

Sherwood's Plot: Fundamental or Empirical

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ABSTRACT: *There are several examples of heuristic rules first proposed from empirical observation, which eventually earned physicochemical validity after the fundamental derivation of a posteriori. This may be the case of Sherwood's plot – for which a sound rationalization from first principles, entailing enthalpy and mass balances, is provided here; it applies to (fine) chemicals undergoing concentration followed by purification at large, where such costs override the whole processing.*

KEYWORDS: *Concentration costs; Purification costs; Heuristic rule; Mass balance; Enthalpy balance.*

INTRODUCTION

Accurate anticipation of the price to be attained in the open market by a given chemical commodity or specialty, following industrial processing, has long been sought – since the difference between price and cost will determine the economic feasibility of the underlying process. One of the earliest (and still most widely utilized) approach to this issue was developed by *Sherwood* [1] - who unfolded a simple relationship between price of a material and its concentration in the source feedstock stream. Such a relationship came from inspection of comprehensive datasets obtained from industrial practice; to encompass the several orders of magnitude of prices and departing concentrations of target compound for which such a relationship turns out valid, *Sherwood's* plot is normally presented in logarithmic form. This type of plot is normally utilized to unfold power-law relationships – and it sounds reasonable to assume that processing costs will increase more (or less) than linearly with a dilution of feedstock. The constant slope of -1 coincidentally found for the best-fit straight line in the

mentioned log-log plot does not compromise its generality; it indeed suggests that price is, in practice, inversely proportional to the concentration of target compounds in the raw material.

The aforementioned heuristic has been confirmed *a posteriori* for a wide variety of materials in dilute solutions – ranging from metal ores to biological drugs (including bacteria, molds, and microalgae as sources), and covering gas separations and even pollutants [2-5]. *Sherwood's* plot was also successfully applied to assess the recycling potential of material waste streams [6] and used products [7]. It is commonly accepted that prices are constrained by supply and demand – and thus dependent on a multitude of socioeconomic variables; however, no product will reach the market unless the associated revenue exceeds its processing costs – as a basic requirement of profitability. Furthermore, separation costs normally override other processing costs in the case of fine chemicals; for instance, [8] claimed that the cost of pure metals prepared from dilute ores is dominated

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by mining and milling costs, but by smelting and refining should concentrated ores be at stake. In any case, Sherwood's plot may be considered to apply as well to separation/purification costs as it does to prices - which will actually coincide in the asymptotic situation of marginal profit.

The functional form underlying Sherwood's plot may be qualitatively justified if separation/purification costs depend directly on amount of material processed per unit amount of pure target product [9]. A more quantitative derivation is, however, possible provided that a few simplifying assumptions or reasonable analogies are made. The complexity of the separation system may indeed scale on the number of target materials or the minimum number of separation steps; or one may instead resort to information theory - since the difficulty in interpreting code words mimics the complexity of separating specific compounds from mixtures [10]. The alternative approach followed here stems from first principles; it is based on enthalpy supplied (or withdrawn) to remove solvent from solution, following a phase change. In fact, withdrawal of contaminating compound(s), generically seen as solvent, from the target compound has classically been achieved via some mechanical method able to split distinct phases - where the former is forced into a distinct phase. This new phase is generated from the source material either via supply of enthalpy in the form of heat, previously obtained from fuel burning (directly as in evaporation and distillation; or indirectly, as in recovery following liquid/liquid extraction and chromatography); or via removal of enthalpy, at the expense of work supplied (as in freezing, freeze-drying, precipitation and crystallization). This analysis applies to fine chemicals that normally undergo early concentration, and subsequent purification as part of the overall separation process.

Theoretical section

Regardless of separator type, the key concept for separation in chemical engineering is removal of solvent, which may unwillingly be accompanied by unwanted solutes. In the absence of losses along the process, the mass of solute, m_s , will remain essentially constant and equal to $m_{s,raw}$, or mass of solute in the raw feedstock available - so any increase in the concentration of solute, C_s , will occur via a decrease in the volume of solvent, V_w .

The solvent is, in general, constituted by free (or bulk) molecules accounting for a total volume $V_{w,f}$, and bound molecules with volume $V_{w,b}$, thus adding up to

$$V_w = V_{w,f} + V_{w,b} \quad (1)$$

During separation, the rate of solvent removal, $-dV_w/dt$ (where t denotes batch time, or plug flow-based space time of separation), will accordingly read

$$-\frac{dV_w}{dt} = \frac{P_{sep}}{\rho_w \Delta h_{sep}} \quad (2)$$

Where P_{sep} denotes separation enthalpy per unit time supplied (or withdrawn) so as to remove solvent of the original liquid solution as a distinct phase, ρ_w denotes mass of solvent per unit volume, and Δh_{sep} denotes enthalpy per unit mass accompanying phase change of solvent. Separation of fine chemicals normally occurs along two sequential stages - concentration and purification, with distinction based on the relative magnitude of $V_{w,f}$ and $V_{w,b}$.

In the case of free solvent, Δh_{sep} will reduce to Δh_f - denoting specific enthalpy change associated with phase change of free solvent molecules. Conversely, bound solvent is normally harder to remove via phase change, due to stronger interaction of its molecules with those of solute(s); Δh_{sep} will accordingly be given by Δh_b , meaning specific enthalpy change associated with phase change of bound solvent molecules. Both Δh_f and Δh_b will be hypothesized hereafter as essentially independent of solute concentration - although one would expect that $\Delta h_b \neq \Delta h_f$.

During the concentration step - often carried out by evaporation or freezing of solvent, or precipitation of solute, or even by liquid/liquid extraction of solvent or solute, $V_{w,f}$ clearly dominates; hence, Eq. (1) simplifies to

$$V_w \approx V_{w,f} \quad (3)$$

while Δh_{sep} abides to

$$\Delta h_{sep} \approx \Delta h_f \quad (4)$$

Insertion of Eqs. (3) and (4) transforms Eq. (2) to

$$-\frac{dV_w}{dt} \approx -\frac{dV_{w,f}}{dt} = \frac{P_{conc}}{\rho_w \Delta h_f} \quad (5)$$

Where separation enthalpy per unit time referring specifically to concentration of solute accompanying formation of a distinct phase of solvent will hereafter be denoted as P_{conc} en lieu of P_{sep} . In view of its differential nature, Eq. (5) requires an initial condition, say

$$V_W|_{t=0} = V_{W,raw} \quad (6)$$

Where $V_{W,raw}$ denotes volume of solvent in the raw feedstock stream; integration of Eq. (5) via separation of variables yields

$$V_{W,raw} - V_{W,conc} = \frac{P_{conc}}{\rho_W \Delta h_f} \Delta t_{conc} \quad (7)$$

with the aid of Eq. (6), where $V_{W,conc}$ denotes volume of feedstock obtained after concentration took place during period Δt_{conc} – provided that $P_{conc}/\rho_W \Delta h_f$ is taken as essentially independent of time. The total cost of concentration, Co_{conc} , should then be proportional to the total amount of enthalpy of phase change required, viz.

$$Co_{conc} = Co_{W,conc} P_{conc} \Delta t_{conc} \quad (8)$$

Where $Co_{W,conc}$ denotes cost of separation per unit amount of enthalpy of phase change in transit during concentration; after solving Eq. (8) for P_{conc} , one may redo Eq. (7) to

$$V_{W,raw} - V_{W,conc} = \frac{Co_{conc}}{\rho_W \Delta h_f Co_{W,conc}} \quad (9)$$

On the other hand, the mass concentration of solute by the end of the concentration step reads

$$C_{s,conc} = \frac{m_{s,raw}}{V_{W,conc}} \quad (10)$$

because the mass of solute in the original raw feedstock, $m_{s,raw}$, remains essentially constant as no losses are considered; by the same token,

$$C_{s,raw} = \frac{m_{s,raw}}{V_{W,raw}} \quad (11)$$

pertaining to the original feedstock. Combination of Eqs. (10) and (11) supports transformation of Eq. (9) to

$$\frac{m_{s,raw}}{C_{s,raw}} - \frac{m_{s,raw}}{C_{s,conc}} = \frac{Co_{conc}}{Co_{W,conc} \rho_W \Delta h_f} \quad (12)$$

where isolation of Co_{conc} finally yields

$$Co_{conc} = \kappa_{conc} \left(\frac{1}{C_{s,raw}} - \frac{1}{C_{s,conc}} \right) \quad (13)$$

– provided that a characteristic, constant parameter κ_{conc} is defined by

$$\kappa_{conc} \equiv \rho_W \Delta h_f m_{s,raw} Co_{W,conc} \quad (14)$$

Note the proportionality of Co_{conc} to the difference of reciprocals of solute concentration in the raw feedstock and after reaching the level preset for the unit operation of concentration; although Co_{conc} increases with a decrease in $C_{s,raw}$ as expected, the increase of the former with an increase in $C_{s,conc}$ is far less significant – owing to the much higher range of $C_{s,conc}$ relative to $C_{s,raw}$, since reciprocals are at stake. This feature is inscribed in the ordinate originally chosen for Sherwood's plot - which refers to cost of pure (target) compound, or compound within a concentration range sufficiently narrow around its true purity. Although $C_{s,conc}$ should in principle be pushed to as high a value as possible – because the subsequent purification cost is normally much higher, a physicochemical limits exists because the rationale for concentration applies only while Eq. (3) is valid. In fact, solvent remains chiefly in free form up to approximately one (sometimes two) orders of magnitude increase in $C_{s,conc}$ relative to $C_{s,raw}$.

Once the concentration step is over, purification is in order; this is characterized by a much higher performance in terms of separation, as it can recover the solute of interest from the remaining solvent (including contaminating solutes). A typical process relevant here is high performance liquid/liquid or solid/liquid extraction as in preparative chromatography, relying on preferential binding of the target solute to a stationary phase – aimed at guaranteeing sufficient selectivity. The phase change is accordingly provided by the mobile phase that preferentially dissolves solvent (or solute), and thus carries it away as a phase distinct from the stationary phase; but still requires supply/withdrawal of enthalpy downstream, so as to close the production cycle. The characteristics of the solvent undergoing purification are normally rather different from those of the original solvent: in fact, the volume of solvent bound to the solute of interest now dominates over free solvent, according to

$$V_W \approx V_{W,b} \quad (15)$$

instead of Eq. (3), thus implying

$$\Delta h_{sep} \approx h_b \quad (16)$$

To be swapped for Eq. (4). The rate of solvent removal will be approximately given by

$$-\frac{dV_W}{dt} \approx -\frac{dV_{W,b}}{dt} = \frac{P_{pur}}{\rho_W \Delta h_b} \quad (17)$$

Using Eq. (5) as template – where P_{pur} denotes separation enthalpy per unit time, required specifically for the phase change of solvent taking place throughout purification; Eq. (17) should abide to the initial condition

$$V_W|_{t=0} = V_{W,conc} \quad (18)$$

Because purification typically follows concentration. Integration of Eq. (17) is again feasible *via* separation of variables at the expense of Eq. (18), and yields

$$V_{W,conc} - V_{W,pur} = \frac{P_{pur}}{\rho_W \Delta h_b} \Delta t_{pur} \quad (19)$$

Based once more on the simplifying hypothesis that $P_{pur}/\rho_W \Delta h_{sep}$ remains essentially constant throughout purification for a period Δt_{pur} – while producing a feedstock volume $V_{W,pur}$. The total cost of purification, Co_{pur} , should again be proportional to the total amount of enthalpy required by the phase change, viz.

$$Co_{pur} = Co_{W,pur} P_{pur} \Delta t_{pur} \quad (20)$$

Where $Co_{W,pur}$ denotes cost of separation per unit amount of enthalpy of phase change in transit during purification. Combination of Eqs. (19) and (20) generates

$$V_{W,conc} - V_{W,pur} = \frac{Co_{pur}}{\rho_W \Delta h_b Co_{W,pur}} \quad (21)$$

– similar in form to Eq. (9), which readily permits isolation of Co_{pur} as

$$Co_{pur} = \rho_W \Delta h_b Co_{W,pur} (V_{W,conc} - V_{W,pur}) \quad (22)$$

Remember that a major working hypothesis is that no target solute is lost during the purification step – i.e. the yield remains unity, which requires a very large

(putatively infinite) selectivity. Concentration of solute throughout purification should satisfy

$$C_{s,pur} = \frac{m_{s,raw}}{V_{W,pur} + V_s} \quad (23)$$

because the volume of residual solvent (containing all other byproducts seen as impurities) bound to solute, $V_{W,pur}$, will now be of the order of magnitude of the volume occupied by solute itself, V_s – unlike happened in Eq. (11) with $V_{W,raw}$; note that V_s should remain essentially constant (at least in an ideal solution). Upon solving for $V_{W,pur}$, Eq. (23) yields

$$V_{W,pur} = \frac{m_{s,raw}}{C_{s,pur}} - V_s \quad (24)$$

and likewise

$$V_{W,conc} = \frac{m_{s,raw}}{C_{s,conc}} - V_s \quad (25)$$

Applying to the concentration step – even though $m_{s,raw}/C_{s,conc} \gg V_s$; insertion of Eqs. (24) and (25) converts Eq. (22) to

$$Co_{pur} = \rho_W \Delta h_b Co_{W,pur} \left(\frac{m_{s,raw}}{C_{s,conc}} - V_s - \frac{m_{s,raw}}{C_{s,pur}} + V_s \right) \quad (26)$$

Where cancellation of symmetrical terms, followed by factoring out of $m_{s,raw}$ gives merely

$$Co_{pur} = \kappa_{pur} \left(\frac{1}{C_{s,conc}} - \frac{1}{C_{s,pur}} \right) \quad (27)$$

– Provided that another characteristic, constant parameter κ_{pur} abides to

$$\kappa_{pur} = \rho_W \Delta h_b m_{s,raw} Co_{W,pur} \quad (28)$$

It is remarkable that the functionality of Co_{pur} on the reciprocals of the germane solute concentrations $C_{s,conc}$ and $C_{s,pur} > C_{s,conc}$ as per Eq. (27) is identical to that prevailing for Co_{conc} on $C_{s,raw}$ and $C_{s,conc} < C_{s,raw}$ in Eq. (13); however, common industrial practice has it that

$$\frac{\kappa_{pur}}{\kappa_{conc}} = \frac{\Delta h_b}{\Delta h_f} \frac{Co_{W,pur}}{Co_{W,conc}} \ll 1 \quad (29)$$

after recalling Eqs. (14) and (28).

The total cost of separation, Co_{sep} , will finally be given by

$$Co_{sep} = Co_{conc} + Co_{pur} \quad (30)$$

Where insertion of Eqs. (13) and (27) generates

$$Co_{sep} = \kappa_{conc} \left(\frac{1}{C_{s,raw}} - \frac{1}{C_{s,conc}} \right) + \kappa_{pur} \left(\frac{1}{C_{s,conc}} - \frac{1}{C_{s,pur}} \right) \quad (31)$$

In view of Eq. (29), one may simplify Eq. (31) to

$$Co_{sep} \approx \kappa_{conc} \left(\frac{1}{C_{s,raw}} - \frac{1}{C_{s,conc}} \right) \quad (32)$$

while

$$C_{s,conc} \approx C_{s,pur} \quad (33)$$

implies

$$\frac{1}{C_{s,conc}} - \frac{1}{C_{s,pur}} = 0 \quad (34)$$

– Which, in turn, supports transformation of Eq. (32) to

$$Co_{sep} \approx \kappa_{conc} \left(\frac{1}{C_{s,raw}} - \frac{1}{C_{s,pur}} \right) \quad (35)$$

Equation (35) is plotted in Fig. 1, laid on actual data retrieved from various sources including [11]; the typical shape of Sherwood's plot is readily grasped.

{insert Fig.1}

Note, in particular, the straight line with slope -1 in the bilogarithmic plot along most of the operational range, encompassing chiefly fine chemicals and bioactive compounds – overridden by the functionality of Eq. (33) on $1/C_{s,raw}$; followed by a bend arising when $1/C_{s,pur}$ is of the same order of magnitude of $C_{s,raw}$ – as happens with such bulk commodities as ethanol or water.

RESULTS AND DISCUSSION

The above derivation considered only transfer of solvent (containing also unwanted solutes) – originally in free form during concentration, or in bound form during purification; hence, transfer of target solute was neglected.

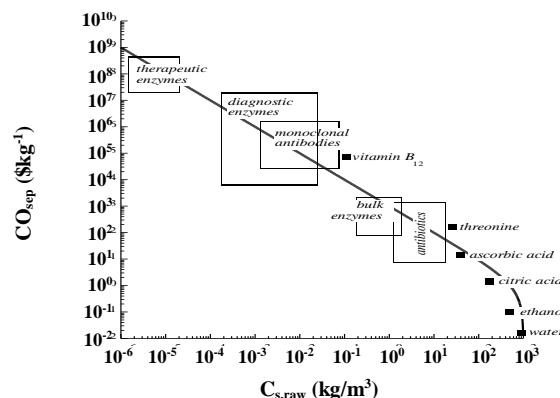


Fig. 1: Variation of separation cost after concentration and purification, Co_{sep} , as a function of concentration of target compound in raw feedstock, $C_{s,raw}$, expressed on a weight basis per unit volume of product, and overlaid on actual data pertaining to usual chemical specialties (and selected commodities).

Although this strategy was followed so as to keep mathematical handling at a tractable level, it is known that purification may, in general, encompass also transfer of target solute from the original to another phase, i.e. transfer of solvent and target solute may occur simultaneously. Furthermore, only separation processes encompassing a first step of concentration and a second step of purification are eligible; therefore, separation processes based on (strongly inter-related) absorber/stripper steps – as happens with gas separations, were left out of this analysis. Extension to said gas separations would also require the variation of phase change enthalpy with the (logarithm of) solute concentration (or partial pressure, for that matter) be taken into account, rather than hypothesizing an essentially constant enthalpy of phase change.

Unlike purification processes, concentration processes yield variations from $C_{s,raw}$ to $C_{s,conc}$ quite above from $C_{s,conc}$ to $C_{s,pur}$. Therefore, costs of concentration usually override those of purification – on an overall basis, rather than a unit mass basis; thus fully justifying why the approximate form labelled as Eq. (35) is normally quite accurate. In any case, the nature and mode of enthalpy in transit accompanying phase change of solvent strongly affects $Co_{w,conc}$ – e.g. freezing is more costly than boiling, and cost of extra solvent for liquid extraction normally lies above cost of enthalpy for conductive transfer. In view of

$$C_{S, \text{pur}} \gg C_{S, \text{raw}} \quad (36)$$

and, consequently,

$$\frac{1}{C_{S, \text{raw}}} \gg \frac{1}{C_{S, \text{pur}}} \quad (37)$$

Eq. (35) is often abbreviated to

$$C_{O, \text{sep}} \approx \frac{K_{\text{conc}}}{C_{S, \text{raw}}} \quad (38)$$

– Which is the form of Sherwood's relationship most commonly employed in (bio)chemical engineering practice. Equation (38) justifies indeed the linear portion of the plot labelled as Fig. 1, with slope equal to -1 as per the bilogarithmic scale elected; however, $1/C_{S, \text{pur}}$ cannot be neglected in the case of such bulk commodities as ethanol or water – and the full form exhibited by Eq. (35) is required to justify the downward bending of the said plot.

The effort to justify an empiric rule based on first principles (as done above) parallels what happened with Arrhenius' empirical law for temperature-dependence of kinetic parameters; the activated state theory, formulated in the 30's by Eyring, theoretically justified its (dominant) negative exponential form by resorting to elementary molecular phenomena – provided that the temperature range under scrutiny is not too wide.

Finally, it should be stressed that enthalpy accompanying a phase change of solvent has been considered as the basis for separation, in either concentration or purification forms, since most separations in (bio)chemical engineering practice resort to (spontaneous) mechanical separation between two bulk phases - one of which did not originally exist. The enthalpy of phase change accounts not only for enthalpy arising from intermolecular binding forces, but also for entropy arising from molecular disorder when going from the original, single solute-poor phase (or phase containing target solute, plus extraneous solutes and solvent) to the new set of solute-rich phase and solute-free phase (or solute-rich and solute-free separate phases). This concept is distinct from separation work, alias Gibbs' energy change accompanying separation – a thermodynamic concept requiring reversible transitions between states, and giving rise to the theoretical minimum describing

said separation (or negative of Gibbs' energy change of mixing).

CONCLUSIONS

The derivation presented in this short communication departed from first principles, and resorted to standard enthalpy and mass balances as tool; it is remarkable how it led so closely to the empirical curve that for decades has been successfully employed by industrial practitioners. Therefore, Sherwood's cost-scaling heuristic goes well beyond a mere result of empirical realization, at least in the case of fine chemicals and bioactive compounds; it indeed holds a mechanistic rationale, provided that separation/purification dominates overall processing costs. This strengthens its value as modelling aid, since the applicability of Eq. (35) has been widely confirmed for a wide variety of chemical specialties in dilute solutions – including antibiotics, enzymes, toxins, and monoclonal antibodies.

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Nomenclature

$C_{O, \text{conc}}$	Total cost of concentration
$C_{O, \text{pur}}$	Total cost of purification
$C_{O, \text{sep}}$	Total cost of separation
$C_{O, W, \text{conc}}$	Cost of separation per unit amount of enthalpy of phase change in transit during concentration
$C_{O, W, \text{pur}}$	Cost of separation per unit amount of enthalpy of phase change in transit during purification
C_s	Mass concentration of solute
$C_{s, \text{conc}}$	Mass concentration of solute by end of concentration step
$C_{s, \text{pur}}$	Mass concentration of solute by end of purification step
$C_{s, \text{raw}}$	Mass concentration of solute in original feedstock
t	Batch time
m_s	Mass of solute
$m_{s, \text{raw}}$	Mass of solute in original raw feedstock

P_{conc}	Separation enthalpy per unit time, used to remove solvent as distinct phase during concentration
P_{pur}	Separation enthalpy per unit time, used to remove solvent as distinct phase during purification
P_{sep}	Separation enthalpy per unit time, used to remove solvent as distinct phase
V_s	Volume of solute
V_w	Volume of solvent
$V_{w,b}$	Volume of bound solvent
$V_{w,conc}$	Volume of solvent in feedstock stream after concentration step
$V_{w,f}$	Volume of free solvent
$V_{w,pur}$	Volume of solvent in feedstock stream after purification step
$V_{w,raw}$	Volume of solvent in raw feedstock stream
Δh_b	Enthalpy per unit mass accompanying phase change of bound solvent
Δh_f	Enthalpy per unit mass accompanying phase change of free solvent
Δh_{sep}	Enthalpy per unit mass accompanying phase change of solvent
Δt_{conc}	Duration of concentration step
Δt_{pur}	Duration of purification step
κ_{conc}	Parameter characteristic of concentration step
κ_{pur}	Parameter characteristic of purification step
ρ_w	Mass of solvent per unit volume

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