Constant Total Pressure Evaporation with Heat Reuse by a Built-in Engine

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A new way of promoting a nonspontaneous process, namely, a built-in engine, is introduced showing that a process with a large temperature coefficient of free energy change [that is, $d(\Delta G)_{T,P}/dT$] can be utilized to promote a nonspontaneous process which has a small temperature coefficient of free energy change. When such a built-in engine is incorporated into an evaporating system, heat reuse in the system can be obtained under a constant total pressure condition.

An auxiliary system consisting of two organic substances which are partially miscible in a certain temperature range and have a critical solution temperature can be used to serve as a built-in engine. One substance is added to the boiling mass of an evaporator to lower its boiling temperature, and the other is added to the condensing side to raise the temperature of the condensing mass. Heat of condensation can be effectively utilized in evaporating the boiling mass. Regeneration of the auxiliary system is achieved by taking advantage of the solubility gap.

Heat reuse is essential to the economy of an evaporation operation. In a conventional operation, the pressure at the condensing side of an evaporator is maintained considerably higher than that at the boiling side in order to obtain the temperature difference required for heat transfer. In the present process, a suitably selected auxiliary system is incorporated within an evaporating system so that such a pressure difference becomes unnecessary. Heat reuse can be obtained under a constant total pressure condition.

The auxiliary system consists of two organic substances which are immiscible with water. One, called a *boiling-point depressor* (or simply a depressor and denoted by β), is added to the boiling mass of an evaporator to lower its boiling temperature. The other, called an *absorbent* (denoted by α), is added on the condensing side to raise the temperature of the condensing mass. With the help of the auxiliary system, it is possible for the temperature of the condensing mass to become higher than that of the boiling mass, even at the same pressure. Heat of condensation can then be effectively utilized in evaporating the boiling mass, and heat reuse is realized.

It is shown that at the same time fresh water is separated from the aqueous solution, mixing of the depressor (β) and the absorbent (α) takes place in the auxiliary system. When the auxiliary system is well chosen, it can be regenerated by simple cooling. Such is the case when the auxiliary system forms a miscibility gap with a critical solution temperature.

It will be shown that the auxiliary system is cyclic in operation and functions as a built-in engine, absorbing the heat of mixing at the evaporator temperature and rejecting heat at a low temperature sink. The system can thus supply the work required in compressing the water vapor distilled from the boiling mass. The principle which underlies this built-in engine concept can be generalized. A process which has a large temperature coefficient of free energy change $\left[\text{that is, } \left|\frac{d(\Delta G)_{T,P}}{dT}\right|\right]$ can be utilized to promote a nonspontaneous process which has a small temperature coefficient of free energy change. This generalized principle is quite far-reaching and may find many applications in various fields. The underlying principles will be discussed in two parts: constant total pressure evaporation with heat reuse and regeneration of the auxiliary system.

CONSTANT TOTAL PRESSURE EVAPORATION WITH HEAT REUSE

In a conventional evaporator, a boiling mass receives heat from condensing steam and gives out superheated steam. The former will be called the *input vapor* and the latter the *output vapor*. Among the temperature of the boiling mass and the condensing temperatures of the input and output vapors, the following relation holds:

$$(T_c)_{\text{input}} > (T_b) > (T_c)_{\text{output}} \tag{1}$$

The output vapor cannot be used without modification as the input vapor for the boiling mass.

In the present process, an auxiliary system is incorporated into the evaporating system to realize the following relation:

$$(T_c)_{\text{input}} = (T_c)_{\text{output}} > (T_b) \tag{2}$$

The output vapor can, then, be used as the input vapor directly.

Depression of the Temperature of a Boiling Mass

When a mixture of two immiscible liquids is heated, the mixture boils at a temperature lower than the boiling points of either. In the present process, an organic substance of proper volatility is added to lower the boiling point of an aqueous solution. In an actual process, countercurrent multistage operation is used, and organic solutions of α and β of various concentrations are added both to the boiling side and the condensing side of the multistage evaporators. This is due to the fact that the eco-

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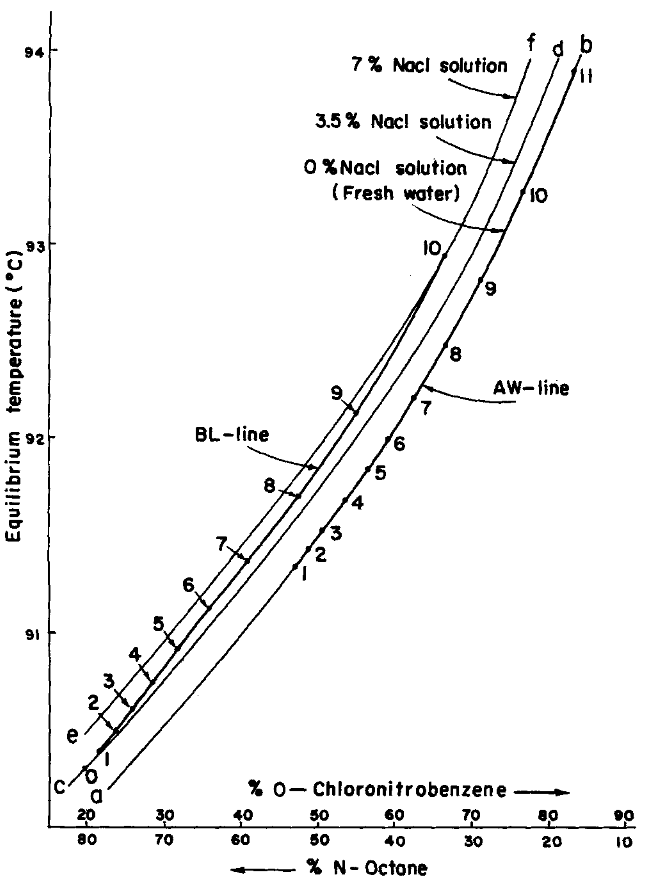


Fig. 1. Equilibrium and operating lines of a constant total pressure evaporating system.

nomical regeneration of the auxiliary system is based on the miscibility gap of the system, and the regeneration operation yields organic solutions of α and β.

The boiling mass in stage n, then, consists of an aqueous solution L'_n and an organic solution of α and β, B'_n. The temperature of the boiling mass in stage n, $(T_b)_n$, is related to the concentration of the two solutions as

$$(T_b)_n = f(\text{conc. of } L'_n, \text{ conc. of } B'_n)$$

This conclusion may be arrived at by applying the phase rule to the boiling equilibrium. Under a constant total pressure operation, the net degree of freedom becomes 2, which may be chosen to be the concentrations of the aqueous and the organic solutions.

Figure 1 shows the temperature of a boiling mass consisting of an aqueous salt solution and an organic solution of n-octane and o-chloronitrobenzene under atmospheric pressure as a function of their compositions (*1*) The lines *ab*, *cd*, and *ef* apply to 0, 3.5, and 7% salt solutions, respectively. The *AW* line, the *BL* line, and the numbered points will be explained later.

The system, n-octane and o-chloronitrobenzene, is not an ideal one owing to the toxicity, the low but significant solubility, and the significant volatility of the latter. A system consisting of an organic fluorine compound as a depressor and a higher boiling paraffin hydrocarbon as an absorbent would be an ideal auxiliary system owing to its nontoxicity and low solubilities in water. Or a paraffin hydrocarbon might be used as a depressor with a higher boiling fluorocarbon or a nitro-compound used as an absorbent.

Elevation of the Temperature of a Condensing Mass

Since it is desired to condense water vapor at a higher temperature, it is only necessary to raise its vapor pressure. In the present process, the vapor recompression is achieved in a distinct way.

When a low volatility absorbent A' is in contact with a mixed vapor of water W and the depressor β, both the absorption of β into A' and the condensation W take place simultaneously at a temperature (T_c) which is higher than the equilibrium condensation temperature of the mixed vapor without the absorbent. This simultaneous absorption and condensation of a mixed vapor will be referred to simply as *condensation of the mixed vapor* in the following discussions.

Since there are three components (water, α, and β) and three phases (water, organic, and vapor) involved in this condensation equilibrium, the degree of freedom of the system is 2. Under a constant total pressure condition, the net degree of freedom becomes 1. The temperature of the condensing mass in stage n, $(T_c)_n$, is thus related to the concentration of the organic solution in the condensing mass as

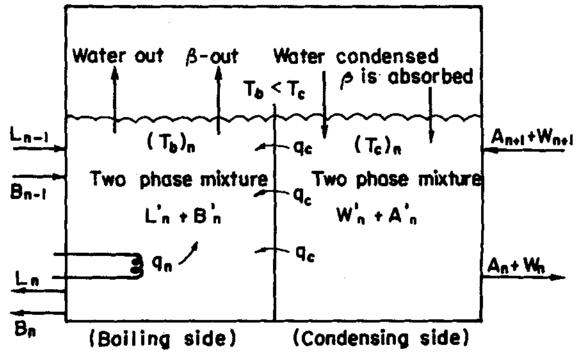
$$(T_c)_n = (\text{conc. of the organic solution } A')$$

The line *ab* in Figure 1 shows the relation between the temperature of a condensing mass $(T_c)_n$ and the composition of the organic solution of n-octane and o-chloronitrobenzene in the condensing mass(*1*).

Constant Total Pressure Vapor Recompression Evaporation

Figure 2 illustrates a constant total pressure evaporator with heat reuse. It shows the condition in stage n of a multistage evaporation system. An organic solution B_{n-1} (β rich) and an aqueous solution L_{n-1} are fed to the boiling side of the n^{th} stage evaporator. Another organic solution A_{n+1} (α rich) and fresh water stream W_{n+1} are added to the condensing side. The evaporator then discharges L_n and B_n from the boiling side and A_n and W_n from the condensing side.

The boiling mass consists of an aqueous solution L'_n and an organic solution B'_n and boils off water vapor and β vapor at temperature $(T_b)_n$. The condensing mass consists of an organic solution A'_n and fresh water W'_n. The mixed vapor distilled from the boiling mass is condensed (β vapor is absorbed into A'_n and water vapor is condensed) at temperature $(T_c)_{n,\text{output}}$. This temperature can be higher than the temperature of the boiling mass if the solution A'_n is sufficiently richer in the absorbent (depending on the concentration of L'_n) than in the solution B'_n. The temperature gain at stage n will be defined as the difference between the two temperatures. Thus



β : Depressor
α : Absorbent
A : Organic solution of α and β(α-rich) added to condensing side
B : Organic solution of α and β (β rich) added to boiling side
q_m: Mak-up heat , q_c: Heat of condensation

Fig. 2. Schematic diagram illustrating constant total pressure upgrading of heat energy.

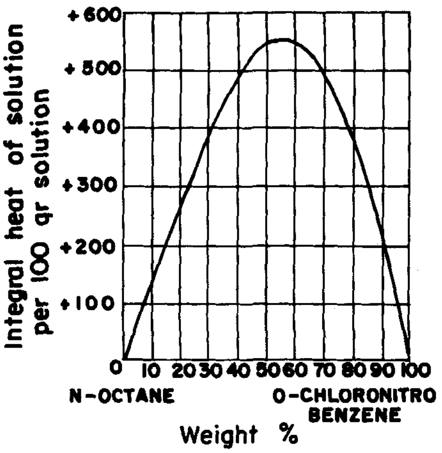


Fig. 3. Integral heat of solution (at 60°C.).

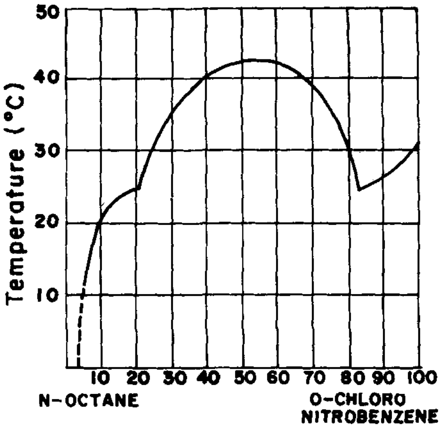


Fig. 5. Miscibility gap for the system *n*-octane and o-chloronitrobenzene.

$$\text{Temperature gain} = (T_c)_{n(\text{output})} - (T_b)_n > 0$$

When the temperature gain is sufficiently large, heat flows from the condensing side to the boiling side at a practical rate. The heat of absorption of β into A'_n and the heat of condensation of the water vapor are utilized in the heating of the boiling mass.

Water is distilled from L_{n-1} to give fresh water by the amount $(W_n - W_{n+1})$, and a more concentrated solution L_n results. In the auxiliary system, β is distilled from B_{n-1} and is absorbed into A_{n+1} to give B_n and A_n. Therefore, the compositions of the A stream and the B stream approach each other. This approach in the compositions of the A and the B streams will be referred to as the *mixing of the two streams* in the following discussions. It may be stated that fresh water is separated from the aqueous solution system while mixing of the organic solutions takes place. Actually, the constant total pressure heat reuse is achieved through the mixing in the organic solutions.

In Figure 2, it is shown that some makeup heat is supplied to the boiling mass. The amount of the makeup heat required can be calculated by applying enthalpy balance to stage n as

$$\begin{aligned}(q_m)_n = {} & (\{L_n(h_L)_n + W_n(h_W)_n\} \\ & - \{L_{n-1}(h_L)_{n-1} + W_{n+1}(h_W)_{n+1}\}) \\ & + (\{B_n(h_B)_n + A_n(h_A)_n\} \\ & - \{B_{n-1}(h_B)_{n-1} + A_{n+1}(h_A)_{n+1}\})\end{aligned}$$

The first bracketed term may be interpreted as the enthalpy change for the separation of water from L_{n-1}. In the case of the sodium chloride solution system (*2*), this term may be neglected in an approximate calculation. The second bracketed term is the enthalpy change due to the compositions of the A and the B streams approaching each other and may be interpreted as the heat of mixing. In each stage, the heat of mixing of the organic solutions should be supplied as the makeup heat.

Figure 3 shows the integral heat of solution at 60°C. for the *n*-octane *o*-chloronitrobenzene system (*1*) from which heat of mixing can be calculated.

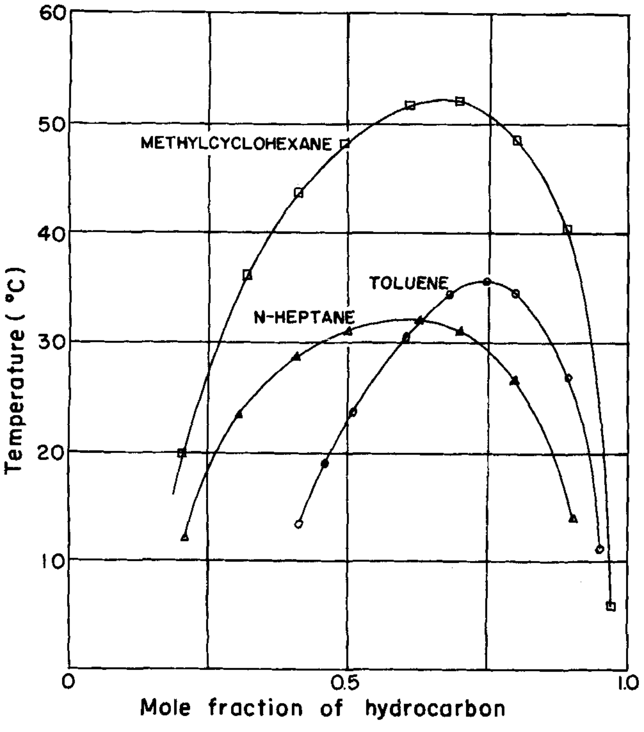


Fig. 4. Binary solubility curves system containing $C_7F_{15}H$ (3).

REGENERATION OF AN AUXILIARY SYSTEM BY THE MISCIBILITY GAP

The organic solutions formed in the evaporating system should be regenerated and recycled. It would be nice to have complete separation into the individual constituents, but it is not necessary. The most economical regeneration uses the phase separation due to the miscibility gap. A pair of organic substances is selected to serve as an auxiliary system. These substances form a miscibility gap at lower temperatures and have an upper critical solution temperature somewhat below the evaporator temperature.

In selecting an auxiliary system, the following opposing effects have to be compromised. The absorbent should have sufficient affinity with the depressor at the evaporator temperature to obtain adequate temperature gain. At the same time, the affinity between them should become sufficiently low at a lower temperature to give a miscibility gap. Figure 4 shows phase diagrams for a fluoro compound and various hydrocarbons (*3*). Figure 5 shows the phase diagram for the *n*-octane and *o*-chloronitrobenzene system (*1*).

MULTISTAGE OPERATION

As has been described previously, the constant total pressure evaporation with heat reuse is based on the idea of recovering the temperature drop for heat transfer by the temperature gain. Thus, the organic solutions in the boiling and condensing sides of an evaporator should be different in their compositions by a certain amount to attain the desired temperature gain. The organic solutions recoverable from a regeneration operation may have a greater difference in their compositions than the amount just described. Therefore, a multistage operation with countercurrent flow of the solutions may be devised to make effective use of the driving forces for both the heat and the mass transfer operations and still maintain sufficient temperature gain in each stage.

Operation Flow Sheet

Figure 6 shows a flow diagram for a multistage (ten stages as shown in the figure) evaporating system based on the present process. Four liquid streams flow through the stages: the L_n, A_n, B_n, and W_n streams. The L_n and B_n streams and A_n and W_n streams flow in pairs parallel to each other within a stage, as will be shown later in connection with the evaporator design (Figure 8), but they flow countercurrent to each other through the stages.

L_n and B_n form a fluid pair and are evaporated as they flow through the successive stages (1 → 10). The salt content of L increases from $(C_L)_0$ to $(C_L)_{10}$, and the composition of B, expressed as depressor content in the solution, drops from $(C_B)_0$ to $(C_B)_{10}$.

A_{11} is fed into stage 10. It absorbs depressor vapor, and its depressor content increases as it flows through stage (10→1) from $(C_A)_{11}$ to $(C_A)_1$. Water vapor condenses as depressor vapor is absorbed in A, and thus forms a W stream. The W stream so formed flows with A making up another fluid pair.

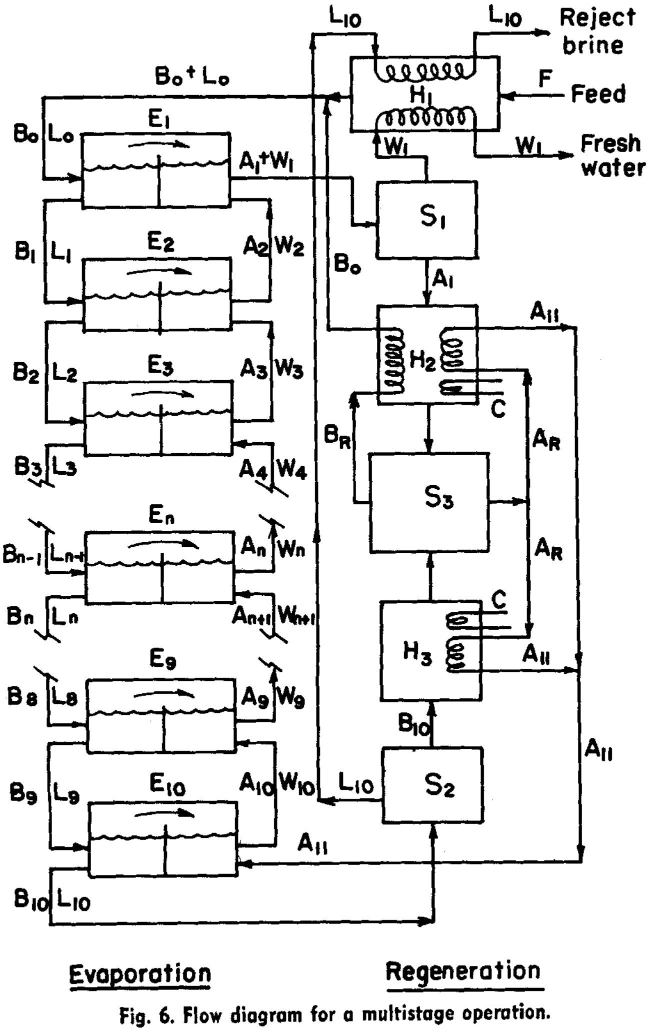


Fig. 6. Flow diagram for a multistage operation.

The aqueous solution feed is heated in the heat exchanger H_1 by the product water W_1 and the reject brine L_{10} and becomes L_o, which is fed into the first stage. The two pairs of fluid streams $A_1 + W_1$ and $B_{10} + L_{10}$ are separated into the organic and aqueous solutions in the separators S_1 and S_2, respectively. W_1 and L_{10} so separated are sent to the heat exchanger H_1 to heat the feed. The organic streams A_1 and B_{10} are cooled in the heat exchangers H_2 and H_3, respectively, by heat exchange with fluids A_R and B_R to be described below and by cooling water C. Cooling water is required to keep the system in thermal balance and to serve as the low temperature sink for the built-in engine to be described. As A_1 and B_{10} are cooled, phase separations take place to give an α rich fluid A_R and a β rich fluid B_R. The mixtures are separated into A_R and B_R streams in the separators S_3. A_R and B_R are heated in the heat exchangers H_2 and H_3, become A_{11} and B_o, respectively, and are recycled.

The operation of a multistage system is illustrated below with the following assumed conditions:

1. $L_o = 100$ parts, $A_{11} = 179$ parts, $B_o = 191$ parts.
2. $(C_L)_o = 3.5\%$ and $(C_L)_{10} = 7\%$.
3. Equal water evaporation in each stage.
4. Sink temperature = 25°C.
5. Operating pressure = 1 atm.
6. n-Octane and o-chloronitrobenzene are used as the depressor and the absorbent, respectively.

From Figure 5, the compositions of the organic solutions regenerated at 25°C. are $(C_B)_o = 80\%\ \beta$ and $(C_A)_{11} = 18.0\%\ \beta$. Water evaporated in each stage and $(C_L)_n$ can be found by material balances. The amount of β evaporated in each stage can be found by applying the principle of steam distillation, and the amounts A_n and B_n and the compositions $(C_A)_n$ and $(C_B)_n$ can then be found. The temperatures $(T_C)_n$ and $(T_b)_n$ for the two phase mixtures $A_n + W_n$ and $B_n + L_n$ can be found from Figure 1.

The results of the calculations are summarized as follows:

1. A_1 and B_{10} are 312.2 parts and 57.8 parts, respectively, and $(C_A)_1 = 53\%\ \beta$ and $(C_B)_{10} = 34\%\ \beta$. These results will be used in calculating the overall makeup heat required.
2. When one refers to Figure 1, the points 0 to 10 on the BL line show the compositions and (T_b) for $B_n + L_n$ for $n = 0$ to $n = 10$. The points 1 to 11 on the AW line show the composition of A_n and the $(T_c)_n$ for $A_n + W_n$ for $n = 1$ to $n = 11$. From these results, it will be seen that the average Δt for heat transfer in each stage is about 1.1°C., or about 2°F.

This Δt value may seem too small. It will be shown that proposed evaporators which are applicable to this process are extremely simple in their construction and could be manufactured at very low costs. Therefore, it is one of the advantages of the present process to use a small Δt for heat transfer in order to obtain a high thermodynamic efficiency.

Makeup Heat Requirement

Makeup heat $(q_m)_n$ has to be supplied to each stage. The total makeup heat $\sum_{n=1}^{N} (q_m)_n$ can be calculated by applying enthalpy balance to the whole evaporator set as follows:

$$\sum_{n=1}^{N} (q_m)_n = [L_N(h_L)_N + W_1(h_W)_1 - L_o(h_L)_o]$$

$$+ [B_N(h_B)_N + A_1(h_A)_1 - B_0(h_B)_0 - A_{N+1}(h_A)_{N+1}]$$

$$\simeq \text{heat of mixing to form } B_N \text{ and } A_1 \text{ from } B_0 \text{ and } A_{N+1}.$$

The first bracketed term represents the enthalpy change *involved in* the separation of water from the aqueous solution. Thermodynamic data are available for the sodium chloride-water system (*2*). This term is small as compared with the second bracketed term and may be neglected in approximate calculations. The second bracketed term represents the enthalpy or heat of mixing B_0 and A_{N+1} to obtain B_N and A_1. Since the mutual solubility of the depressor and the absorbent increases with temperature, the enthalpy of mixing is a positive quantity.

In a practical operation, the easiest way of adding makeup heat is to add makeup steam $(S_m)_n$ to each stage. The total makeup steam required can be calculated approximately by

$$\sum_{n=1}^{N} (S_m)_n$$

$$= \frac{B_N(h_B)_N + A_1(h_A)_1 - B_0(h_B)_0 - A_{N+1}(h_A)_{N+1}}{H_W - (h_W)_1}$$

$$= \frac{\text{heat of mixing to form } B_N \text{ and } A_1 \text{ from } B_0 \text{ and } A_{N+1}}{\text{latent heat of condensation of steam}}$$

The heat of mixing given in the numerator can be found approximately by taking the difference between the sum of the integral heats of solution of B_N and A_1 and the sum of the integral heats of solution of B_0 and A_{N+1}. For the example illustrated in the last section, this heat of mixing *is found to* be 800 cal./100 g. of L_0 from Figure 3 and from the results summarized in the last section. The performance ratio, defined as the pounds of water produced per pound of steam used, is calculated as 33.6. Additional heat is required to make up the losses caused by the *inefficiencies* in the heat exchange operations. So, the actual performance ratio will be lower than this value.

The minimum work of separation of seawater with 50% recovery has been calculated as 4.15 kw.-hr./1,000 gal. (*4*). When one assumes that a reversible heat engine operating between 90° and 25°C. is used to supply this amount of work, the heat input at the high temperature level is 23.2 kw.-hr./1,000 gal. From this value, the ideal performance ratio is calculated to be 103. Thus, the present process when properly carried out may give a very favorable steam economy. The performance ratio will further be improved by increasing the operating temperature range.

The Built-in Engine Principle

The conventional ways of promoting a nonspontaneous process are by changing the operating condition, by supplying work to the system, and by free energy coupling with a matching spontaneous process.

A process which is nonspontaneous at a certain operating condition may become a spontaneous one at another operating condition. When both the reactants and the products are in the condensed state, the operating pressure does not materially shift the equilibrium. For a nonspontaneous process, whose temperature coefficient of free energy change is small, the reversal of the ΔG value (that is, making the ΔG value negative) may not take place within a practicable temperature range. For these reasons, *it is* impracticable to attempt to separate fresh water from a saline solution by simply changing the operating condition.

Electrolysis and vapor recompression evaporation are examples of the second approach. Work in an amount greater than the $\Delta G_{T,P}$ value of the process is supplied to the system to force the nonspontaneous process to proceed.

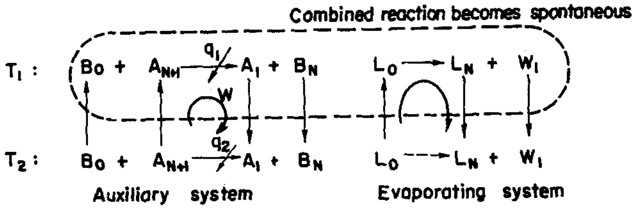


Fig. 7. Built-in engine principle.

The third approach is based on the idea that a spontaneous process ($\Delta G_{T,P} < 0$) may be coupled with a nonspontaneous process ($\Delta G_{T,P} > 0$) so that the overall combined process becomes a spontaneous one. The osmious process (5) is an example of this approach, in which the diffusion of ions from a very concentrated salt solution into a brackish water compartment causes desalting of another portion of the brackish water.

The built-in engine principle is based on two ideas: promoting a nonspontaneous process by free energy coupling with a matching auxiliary process which is spontaneous and regenerating the auxiliary system by either heating or cooling. This principle is embodied in the present process and will be explained in connection with the process.

With reference to Figure 7, under a constant pressure P and evaporator temperature T_1 the separation of fresh water from saline water is nonspontaneous, but the mixing of the organic solutions in the auxiliary system is a spontaneous one. When the two systems are coupled together, the positive value of ΔG of the former system is absorbed into the greater negative value of ΔG of the latter system and both transformations proceed to the right. The two systems have formed a free energy coupling. The task of reversing the ΔG value is now taken care of by the auxiliary system.

The transformation in the auxiliary system has a large temperature coefficient of free energy change and easily changes the direction of its transformation when the operating temperature is varied. It proceeds in one direction at evaporator temperature T_1 and reverses its direction at the regeneration temperature T_2. The auxiliary system thus follows a cyclic process, absorbing the heat of mixing at T_1 and rejecting heat at T_2. Therefore, *it* constitutes an engine which is incorporated within the operating system and may be properly called a *built-in engine.*

THE EVAPORATOR DESIGNS

The characteristic feature of the present process is that both the condensing and the boiling sides of an evaporator are under the same pressure. Therefore, there is little concern about the strength of materials, and construction can be greatly simplified. Extremely thin metallic plates may be used in the construction of the evaporator, and very large evaporators may be constructed. Two new evaporator designs, a supermultiple parallel plate evaporator and a spiral evaporator, are described.

Parallel Vertical Plate Evaporator

As shown in Figure 8, a parallel vertical plate evaporator is made up of parallel vertical heat conducting plates so that two successive plates form a compartment. An entrainment separating device may be inserted in each compartment. All the liquid streams involved are allowed to flow on the surface of the conducting plates as falling films. A liquid mixture of an aqueous solution L and an organic solution *B* flows on one side of a plate, and a mixture of an organic solution *A* and condensate stream *W* flows on the other side of the plate. Boiling takes place on one side of the plate, and condensation takes place on the other. Heat of condensation is transferred to the boiling liquid through the conducting plate.

The fluid pairs are parallel fed to all the compartments throughout the same stage. The temperature gain balances out the temperature drop for heat transfer, and there is no limit to the number of compartments which can be used. If each compartment is considered as an effect, the evaporator may be called a *supermultiple effect evaporator,* since there is no limit to the number of effects which can be used.

The surface of the metallic plates may be extended to increase the heat transfer area. Other modifications may be adopted to obtain a stable surface film. Makeup steam is added at each effect or cell.

Spiral Plate Evaporator

A spiral plate evaporator is a modification of the parallel vertical plates evaporator. As shown in Figure 9, it is made up of a long metal sheet wound in a spiral form. It may or may not be compartmented. A liquid distributor is placed on the top of the spiral to direct the flow of the fluid streams; a collector plate is placed at the bottom to collect the liquid streams. It will be noticed that a spiral evaporator is extremely simple in construction, and its manufacturing cost should be extremely low.

In the proposed evaporators, the vapor distilled from a boiling mass is condensed immediately a short distance away. Therefore, the flow velocity of the vapor is very low, and the entrainment separation problem is greatly simplified.

Boiling is expected to take place at the phase boundaries of the two solutions in a boiling mass rather than on the surface of the metal plate. Hence, scale deposit is less likely to develop on the surface of the metal plate.

SUMMARY

The principle of the built-in engine is introduced. It offers a way to promote a nonspontaneous process, which cannot in practice be made into a spontaneous one, by varying the operating temperature.

When a suitably selected auxiliary system is incorporated into an evaporation operation to serve as a built-in engine, a constant total pressure evaporation with heat reuse can be realized.

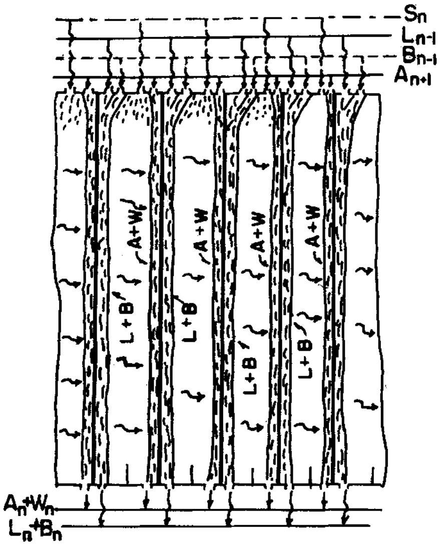


Fig. 8. Construction of n^{th} stage.

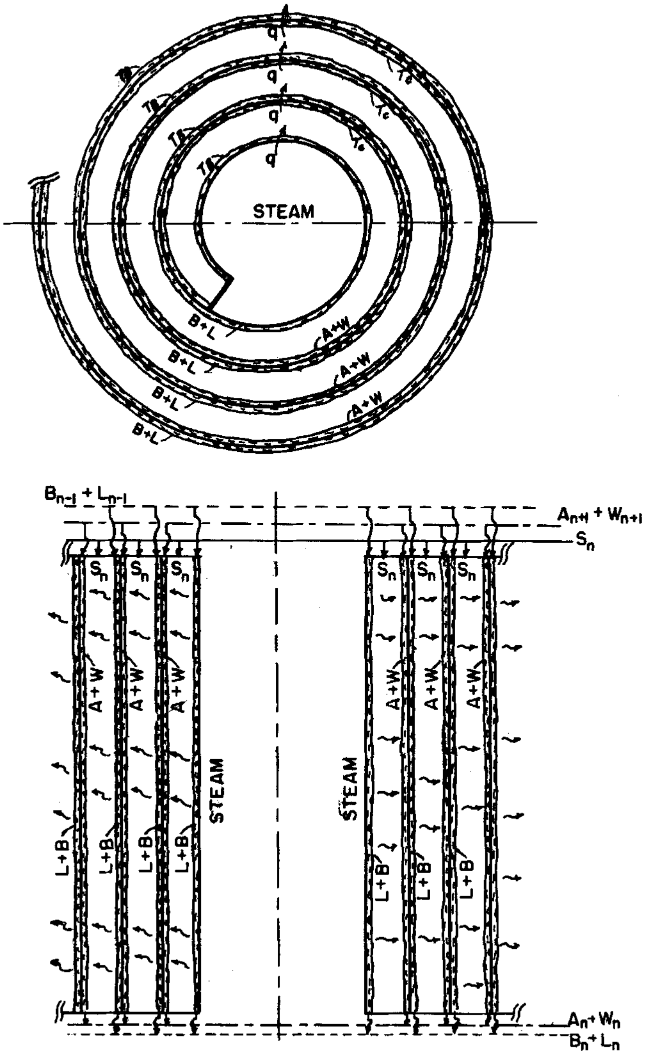


Fig. 9. Spiral vertical plate evaporator.

The proposed evaporators which are applicable to this process are extremely simple in their construction.

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NOTATION

A_n = organic solution of α and β leaving the condenser of stage n evaporator

A_n' = organic solution of α and β existing in the condenser of stage n evaporator

B_n = organic solution of α and β leaving the boiling side of stage n evaporator

B_n' = organic solution of α and β existing in the boiling mass of stage n evaporator

h_A = enthalpy per pound of A stream
h_B = enthalpy per pound of B stream
h_L = enthalpy per pound of L stream
h_W = enthalpy per pound of W stream.
H_W = enthalpy per pound of water vapor
L_n = aqueous solution leaving stage n evaporator
L_n' = aqueous solution in the boiling mass of stage n evaporator
N = total number of stages
q_m = makeup heat
S_m = makeup steam
T_b = temperature of a boiling mass
T_c = temperature of a condensing mass
α = absorbent used to raise condensation temperature
β = boiling-point depressor

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Concentrated Polymer Solution: Part II.

Dependence of Viscosity and Relaxation Time on Concentration and Molecular Weight

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A previously presented molecular theory for non-Newtonian viscosity in moderately concentrated polymer solutions is extended here to a specific consideration of the influence of solute concentration c and molecular weight M on the limiting viscosity η_0 and the relaxation time λ. Estimates of the M,c dependence of several intermediate functions are necessary including that of Kirkwood's friction coefficient. The prediction $\eta_0 \sim (cM^{0.625})^2$ is in good agreement with the empirical observation that η_0 is a function of the parameter $cM^{0.68}$, but is inadequate for extremes of M and c. Plausibility arguments are advanced to suggest $\lambda \sim \eta_0 c^{-2}$ rather than $\lambda_{\text{dil.}} \sim M\eta_0 c^{-1}$ predicted by dilute solution theory and widely accepted. This would explain the utility of the factor c^2 used in recent rheological correlations, and would reconcile some conflicting reports of $\lambda(M)$ measurements.

A rather general formulation for the stress tensor in solutions of flexible polymers has been given by Fixman (*6*). This was discussed recently by Williams (*20*), who attempted to specialize it to the case of concentrated solutions by emphasizing intermolecular force effects. Williams introduced several mathematically tractable and physically plausible approximations for the intermediate functions needed to calculate the stress during shear flow.

One of these functions was $\nu(\mathbf{R})$, the spatial distribution of a polymer's segments with respect to its center ($\mathbf{R} = 0$). When a shear-dependent approximation to ν was inserted into the general intermolecular potential expression (*7*)

$$V(\mathbf{r}) = A \int \nu(\mathbf{R})\, \nu(\mathbf{r} + \mathbf{R})\, d\mathbf{R} \qquad (1)$$

where $\mathbf{r}$ is the vector between polymer molecular centers and A is a characteristic constant, there was obtained

$$V = \frac{A}{\sqrt{1 + \lambda^2\gamma^2}} \left(\frac{B}{2\pi}\right)^{3/2} \exp\left\{\frac{-B}{2(1 + \lambda^2\gamma^2)} \left[(x - \lambda\gamma z)^2 + (1 + \lambda^2\gamma^2)y^2 + (1 + 3\lambda^2\gamma^2)z^2\right]\right\} \qquad (2)$$

with $\gamma = dv_x/dx$ as the shear rate, λ an unspecified time constant, and B effectively a scale factor for a polymer molecule.

Since it was assumed (*6*) that potentials were pairwise additive, the stresses could be calculated by computing certain averages with respect to the pair correlation function $g(\mathbf{r})$. For a state of shear, $g(\mathbf{r})$ can be perturbed as (*15*)

$$g = g_o(r)\left[1 + \frac{\xi\gamma}{kT} \cdot Cf(r) \cdot h(\theta, \phi) + \ldots .\right] \qquad (3)$$

where ξ is Kirkwood's friction coefficient (in polymer pair space) and C is a constant arising from the integration performed to determine $f(r)$. It was then necessary to choose a second function $g_o(r)$, the radial distribution function. Because polymer molecular domains overlap in concentrated solutions, the value $g_o \cong 1$ was used (*2*, *8*); physically this means that the liquid contains a uniform density of polymer molecules. The form of $f(r)$ in Equation (3) was also determined through application of $g_o = 1$.

When these expressions for $V(r)$ and $g(r)$ were introduced into the integrals describing stress, the non-Newtonian viscosity η was evaluated directly in terms of well-known functions. Results were written as

$$\frac{\eta - \eta_s}{\eta_o - \eta_s} = S(\lambda\gamma) = 1 - \frac{9}{14}\lambda^2\gamma^2 \ldots \qquad (4)$$