On the Andrecovich and Westerberg Box Display

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The issue of how best to integrate distillation columns into processes so that reboiler heat may be supplied with minimum import of energy has interested many workers over the years. Andrecovich and Westerberg's (1985a, b, c) computations for mixtures that are ideal, or nearly so, revealed that the temperature difference across the column, ΔT, and the reboiler or condenser duty, Q, increase with increase in column pressure and hence temperature. However, although they observed that each quantity varies linearly with temperature, they also observed that the variation is often so slight that each may be taken as independent of temperature, to a useful first approximation. This lesson was then incorporated into synthesis strategies. In particular, it proved useful to represent a column by a rectangular box, on a plot of temperature vs. heat flow (or enthalpy), so that the possibility of column integration might be assessed: the dimensions of the box are taken to be independent of its whereabouts on the plot. This idea was taken up by Hindmarsh and Townsend (1984), who demonstrated the advantage of combining the box display with a background process grand composite curve (Linnhoff and Townsend, 1983). Their case studies showed clearly the power of the box display when applied to industrial problems.

The purpose of this note is to use simple, approximate analyses to shed light on Andrecovich and Westerberg's powerful observations.

Analysis for ΔT

We begin by integrating the Clausius-Clapeyron equation for vapor-liquid equilibrium under the usual simplifying assumptions:

a. The liquid molar volume is negligible compared to the vapor molar volume

b. The vapor is ideal

c. The latent heat of evaporation of component i, ΔH_i, is independent of temperature

The result, the Clapeyron equation, is here written as

$$\ln p_i^* = \frac{\Delta S_i}{R} - \frac{\Delta H_i}{R}\frac{1}{T} \tag{1}$$

where ΔH_i, being by assumption independent of temperature, is taken to be equal to its value at the normal boiling point. It will be recalled that although assumption (c) is usually not very accurate, compensating changes in the temperature dependence of the difference between the vapor and liquid compressibilities result in Eq. 1 being usefully accurate (Reid and Sherwood, 1958). We also invoke Trouton's rule for nonpolar components,

$$\Delta S_i = 88\ \text{J/mol} \cdot \text{K, all } i \tag{2}$$

Consider a binary distillation column producing high-purity products that has an internal pressure drop which is small compared to the total pressure. Then, letting 1 denote the more volatile component (MVC)

$$\ln P \approx \ln p_1^*(T_{CO}) = \frac{\Delta S_1}{R} - \frac{T_{b1}\Delta S_1}{R}\frac{1}{T_{CO}} \tag{3}$$

$$\ln P \approx \ln p_2^*(T_{RE}) = \frac{\Delta S_1}{R} - \frac{T_{b2}\Delta S_1}{R}\frac{1}{T_{RE}} \tag{4}$$

Subtracting and rearranging,

$$T_{RE} - T_{CO} = \Delta T = T_{CO}\frac{\Delta T_b}{T_{b1}} \tag{5}$$

That is, the temperature difference across the column is directly proportional to the condenser temperature, the proportionally constant being the difference in the pure-component normal boiling points divided by the normal boiling point of the MVC.

This is a special case of the linearity observed by Andrecovich and Westerberg for multicomponent mixtures, showing that their result is thermodynamically well-based.

Equation 5 also supports their observation that ΔT is fairly insensitive to T_{CO}: first we deduce from Eq. 5 that

$$\delta\Delta T = \frac{\Delta T_b}{T_{b1}} \delta T_{CO} \tag{6}$$

and then we consider two particular cases:

- Toluene/cycloheptane, with $(\Delta T_b, T_{b1}) = (8.1, 383.8)$
- Benzene/toluene, with $(\Delta T_b, T_{b1}) = (30.1, 353.7)$

Then for $\delta T_{CO} = 40$ K, $\delta\Delta T$ equals 0.84 and 3.4 K, respectively, both of which are less than 10% of the ΔT calculated from Eq. 5 with $T_{CO} = 410$ K, which are 8.7 and 34.9 K.

Moreover, Eq. 6 may be useful for multicomponent distillations: for the two splits of the ternary mixture benzene (60%)/toluene (30%)/cycloheptane (10%), the values $\delta\Delta T = 0.84$ and 3.4 K for $\delta T_{CO} = 40$ K in the neighborhood of $T_{CO} = 410$ K agree well with the values read from Figure 2 of Andrecovich and Westerberg (1985b).

Analysis for *Q*

Here we begin by assuming ideality so that

$$\ln \alpha = \ln p_1^* - \ln p_2^* \tag{7}$$

Substitution of Eqs. 2–4 then yields a familiar expression for the relative volatility as a function of temperature

$$\ln \alpha = 10.6 \frac{\Delta T_b}{T} \tag{8}$$

If the assumptions of the McCabe-Thiele method are satisfied and the column operates close to its minimum reflux ratio, then for a bubble-point feed (Paterson, 1987)

$$Q = (R_m + 1) z \Delta H = \left[\frac{1}{(\alpha - 1) z} + 1\right] z \Delta H \tag{9}$$

If we further assume that the two components are close-boiling, so that $\alpha - 1 \ll 1$, then, as is well known, a Taylor series yields $\ln \alpha = \ln [1 + (\alpha - 1)] \approx (\alpha - 1)$, so that Eq. 9 becomes

$$Q \approx \Delta H \left(\frac{T}{10.6\, \Delta T_b} + z\right) \tag{10}$$

At first sight, we here have the Andrecovich and Westerberg result, since Q appears to be linear in T and a sample calculation with, say, $z = 0.5$, $\Delta T_b = 8.1$ K, $T = 410$ K, shows that a δT of 40 K increases Q by 9.2%; again, a change smaller than 10%. However, *this* interpretation neglects the decline of ΔH with increase in T. To allow for this, we ought strictly to abandon the Clapeyron equation, deduced on the assumption of a constant ΔH. However, as explained above, the formal requirement of a constant ΔH is largely illusory, so that it becomes a legitimate approximation to accept Eq. 10 and consider the variation of ΔH within it.

A convenient tool is the Watson (1943) equation relating the values of ΔH at two different reduced temepratures,

$$\Delta H^{(2)} = \Delta H^{(1)} \left[\frac{1 - T_r^{(2)}}{1 - T_r^{(1)}}\right]^{0.38}, \tag{11}$$

which manipulates to the convenient form

$$\frac{\delta \Delta H}{\Delta H} = -0.38 \frac{1}{T_c - T} \delta T. \tag{12}$$

As a sample calculation, we consider toluene ($T_c = 591.7$ K) at around 410 K with $\delta T = 40$ K, and find that ΔH declines by about 8.4%. This clearly cancels most of the rise in Q calculated above, confirming that the dependence of Q on T is indeed small.

We now see why Q is approximately independent of T: the effect of declining ΔH with increasing T largely nullifies the effect of increasing reflux ratio. Moreover, it is a commonplace of applied mathematics that if one variable is a mild and continuous function of a second variable, then the relationship may be approximated as linear for many practical purposes. This is the justification for Andrecovich and Westerberg to take Q as linear in T.

Remark

Hindmarsh and Townsend (1984) emphasize that a change in operating temperature will not move a column design into a new capital cost regime if the column pressure remains in the range 1–10 bar. An explicit approximate expression for a new pressure $P^{(2)}$ as a function of temperature may therefore be useful. From Eqs. 1 and 2 there follows

$$\ln P^{(2)} = 10.6 \left[1 - \frac{T_{CO}^{(1)}}{T_{CO}^{(2)}}\right] + \frac{T_{CO}^{(1)}}{T_{CO}^{(2)}} \ln P^{(1)} \tag{13}$$

Equation 13 offers useful accuracy even for multicomponent problems: in the example problem of Hindmarsh and Townsend, columns 2 and 4 are to have their condenser temperatures raised from 371 and 406 K, respectively, to 395 and 421 K, to permit integration with the reboilers of columns 1 and 3. Equation 13 predicts that the pressures of columns 2 and 4 will then increase from their initial values of 1.4 bar to new values of 2.6 and 2.0 bar, respectively. The corresponding values reported by Hindmarsh and Townsend are 2.7 and 2.1 bar; agreement is sufficiently good to suggest that Eq. 13 will be useful for checking for a change of cost regime.

Conclusions

Simple analyses of (binary) distillation support and illuminate the approximations summarized from computational experience by Andrecovich and Westerberg.

Notation

ΔH = enthalpy of evaporation
P = pressure
p^* = saturated vapor pressure
Q = reboiler or condenser duty
R = gas constant

R_m = minimum reflux ratio
ΔS = entropy of evaporation at T_b
T = absolute temperature
ΔT = column temperature difference
T_b = normal boiling point
ΔT_b = difference in normal boiling points
T_c = critical temperature
T_{CO} = condenser temperature
T_r = reduced temperature, = T/T_c
T_{RE} = reboiler temperature
z = mole fraction of MVC in column feed
α = relative volatility
δ = small change in

Subscripts

$i, 1, 2$ = component number

Superscripts

$(1), (2)$ = at two different conditions

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