\partial y_2} \right)_{u_1} dy_2 \quad (16)$$

or

$$dy_1 = \hat{g}_{11} du_1 + \hat{g}_{12} dy_2 \quad (17)$$

How are these partial derivatives (gains) related to the ones in Eq. 14-15 ? Simple algebra shows that the answer is

$$\hat{g}_{11} = g_{11} - g_{12}g_{21}/g_{22} \quad (18)$$

$$\hat{g}_{12} = g_{12}/g_{22} \quad (19)$$

This result may also be obtained from more systematic methods, for example the Jacobian transformations used in thermodynamics (eg., Callen, 1960, p.128).

Several authors have recently applied variable transformations to derive consistent models for distillation columns. For example, Häggblom and Waller (1988) showed how gains for one distillation configuration (selecting two independent variables from the set  $L, V, D$  and  $B$ , see Fig. 2) may be derived when data for another configuration are known, and Mijares et al. (1985) applied the method of Jacobian transformations to compute the Relative Gain Array for various configurations. However, no one has pointed out the close connection between these variable transformations for distillation columns and those of classical thermodynamics.

The issue of variable transformations is quite straightforward and is not dealt with in any detail in this paper. Instead the focus is on the Gibbs-Duhem kind of consistency relationships which so far has been overlooked within the field of process control.

## 2.4 Differences

Before embarking on this, however, it should be noted that there are also important differences between thermodynamics and steady state process control models. One is that the partial derivatives in thermodynamics usually are important properties in themselves. For example, in Eq. 7 we have  $\left(\frac{\partial G}{\partial p}\right)_T = V$ ,  $\left(\frac{\partial G}{\partial T}\right)_p = -S$  and  $\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} = \mu_i$  where  $\mu_i$  denotes the chemical potential. On the other hand, in process control usually only the numerical value of the partial derivatives (gains) are of interest. The powerful method of Legendre transformations used in thermodynamics (eg., Modell and Reid, p. 104) which forms the basis of the famous Bridgman tables, will therefore not generally have its equivalence for process control models.

Another difference are the laws of thermodynamics which do not have a direct counterpart in other examples. However, in process control examples there may exist other relationships which put additional constraints on the equations. One fundamental relationship which often applies is the steady state material balance. For example, for the flash tank example in the Introduction, the steady-state overall material balance is  $F = F_L + F_V$  and the component material balance is  $Fz = F_Lx + F_Vy$ . These exact equations may be used to derive consistency relations between the gain elements for  $x$  and  $y$ . For example, with  $F$  and  $z$  constant we derive  $F_L dx + F_V dy = -(y - x)dF_V$  which yields the following consistency relationship for the gains related to changes in  $Q$ :

$$F_L g_{xQ} + F_V g_{yQ} = -(y - x)g_{F_V Q} \quad (20)$$

Skogestad and Morari (1987) and Häggblom and Waller (1988) have used component material balances to derive similar consistency relationships for distillation column models.

## 3 The Gibbs-Duhem equation of thermodynamics

### 3.1 Simple derivation

As discussed above the Gibbs energy may be written as a total differential of the independent variables  $p$ ,  $T$  and  $n_i$ .

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,\{n_i\}} dT + \left(\frac{\partial G}{\partial p}\right)_{T,\{n_i\}} dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\{n_j, j \neq i\}} dn_i \quad (21)$$

$$= -SdT + Vdp + \sum_i \mu_i dn_i \quad (22)$$

Here we know from physical insight that  $G$  and  $n_i$  are extensive variables, while  $T$  and  $p$  are intensive variables. Imagine that the actual system was obtained by mixing a large (infinite) number of identical smaller subsystems. Mathematically this mixing process corresponds to integrating Eq.21 from zero size to actual conditions with all intensive properties constant (that is,  $dp = 0$ ,  $dT = 0$ ,  $\mu_i$  constant). This yields

$$G = \left(\frac{\partial G}{\partial T}\right)_{p,\{n_i\}} \cdot 0 + \left(\frac{\partial G}{\partial p}\right)_{T,\{n_i\}} \cdot 0 + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\{n_j, j \neq i\}} n_i \quad (23)$$

or

$$G = \sum_i \mu_i n_i \quad (24)$$

Equation 24 is referred to as the Integrated Gibbs-Duhem (IGD) equation in the following. Differentiating this equation yields

$$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad (25)$$

and by subtracting Eq.22 we obtain the “true” Gibbs-Duhem equation

$$SdT - Vdp + \sum_i n_i d\mu_i = 0 \quad (26)$$

This equation provides a consistency relationship between allowable variations in the variables  $T$ ,  $p$  and  $\mu_i$ . However, we shall focus on the closely related Integrated Gibbs-Duhem equation which has a clearer physical interpretation.

### 3.2 Rigorous derivation

A more rigorous derivation is instructive since the necessary assumptions then become clearer. The derivation given here is taken from Modell and Reid (1983) and is based on Euler’s theorem of homogeneous functions. Consider a variable  $y$  which is a function of the independent variables  $a, b, c, d$ .

$$y = y(a, b, c, d) \quad (27)$$

Differentiating yields the linear relationship

$$dy = \left( \frac{\partial y}{\partial a} \right)_{b,c,d} da + \left( \frac{\partial y}{\partial b} \right)_{a,c,d} db + \left( \frac{\partial y}{\partial c} \right)_{d,a,b} dc + \left( \frac{\partial y}{\partial d} \right)_{c,a,b} dd \quad (28)$$

$a, b$  are intensive variables and  $c, d$  are extensive variables. Assume that increasing  $c$  and  $d$  by a factor  $k$ , with  $a$  and  $b$  constant, results in an increase in  $y$  by a factor  $k^h$  (we see that  $h = 0$  if  $y$  is an intensive variable and  $h = 1$  if  $y$  is an extensive variable). Mathematically,  $y$  is assumed to be homogeneous to the degree  $h$  in  $c$  and  $d$ , that is

$$y(a, b, kc, kd) = k^h y(a, b, c, d) \quad (29)$$

Differentiating this expression and collecting terms making use of the fact that  $a, b, c, d$  and  $k$  are *independent* variables yields Euler’s theorem:

$$h \cdot y = \left( \frac{\partial y}{\partial c} \right)_{d,a,b} c + \left( \frac{\partial y}{\partial d} \right)_{c,a,b} d \quad (30)$$

This is the general form of Integrated Gibbs-Duhem equation which is applicable to steady-state models in general. Note that Eq.30 may be obtained directly from Eq.28 by formally integrating Eq.28 from zero to actual conditions with the intensive variables  $a, b$  constant (and also  $y$  constant if  $h = 0$ ).

*Application of Eq.30 to thermodynamics.* To rederive Eq.24 write  $G$  as a function of the independent variables

$$G = y(T, p, \{n_i\}) \quad (31)$$

and use the fact that an increase in all  $\{n_i\}$ 's by a factor  $k$  with  $T$  and  $p$  constant increases  $G$  by a factor  $k$ , that is,

$$y(T, p, \{kn_i\}) = ky(T, p, \{n_i\}) \quad (32)$$

Equation 30 then yields

$$G = \sum_i n_i \left( \frac{\partial f}{\partial n_i} \right)_{T, p, \{n_j, j \neq i\}} = \sum_i \mu_i n_i \quad (33)$$

which is identical to Eq.24.

## 4 The Gibbs-Duhem equation of process control

The consistency relationships for the general case are derived using the following procedure:

**Step 1.** Identify the independent variables (inputs and disturbances in control).

**Step 2.** Physical assumption: Increasing all the independent *extensive* variables by a factor  $k$  (with the independent *intensive* variables constant) increases all the dependent extensive variables by a factor  $k$  and keeps *all* the dependent intensive variables constant.

**Step 3.** Formulate the physical insight from Step 2 mathematically (Eq.29) and derive the Gibbs-Duhem consistency relationship (Eq.30).

The use of this method is best illustrated by examples as is shown below.

The key idea in Step 2 is that the properties of the system may be maintained when the throughput is increased. This is usually referred to as “scaling” of flows in process design. It is stressed that *all* intensive variables should be kept constant. If there is an intensive variable which will vary (eg., a temperature), then there is a need to introduce an additional extensive variable to keep it constant (eg., a heat duty).

One underlying assumption for Step 2 is that the “efficiency” of the system, which may be viewed as an intensive variable, is unchanged. For example, in the mixing tank example we must assume that the separator efficiency is unchanged when the load is increased. Similarly, for a distillation column we must assume that the tray efficiency remains constant. This assumption is generally satisfied if the data are obtained by simulations using a theoretical model. However, if data are obtained from a real system this may not apply.

If a given set of data does *not* satisfy the fundamental Gibbs Duhem relationships (Eq.30) there are three possibilities:

1. There is something wrong in the physical assumption (Step 2) such that the relation does not apply.
2. The data are inconsistent due to measurement error or numerical errors.



3. The data are inconsistent due to nonlinearity in the process (the change made was too large or the operating point has changed).

Obtaining consistent data from experiments is always very difficult. However, simulations may also yield inconsistent data due to either i) numerical errors if the change is too small, or ii) nonlinearity if the change is too large. The Gibbs-Duhem relationships may be used to evaluate these effects and to decide on a reasonable size for the change.

## 5 Applications

### 5.1 Flash Tank with chemical reaction.

Consider again the flash tank in Fig.1 used in the Introduction, but include also the possibility that the approach to equilibrium (“efficiency”) may vary. We must then include an additional extensive variable which we may adjust to keep the efficiency constant. We make the physical assumption that the efficiency depends on the liquid residence time, that is, on the liquid volume  $V_L$ . This will be the case, for example, if there is a chemical reaction taking place in the liquid phase. We shall use the three-step procedure to obtain consistency relations.

1. Independent variables are  $F, Q, z$  and  $V_L$  (liquid volume), that is, the linear model becomes

$$dy = g_{yF}dF + g_{yQ}dQ + g_{yz}dz + g_{yV_L}dV_L \quad (34)$$

where  $y$  is any dependent variable.

2. Physical assumption: Increasing the extensive variables  $F, Q, V_L$  by the same factor keeps all intensive variables constant.
3. Combining these physical assumptions with Eq.30 (or equivalently, integrate Eq.34 from zero to actual conditions) yields

$$h \cdot y = g_{yF}F + g_{yQ}Q + g_{yV_L}V_L \quad (35)$$

where  $h = 0$  if  $y$  is an intensive variable and  $h = 1$  if  $y$  is an extensive variable.

There are numerous applications of this relationship. For example, if we know the effects  $g_{yF}$  and  $g_{yQ}$  of changes in feed rate and heat input, then we may derive “for free” the effect  $g_{yV_L}$  of a change in liquid volume. To obtain additional insight consider two special cases:

*Case 1.*  $g_{yV_L} = 0$ . This is the case when the liquid residence time has no effect on the steady-state operation, that is, the product streams are in equilibrium. The case when  $y$  is an intensive variable was considered in the Introduction (recall Eq.4). Here, let  $y$  represent the vapor flow  $F_V$  which is an extensive variable. Eq. 35 yields the consistency relationship

$$F_V = \left( \frac{\partial F_V}{\partial F} \right)_{Q,z} F + \left( \frac{\partial F_V}{\partial Q} \right)_{F,z} Q \quad (36)$$

or equivalently in terms of relative changes

$$\left(\frac{\partial F_V/F_V}{\partial F/F}\right)_{Q,z} + \left(\frac{\partial F_V/F_V}{\partial Q/Q}\right)_{F,z} = 1 \quad (37)$$

As a numerical example assume that the first term in Eq.37 is 0.8, that is, a 10% increase in  $F$  increases  $F_V$  by 8% (neglecting nonlinear effects). Eq.37 then tells us that the second term must be 0.2, that is a 10% increase in  $Q$  must increase  $F_V$  by 2%.

*Case 2.*  $Q = 0$ . This is the case with no heat input. Let  $y$  denote an intensive variable, for example, the fractional conversion. Eq.30 yields

$$\left(\frac{\partial y}{\partial F}\right)_{V_L,z} F = - \left(\frac{\partial y}{\partial V_L}\right)_{F,z} V_L \quad (38)$$

In words, this equation tells us that the effect of an increase in the feed rate  $F$  by, say, 1% is equivalent to a decrease in the volume  $V_L$  by 1%. This is of course no surprise since both these changes correspond to a decrease in the residence time  $\tau = V_L/F$  by 1%, and with  $z$  constant we expect  $y$  to depend on  $\tau$  only.

## 5.2 Blending system.

Stephanopolous (1984, p. 502-503) considers the blending system shown in Fig.3. Two streams with flow rates  $F_1 = 133.4$  and  $F_2 = 66.6$  are mixed to form the product stream with flow rate  $F$ . Let  $x_1, x_2$ , and  $x$  represent some property of these streams, eg. density, mole fraction, temperature or pH. With constant values of  $x_1$  and  $x_2$  the linear steady-state model becomes

$$dF = g_{FF_1} dF_1 + g_{FF_2} dF_2 \quad (39)$$

$$dx = g_{xF_1} dF_1 + g_{xF_2} dF_2 \quad (40)$$

Assume we want to use  $F_1$  and  $F_2$  (inputs) to control  $F$  and  $x$  (outputs) using single loops. To decide on the appropriate pairing we shall compute the Relative Gains (Bristol, 1966). The relative gain between  $F$  and  $F_1$  is defined as

$$\lambda_{11} = \frac{(\partial F/\partial F_1)_{F_2}}{(\partial F/\partial F_1)_x} = \frac{g_{11}}{\hat{g}_{11}} \quad (41)$$

which is equivalent to (see Eq.18):

$$\lambda_{11} = \frac{g_{11}}{\hat{g}_{11}} = \left(1 - \frac{g_{FF_2} g_{xF_1}}{g_{FF_1} g_{xF_2}}\right)^{-1} \quad (42)$$

One might expect to need some model of the blending process to evaluate the  $g$ 's and compute the relative gain. For example, Stephanopolous (1984) assumed  $x_1, x_2, x$  to represent mole fractions and used the steady-state material balances

$$F = F_1 + F_2 \quad (43)$$

$$F x = F_1 x_1 + F_2 x_2 \quad (44)$$

to evaluate the relative gain numerically and obtained  $\lambda_{11} = 0.60$ . We shall now use the Gibbs-Duhem consistency relationship to show that the correct value is 0.67. The reason for the error in Stephanopolous is numerical round-off errors. However, more importantly, we shall show that the value of the relative gain is independent of what property  $x$  represents (that is, Eq.44 is not needed). We have

1. Independent variables  $F_1$  and  $F_2$ .
2. Physical assumption: Increasing  $F_1$  and  $F_2$  by the same factor keeps all intensive variables constant.
3. The IGD-relationship (Eq.30) yields

$$F = g_{FF_1} F_1 + g_{FF_2} F_2 \quad (45)$$

$$0 = g_{xF_1} F_1 + g_{xF_2} F_2 \quad (46)$$

Note that these consistency relationships between the gain elements have been derived without using any model of the blending system. However, to evaluate the relative gain we need to assume that the total material balance  $F = F_1 + F_2$  applies. We then have

$$g_{FF_1} = \left( \frac{\partial F}{\partial F_1} \right)_{F_2} = 1; \quad g_{FF_2} = \left( \frac{\partial F}{\partial F_2} \right)_{F_1} = 1 \quad (47)$$

(note that this is consistent with Eq.45). Furthermore, from Eq.46 we have

$$g_{xF_1}/g_{xF_2} = -F_2/F_1 \quad (48)$$

and inserting Eqs.47 and 48 into Eq.42 yields

$$\lambda_{11} = (1 + F_2/F_1)^{-1} = F_1/F = 0.67 \quad (49)$$

The value of the relative gain between  $F_1$  and  $F$  is equal to  $F_1/F$  irrespective of what property  $x$  represents. Consequently, if we use the rule that one should pair variables with relative gains close to 1 (Bristol, 1966), one should always use the largest stream to control the flow rate of the blend and the smallest stream to control the property of the blend. This is certainly consistent with any engineers intuition.

### 5.3 Distillation Column.

Consider the distillation column in Fig.2.

1. Assumption: Independent extensive variables are  $F, L$  and  $V$  where  $F$  is the feed rate,  $L$  is the reflux rate and  $V$  may represent boilup rate, heat input or steam rate (note that  $V$  here is a flow rate (or heat rate) and not a volume). This choice of independent variables is usually called the  $LV$ -configuration or

$LV$ -structure. In addition, there are a number of independent intensive variables  $\underline{\alpha} = (z_F, p, q_F, \dots)$ . The column model is then given by

$$y = y(F, L, V, \underline{\alpha}) \quad (50)$$

The linearized model becomes

$$dy = g_{yF}^{LV} dF + g_{yL}^{LV} dL + g_{yV}^{LV} dV + \sum_i g_{y\alpha_i}^{LV} d\alpha_i \quad (51)$$

where  $y$  may represent, for example, the product flow rates  $D, B$  or the product compositions  $y_D, x_B$ .

2. Physical assumption: Increasing  $F, L$  and  $V$  by the same factor keeps all intensive variables constant.
3. The Gibbs-Duhem consistency relationship Eq.30 yields

$$h \cdot y = g_{yF}^{LV} F + g_{yL}^{LV} L + g_{yV}^{LV} V \quad (52)$$

If  $y$  is an intensive variable, for example, top compositions  $y_D$  then Eq.52 yields

$$g_{y_D F}^{LV} = -g_{y_D L}^{LV} \frac{L}{F} - g_{y_D V}^{LV} \frac{V}{F} \quad (53)$$

or on matrix form for both top and bottom composition

$$\underline{g}_F^{LV} = \begin{pmatrix} g_{y_D F}^{LV} \\ g_{x_B F}^{LV} \end{pmatrix} = -G^{LV} \begin{pmatrix} L/F \\ V/F \end{pmatrix} \quad (54)$$

where  $G^{LV}$  is the steady-state gain matrix

$$= G^{LV} = \begin{pmatrix} g_{y_D L}^{LV} & g_{y_D V}^{LV} \\ g_{x_B L}^{LV} & g_{x_B V}^{LV} \end{pmatrix} \quad (55)$$

This interesting result tells us that we may compute the effect of a change in feed rate, if we know the effects of changes in reflux and boilup. The result may seem trivial, but in fact seems to be unknown in the literature. The following example shows that published data for the much quoted Wood and Berry column does not satisfy these consistency relationships.

### 5.3.1 Numerical examples

Wood and Berry column example. From pulse testing of an experimental column separating methanol and water, Wood and Berry (1973) obtained the following gain data

$$G^{LV} = \begin{pmatrix} 12.8 & -18.9 \\ 6.6 & -19.4 \end{pmatrix} \quad (56)$$

Here  $y_D$  and  $x_B$  represent wt.% methanol in the products,  $L$  is the reflux rate, and  $V$  is the steam rate to the reboiler. Data for compositions and flows at the nominal

operation point are given in Table 1. Note that all the flows are in mass units. This means that although the assumption of constant molar flows applies quite well to the methanol-water system, the mass flows will vary through the column due to variations in mole weight. The reflux is not saturated, but is heated to a constant temperature, which may be viewed as an additional independent variable. However, since this is an *intensive* variable, Eq.54 still applies and we may use it to estimate the gains for a change in feed rate

$$\underline{g}_F^{LV} = - \begin{pmatrix} 12.8 & -18.9 \\ 6.6 & -19.4 \end{pmatrix} \begin{pmatrix} 1.95/2.45 \\ 1.71/2.45 \end{pmatrix} = \begin{pmatrix} 3.0 \\ 8.3 \end{pmatrix} \quad (57)$$

These values should be compared with experimental gains for the column reported by Ogunnaike and Ray (1979)

$$\underline{g}_F^{LV}{}_{exp} = \begin{pmatrix} 3.8 \\ 4.9 \end{pmatrix} \quad (58)$$

We see that the feed gain for  $y_D$  is reasonably consistent, but the one for  $x_B$  is not.

Simulation of Wood and Berry column. Tray-by-tray simulations using the data in Table 1 gave an almost exact match to the published steady-state data of Wood and Berry. Tray temperatures were consistently about 1.5°C higher than reported, but otherwise matched the experimental profile. The results were obtained using 8 theoretical stages, the UNIQUAC equation to describe the non-ideal vapor-liquid equilibrium, and assuming the enthalpy contents of the steam to be 2150 kJ/kg. Steady-state gains were obtained numerically by making increases in the independent variables  $L$ ,  $V$  and  $F$  of magnitudes 0.1% and 1.0%, respectively. The results are summarized in Table 2 and 3. The numerical values of the gains are different from those published by Wood and Berry, but the differences are not larger than may be expected taking into account experimental error, changes in operating point, nonlinearity and the fact that the experimental data was fitted to a simplified model.

The issue of nonlinearity becomes evident when comparing Tables 2 and 3. Although the individual gains are not too different in the two cases, we note that whereas the feed gains computed from small changes in flows (Table 2) are reasonably consistent, the ones based on large changes are not. In the first case with 0.1% flow increases, the changes in compositions are only on the order 0.01 to 0.06 wt.% and numerical inaccuracies may easily occur when evaluating the gains. In the second case with 1.0% flow increases, the changes in compositions are in the order 0.1 to 0.7 wt.%, and the results clearly show that nonlinearities cause inconsistency in the data. For example, for a 1% increase in feed rate the numerical value of  $g_{x_B F}$  was found to be 4.13, whereas the value obtained from the consistency relationship using the gain matrix was only 0.64. Note that the gain data in Tables 2 and 3 are obtained from a simulation model where the physical assumptions for the consistency relationship hold exactly.

Another striking difference is that the relative gain for the two cases is 9.1 and -2.0, respectively. The last value is obviously in error since it may be shown that the relative gain for the LV-configuration should always be larger than 1 (Skogestad et al., 1989). For comparison, the relative gain of the experimental gain matrix (Eq.56) is 2.0.

The results in Table 1 and 2 clearly illustrate the difficulties in obtaining consistent steady-state gains for distillation columns even when using an accurate simulation

program. The results may be improved, for example, by using two-sided difference approximations or by evaluating the gains with  $D$  constant (to get a good estimate of the effect of internal flow changes; Skogestad, 1988). Of course, the difficulties in obtaining consistent gains from experiments are even larger, and the inconsistencies in the experimental gains found between Eqs.57 and 58 above is hardly surprising.

Waller et al. example. From experiments on a 15 stage pilot plant column separating ethanol and water Waller et al. (1988) obtained the following gains

$$\begin{pmatrix} dT_4 \\ dT_{14} \end{pmatrix} = \begin{pmatrix} -0.045 & 0.048 \\ -0.23 & 0.55 \end{pmatrix} \begin{pmatrix} dL \\ dV \end{pmatrix} + \begin{pmatrix} -0.001 \\ -0.16 \end{pmatrix} dF \quad (59)$$

where  $T_4$  and  $T_{14}$  are temperatures at selected trays in the column and  $V$  is the steam flow to the reboiler. The nominal flow rates in kg/h are  $F = 200$ ,  $L=60$  and  $V = 72$ . Reflux temperature is assumed constant. The gains were reconciled to satisfy the material balance consistency relationships (similar to Eq.20) but they do not satisfy the Gibbs-Duhem consistency relationships: Using Eq.54 we derive

$$\underline{g}_F = \begin{pmatrix} 0.045 \cdot 60/200 - 0.048 \cdot 72/200 \\ 0.23 \cdot 60/200 - 0.55 \cdot 72/200 \end{pmatrix} = \begin{pmatrix} -0.004 \\ -0.13 \end{pmatrix} \quad (60)$$

which is somewhat different from the reported values of  $\begin{pmatrix} -0.001 \\ -0.16 \end{pmatrix}$ .

### 5.3.2 Some extensions

Unsaturated reflux. If the reflux temperature is not at its saturated value but, may vary due to subcooling then the overall cooling duty  $Q_D$  is no longer a dependent variable. It must then be added as a independent variable and the independent extensive variables become  $F, L, V$  and  $Q_D$ . In this case an additional term  $g_{yQ_D} Q_D$  must be added to Eq.52 and the other gains must be evaluated with  $Q_D$  constant. However, if the reflux temperature is kept constant (even though it may be subcooled) then Eq.52 holds as dicussed in the Wood and Berry example above.

More complex columns. If the column has a side stream (flow rate  $S$ ) or an intermediate cooler (duty  $Q_S$ ) then  $S$  and  $Q_S$  must be added as an independent extensive variable, and Eq.52 must be changed accordingly by adding the terms  $g_{yS} S + g_{yQ_S} Q_S$ .

Other control configurations. Depending on the control configuration a lot of other options for independent variables exist. For example, if  $L$  is used for level control then independent variables are  $F, D$  and  $V$  (DV configuration), and a relationship similar to Eq.52 is derived:

$$h \cdot y = g_{yF}^{DV} F + g_{yD}^{DV} D + g_{yV}^{DV} V \quad (61)$$

Another configuration that is proposed as a good choice for many columns is the  $RS$ -configuration with  $F, R = L/D$  and  $S = V/B$  as independent variables. Since  $R$  and  $S$  are intensive variables the consistency relationship becomes

$$h \cdot y = g_{yF}^{RS} F \quad (62)$$

For example, if  $y$  represents top composition, then Eq.62 says that  $\left(\frac{\partial y_D}{\partial F}\right)_{R,S} = 0$ . This results simply says that product compositions are not affected by changes in feed rate provided all flow ratios are kept constant. If  $y = D$  then Eq.62 tells that  $D = \left(\frac{\partial D}{\partial F}\right)_{R,S} F$  which hardly is a surprising result.

Compositions as independent variables. This may be the case, for example, if  $L$  is used to control  $y_D$  such that  $y_D$  may be viewed as an independent variable instead of  $L$ . The IGD equation becomes

$$h \cdot y = \left(\frac{\partial y}{\partial F}\right)_{y_D, V} F + \left(\frac{\partial y}{\partial V}\right)_{y_D, F} V \quad (63)$$

Note that Eqs.61-63 alternatively could have been derived from Eq.52 by using variable transformations of the kind discussed in Section 2.3.

## 6 Conclusion

It has been shown that Eulers equation

$$h \cdot y = \left(\frac{\partial y}{\partial c}\right)_{d, a, b} c + \left(\frac{\partial y}{\partial d}\right)_{c, a, b} d \quad (30)$$

may be used to check consistency of steady-state models. Its derivation is related to that of the Gibbs-Duhem equation of thermodynamics and is based on using physical insight to identify the independent extensive variables.

The relationship is exact, but of course limited to cases where the physical assumption applies. A typical situation where the relationships do not apply is when the efficiency of the system is varying, for example, for a distillation column operating close to flooding conditions. In this case it is possible to include additional extensive variables, for example the column diameter, which may be adjusted to keep the efficiency constant. However, the usefulness of the consistency relationships may be somewhat limited in this case.

## 7 Nomenclature

$g_{y_i u_j} = g_{y_i u_j}^{u_k} = g_{ij} = \left(\frac{\partial y_i}{\partial u_j}\right)_{u_k \neq j}$  - steady state gain (effect of small change in  $u_j$  on  $y_i$ )

$h$  - integer variable which is 0 if  $y$  is intensive and 1 if  $y$  is extensive

$u$  - independent variable

$y$  - dependent variable

$\lambda_{ij} = \frac{(\partial y_i / \partial u_j)_{u_k \neq j}}{(\partial y_i / \partial u_j)_{u_k \neq i}}$  - relative gain between variables  $y_i$  and  $u_j$ .

## 8 References

- Bristol, E.H., 1966, "On a new measure of interactions for multivariable process control", *IEEE Trans. Automat. Control*, **AC-11**, 133-134.
- Callen, H. B., 1960, *Thermodynamics*, Wiley, New York.
- Hägglom, K.E. and K.V. Waller, 1988, "Transformations and consistency relations of distillation control structures", *AIChE Journal*, **34**, 10, 1634-1648.
- Mijares, G., C.D. Holland, R. McDaniel, C.R. Dollar and S.E. Gallun, 1985, "Analysis and evaluation of the relative gains for nonlinear systems", *Computers & Chemical Engineering*, **9**, 1, 61-70.
- Modell, M. and R.C. Reid, 1983, *Thermodynamics and its applications*, 2nd Edition, Prentice-Hall, Englewood Cliffs, NJ.
- Ogunnaike, B.A. and W.H. Ray, 1979, "Multivariable controller design for linear systems having multiple time delays", *AIChE Journal*, **25**, 6, 1043-1057.
- Skogestad, S. and M. Morari, 1987, "A systematic approach to distillation column control", *I. Chem. E. Symposium Series*, bf 104, A71-A86.
- Skogestad, S., 1988, "Disturbance rejection in distillation columns", *Preprints CHEM-DATA 88*, 19th European Conf. On The Use of Computers in Chem. Eng., Göteborg, Sweden, June 1988.
- Skogestad, S., E.W. Jacobsen and P. Lundström, 1989, "Modelling requirements for robust control of distillation columns", Submitted to *Chem. Eng. Sci.*
- Stephanopoulos, G., 1984, *Chemical process control*, Prentice-Hall, New York.
- Waller, K.V, K.E. Hägglom, P.M. Sandelin and D.H. Finnerman, 1988, "Disturbance sensitivity of distillation control structures", *AIChE Journal*, **34**, 5, 853-858.
- Wood, R.K. and M.W. Berry, 1973, "Terminal composition control of a binary distillation column", *Chem. Eng. Sci.*, **28**, 1707-1717.



**Table 1.** Data for simulation of Wood and Berry distillation column.

System	Methanol-Water
UNIQUAC parameters	-301.6449, 498.5938
Pressure (atm)	1.0
No. of theoretical stages, $N$	8
Feed stage, $N_F$ (1 is reboiler)	4
Feed composition, $z_F$ (wt.%)	46.5
Top composition, $y_D$ (wt.%)	96.0
Btm composition, $x_B$ (wt.%)	0.5
Feed rate, $F$ (mass/time)	2.45
Distillate, $D$ (mass/time)	1.18
Bottom product, $B$ (mass/time)	1.27
Reflux, $L$ (mass/time)	1.95
Steam @ 2150 kJ/kg, $V$ (mass/time)	1.71
Feed: Liquid	

**Table 2.** Gains obtained numerically by 0.1% increase in  $L$ ,  $V$  and  $F$ .

$$G^{LV} = \begin{pmatrix} 20.20 & -37.51 \\ 4.92 & -10.26 \end{pmatrix}$$

$$g_F^{LV} = \begin{pmatrix} 10.10 \\ 3.25 \end{pmatrix}$$

Relative gain:

$$\lambda_{11}(G^{LV}) = 9.1$$

Check of feed gain using consistency relationship Eq.54:

$$g_F^{LV} = -G^{LV} \begin{pmatrix} L/F \\ V/F \end{pmatrix} = \begin{pmatrix} 9.79 \\ 3.42 \end{pmatrix}$$

**Table 3.** Gains obtained numerically by 1.0% increase in  $L$ ,  $V$  and  $F$ .

$$G^{LV} = \begin{pmatrix} 19.77 & -38.32 \\ 5.99 & -7.75 \end{pmatrix}$$

$$g_F^{LV} = \begin{pmatrix} 9.72 \\ 4.13 \end{pmatrix}$$

Relative gain:

$$\lambda_{11}(G^{LV}) = -2.0$$

Check of feed gain using consistency relationship Eq.54:

$$g_F^{LV} = -G^{LV} \begin{pmatrix} L/F \\ V/F \end{pmatrix} = \begin{pmatrix} 11.02 \\ 0.64 \end{pmatrix}$$