ENERGETIC INTERPRETATION OF DISTILLATION BASED ON
NON-EQUILIBRIUM THERMODYNAMICS

Z. FONYÓ

(Polytechnical University, Department of Chemical
Engineering, Budapest)

Distillation is dealt with as a steady state
system of the first degree. The energetic aim in dis-
tillation is that the entropy produced by the heat
transport is utilized as completely as possible by the
entropy consumption of the component separation. Ex-
pressions are given for the entropy production of the
heat transport emerging at distillation in both the
reversible and the real cases. In conclusion, the
thermodynamic interpretation of the driving force, ef-
ficiency and dynamic behaviour of distillation is in-
dicated.

INTRODUCTION

The first comprehensive thermodynamic analysis of distilla-
tion is due to PLATONOV and co-workers [1, 2, 3, 4, 5, 6]. Their
papers deal with the energetic improvement of distillation. The
possibilities of the thermodynamic expression for the driving
force and the dynamical characteristics (efficiency) of distilla-
tion were pointed out by KAFAROV and VIGDOROV [7, 8, 9]. In addi-
tion, the general work of SZOLCSÁNYI on the energetics of separa-
tion processes predominates, explaining the theory of steady sys-
tems of the first degree and enabling the energetic interpretation

of the coupled processes by treating the entropy consuming and entropy producing processes separately [10, 11, 12].

The aim of the present paper is the <u>uniform energetic inter-</u> <u>pretation of distillation</u> based on non-equilibrium thermodynamics, that may in the future be of assistance in the energetic improvement of this operation, i.e. in the practical implementation of the principles that could be initiated from thermodynamic considerations. During the development of the principles given in this paper the works of HASELDEN [13], TIMMERS [15], PRATT [16], FRATSCHER [14], KING [17] and STUPIN [18] published in this field were used, in addition to those mentioned earlier.

DISTILLATION COLUMN AS A FIRST DEGREE STEADY SYSTEM

Although the linearity of the integral expressions for the transfer processes is questionable in the irreversible thermodynamics, the linearity of the phenomenological equations will be assumed in the mathematical treatment. This proved to be appropriate, and it was possible to interpret the empirical data by the relationships that were derived. In general the entropy source density in this theory is:

$$\phi = \bar{\bar{L}}_{jk}' \bar{\bar{X}}_k : \bar{\bar{X}}_j \tag{1}$$

Disregarding the relaxation processes, the function of entropy source density of a steady system with two variables, which is of the first degree with regard to flux 1 is

$$\frac{\partial \phi}{\partial X_2} = (L_{12}' + L_{21}')X_1 + 2 L_{22}'X_2 = 0 \tag{2}$$

at the local minimum

$$\phi = L_{11}' X_1^2 [1 - \frac{(L_{12}' + L_{21}')}{4\ L_{11}L_{22}}] = L_{11}' X_1^2 (1 - p^2) \tag{3}$$

where p is the coupling factor, i.e. the degree of the coupling of the entropy processes.

In the case of distillation, the heat flow is flux 1, maintained by an X_1 driving force of constant value due to an external force, and flux 2 is the resulting transfer component flow, which is extinguished because of the ONSAGER relations [19]. In the present case, the entropy produced by the heat transport of the column is decreased by the entropy consuming process of the component separation. The range of the coupling factor is

$$0 \le p \le 1 \tag{4}$$

It is clear that at p = 0 the system is completely irreversible, since $\phi = L_{11} X_1^2$ i.e. only the entropy producing process takes place. If p = 1, ϕ = 0 i.e. the system is reversible, the entropy produced by the heat flow is completely consumed by the entropy consuming process of the component separation.

With respect to energetics in the case of distillation, it should be ensured that the <u>entropy produced by the heat transport</u> <u>be utilized as completely as possible by the entropy consumption</u> <u>of the component separation</u>.

ENTROPY PRODUCTION OF HEAT TRANSPORT

Reversible Rectification

The realization of reversible distillation is well known [1, 2, 20, 21, 22, 23, 24], and will not be dealt with here.

The driving force of the heat flow is the change in the reciprocal of the temperature. From RAOULT's law and the CLAUSIUS--CLAPEYRON Equation can be derived:

$$P = \sum_i \bar{p}_i x_i$$

$$\frac{dP}{dT} = \sum_i \bar{p}_i \frac{dx_i}{dT} + \sum_i x_i \frac{d\bar{p}_i}{dT} = 0 \quad (p = const.) \tag{5}$$

$$\frac{dp_i}{dT} = \frac{x_i \bar{p}_i}{RT^2} \; (V_x = 0; \; V_y = \frac{RT}{\bar{p}_i}) \; (i = 1, 2, \ldots n) \tag{6}$$

Assuming identical latent heats, Equations (5) and (6) and the $\sum_i dx_i = 0$ relation give the driving force of the heat flow:

$$d(\frac{1}{T}) = \frac{R}{\lambda} \sum_i (K_i - 1) \; dx_i \tag{7}$$

Assuming equilibrium at each level of the column, the component and mass balances give the vapour stream in the rectification zone as

$$V = \frac{1}{K_i - 1} (\frac{x_{iD}}{x_i} - 1) \; D \quad (i = 1, 2, \ldots n) \tag{8}$$

Similarly the vapour stream in the stripping zone is

$$V' = \frac{1}{K_i - 1} (1 - \frac{x_{iB}}{x_i}) \; B \quad (i = 1, 2, \ldots n) \tag{9}$$

(The values of V and V' can be given for any component and since $K_i = K_i(T,p,x)$, its value changes along the height of the column.) The entropy production of the heat transport for the full height of the column (flux x driving force) is

$$\phi_Q = \int_{x_{iB}}^{x_{iD}} I_Q \; d(\frac{1}{T}) = \int_{x_{iF}}^{x_{iD}} V\lambda d(\frac{1}{T}) + \int_{x_{iB}}^{x_{iF}} V'\lambda d(\frac{1}{T}) \tag{10}$$

or by substituting Equations (7), (8), (9)

$$Q = RD \sum_i \int_{x_{iF}}^{x_{iD}} (\frac{x_{iD}}{x_i} - 1) \, dx_i + RB \sum_i \int_{x_{iB}}^{x_{iF}} (1 - \frac{x_{iB}}{x_i}) dx_i$$

$$\phi_Q = R(D \sum_{i=1}^{n} x_{iD} \ln x_{iD} + B \sum_{i=1}^{n} x_{iB} \ln x_{iB} - F \sum_{i=1}^{n} x_{iF} \ln x_{iF}) \quad (11)$$

Since the entropy production of the heat transport given by Equation 11 is equal to the entropy consumption in an isotherm--isobar separation of a mixture, known from thermodynamics (entropy of mixing) [19], but with an opposite sign, so the overall entropy source density is zero:

$$\phi = \phi_Q + \phi_c = 0 \quad (12)$$

and the coupling factor $p = 1$.

Adiabatic Rectification

Supposing a constant molar overflow, the entropy production of the heat transport under adiabatic circumstances is

$$\phi_Q = \frac{(R + 1) \, D\lambda T_B - [(R + 1) \, D + (q - 1) \, F]\lambda T_D}{T_D \, T_B} \quad (13)$$

It can be shown that under adiabatic circumstances, the entropy production is greater than in the reversible case even at the R_{min} value, i.e. in a column of infinite dimensions (11), since the vapour stream along the entire height of the column is equal to the minimum value of the vapour stream of the "greatest value". The over-all entropy source density is:

$$\phi = \phi_Q + \phi_c > 0 \quad (14)$$

and the coupling factor:

$$0 < |p| < 1$$

Squared Off Cascade, Thermally Coupled Distillation System

        In the case of reversible rectification with the complete
elimination of the heavy key component in the enriching section,
the internal reflux ratio at level h (m^{th} plate) of the column is:

$$\left(\frac{L}{V}\right)_m = R_h = \frac{V_m - D}{V_m} = 1 - \frac{D}{V_m} \tag{15}$$

Since the value of the equilibrium ratio generally diminishes
upward in the column, $\frac{dR_h}{dm}$ is positive if the plates are numbered
from the top down to the bottom:

$$\frac{d\left(\frac{L}{V}\right)}{dm} = \frac{D}{V_m^2}\frac{dV}{dm} = \frac{dR_h}{dm} > 0 \tag{16}$$

D and V are positive, so (dV/dm) must also be positive, thus the
vapour stream must grow downward in the column, that means a gra-
dual heat withdrawal along the enriching section. By a similar
treatment it can be shown that for the realization of a reversible
rectification, a gradual addition of heat is necessary in the
stripping section.

        The gradual addition and withdrawal of heat are carried out
in practice by using squared off cascades [16, 25,27] or thermally
coupled distillation systems [1, 3, 26, 27]. In these systems the
entropy production of the heat transport in rectification is less
than in the usual adiabatic case,its value, however, cannot attain
the value calculated by Equation (11), since the establishment of
a reversible rectification requires other conditions too [24] (for
instance infinite column sizes, first degree rectification, and a
zero pressure drop, etc.). The value of the coupling factor is
here:

$$0 < |p| < 1$$

(If p = 0, i.e. only heat transport takes place and there is no
component separation and there is no rectification.)

GENERAL THERMODYNAMIC EXPRESSION FOR THE DRIVING FORCE

In thermodynamics the number of transfer units can be defined in general as follows:

$$N_{term} \simeq \int_0^{L_N} \frac{dL_h}{-L_h^*} = \int_0^{S_{ch}} \frac{dS_{ch}}{-S_{ch}^*} \tag{17}$$

(Only the entropy consuming processes are dealt with.)

$$dS_{ch} = \sum_i y_{iD} \, d\left(\frac{G_{ih}}{T}\right) = R \sum_i y_{iD} \, d \ln y_{ih}^g$$

$$S_{ch}^* = \sum_i y_{iD} \left(\frac{G_{ih}^f}{T_h^f} - \frac{G_{ih}^g}{T_h^g}\right) = R \sum_i y_{iD} \ln \frac{y_{ih}^f}{y_{ih}^g} \tag{18}$$

(The above inequalities are strictly valid only under small or moderate pressures, in general fugacities should be written instead of mole fractions in the above relations.)

Substituting, the number of thermodynamic transfer units in the enriching section is:

$$N_{term} = \int_{y_{io}}^{y_{ih}} \frac{\sum_i y_{iD} \, d \ln y_{ih}}{\sum_i y_{iD} \ln \frac{y_{ih}^*}{y_{ih}}} \tag{19}$$

where y_{ih}^* is the equilibrium concentration calculated from the other phase. For the upper part of the column when the pure most volatile component is the overhead product:

$$\lim_{\substack{y_{BD} \to 0 \\ y_{CD} \to 0}} (N_{term}) = \int_{y_{Ao}}^{y_{Ah}} \frac{y_{AD} \, d \ln y_{Ah}}{y_{Ad} \ln \frac{y_{Ah}^*}{y_{Ah}}} = \int_{y_{Ao}}^{y_{Ah}} \frac{d \ln y_{Ah}}{\ln \frac{y_{Ah}^*}{y_{Ah}}} \tag{20}$$

But in this case $y_{Ah}^* - y_{Ah} = \Delta^*$ approaches zero, so Eq. (20) turns into the number of diffusional transfer units as expressed by CHILTON and COLBURN:

$$\lim_{\substack{y_{BD} \to 0, \Delta^* \to 0 \\ y_{CD} \to 0, \\ \vdots}} (N_{term}) = \int_{y_{Ao}}^{y_{Ah}} \frac{dy_{Ah}}{y_{Ah} \ln \left(1 + \frac{\Delta^*}{y_{Ah}}\right)} = \int_{y_{Ao}}^{y_{Ah}} \frac{dy_{Ah}}{y_{Ah}^* - y_{Ah}} = NTU \tag{21}$$

using the relationship:

$$\lim_{\Delta^* \to 0} \left[\ln \left(1 + \frac{\Delta^*}{y_{Ah}}\right) \right] = \frac{\Delta^*}{y_{Ah}}.$$

THERMODYNAMIC PLATE EFFICIENCY

If a rectification column is analyzed using the concept of the equilibrium stage, the thermodynamic plate efficiency, similarly to the above derivation, is

$$n_{term} = \frac{L_N}{L_N^*} = \frac{\sum_i y_{iD} \ln \frac{y_{iN}}{y_{i(N+1)}}}{\sum_i y_{iD} \ln \frac{y_{iN}^*}{y_{i(N+1)}}} \tag{22}$$

the n_{term} turns into the MURPHREE plate efficiency if pure component A is obtained in the enriching section, and $\Delta^* \to 0$, $\Delta \to 0$:

$$\lim_{\substack{\Delta^* \to 0 \ y_{BD} \to 0 \\ \Delta \to 0 \ y_{CD} \to 0 \\ \vdots}} (n_{term}) = \frac{y_{AD} \ln \frac{y_{AN}}{y_{A(N+1)}}}{y_{AD} \ln \frac{y_{AN}^*}{y_{A(N+1)}}} = \frac{y_{AN} - y_{A(N+1)}}{y_{AN}^* - y_{A(N+1)}} = n_M \tag{23}$$

The analysis of the entropy producing process of the heat transport yields the thermal plate efficiency defined by STANDART [30]:

$$\eta_{\text{term}}^{\text{St}} = \frac{L_N'}{L_N'^*} = \frac{V_N H_N - V_{N+1} H_{N+1} + r_N Q_N}{V_N^* H_N^* - V_{N+1} H_{N+1} + r_N Q_N} \tag{24}$$

The expressions of the number of transfer units and plate efficiency in the stripping section can be interpreted thermodynamically in a similar way.

ANALYSIS OF THE DYNAMIC BEHAVIOUR

A new method of analysis of dynamic behaviour is the analysis of the entropy production. The GLANSDORF-PRIGOGINE principle [28] can also be verified for discontinuous systems [29] (transfer model). According to this theorem, the production of entropy is at minimum in steady state which is stable with respect to internal changes. Since perturbations are moderated by time, the entropy production decreases approaching the steady state:

$$\frac{d\phi}{dt} \leq 0 \tag{25}$$

For instance, assuming a disturbance of the steady state in rectification caused by a change in the concentration difference (X_2') while the temperature difference is kept at a constant value $(X_1 = \text{const.})$:

$$X_2' \longrightarrow X_2 = X_2' + \delta X_2 \tag{26}$$

the I_2 stream is

$$I_2 = L_{21} X_1 + L_{22} X_2 = L_{21} X_1 + L_{22} X_2' + L_{22} \delta X_2 = I_2' + L_{22} \delta X_2$$

Since in steady state $I_2' = 0$

$$I_2 = L_{22} \delta X_2 \tag{27}$$

and the diagonal elements of the matrix of the transport coefficients are positive $(L_{22} > 0)$,

$$I_2 = L_{22} \delta X_2 > 0 \tag{28}$$

so the δX_2 change in the driving force and the I_2 stream caused by δX_2 are of the same sign.

The entropy production is

$$\phi = L_{11}X_1^2 + 2\ L_{12}X_1(X_2' + \delta X_2) + L_{22}(X_2' + \delta X_2)^2 =$$

$$= \phi_{min}' + 2\ I_2' + L_{22}(\delta X_2)^2 = \phi_{min}' + L_{22}(\delta X_2)^2 \qquad (29)$$

and

$$L_{22}(\delta X_2)^2 = \phi - \phi_{min}'$$

The increase in the entropy production is proportional to the square of the change in the driving force (change of the concentration driving force). From the foregoing it is clear that the pursuit of the minimum entropy production can also be interpreted from dynamic considerations.

USED SYMBOLS

B   molar mass stream of the bottom product

D   molar mass stream of the overhead product

F   molar mass stream of the feed

G   free energy

H   enthalpy of the vapour

I   flow

K   equilibrium ratio

L'   transport coefficient

L   molar liquid stream

L_N the separation work of the Nth plate

N_{term} number of thermodynamic transfer units

NTU   number of the diffusion transfer units

P total pressure

$\bar{p}$ vapour pressure

p coupling factor

q the liquid fraction of the feed

Q_N the heat loss stream of the Nth plate

r_N the heat loss fraction of the vapour stream of the Nth plate

R reflux ratio

S entropy

T absolute temperature

t time

V molar vapour stream in the rectification section

V' molar vapour stream in the stripping section

X driving force

δX change in the driving force

x liquid mole fraction

y vapour mole fraction

Δ $y_{AN} - y_{A(N+1)}$

Δ $y^{*}_{AN} - y_{A(N+1)}$

ϕ entropy source density

λ latent heat

Indices

$A,B,C...$ components

j,k transport coefficient endices

i component index

n the number of components

N the number of plate

Q   relates to the heat transport

C   relates to the component transport

m   minimum value

h   level of height

f   liquid phase index

g   vapour phase index

*   equilibrium value

Relations are written in a dimensionless form, their homogeneity
should be ensured in substitutions.

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РЕЗЮМЕ

     Дестилляция рассматривается автором, как стационарная систе-
ма первого порядка. С точки зрения энергетики ставится   целью   ис-
пользование наибольшей части энтропии, выделяемой транспортом теп-
ла для сепарации компонентов. Описываются выражения для вычисления
производства энтропии теплопередачи для   реверсивного и   реального
процесса. Наконец, сообщается термодинамическое истолкование   дви-
жущей силы, эффективности динамического поведения ректификации.