Total heat above 32° F. in the fatty acid distilled = Heat taken up by condensing water + Heat lost by evaporation of condensing water + Heat lost by radiation from condenser shell

− [Total heat above 32° F. of steam entering condenser − Total heat above 32° F. in steam leaving condenser − Heat above 32° in water carried over with stock into settling tank]

+ Heat to raise stock in condenser drum from 32° F. to drum temperature + Heat to raise stock from catch basin from 32° F. to condenser temperature

Substituting the proper figures in this heat balance, and dividing by the quantity of fatty acid distilled, we find: Total heat above 32° F. per lb. of fatty acid distilled = 315.3 B. t. u. for Test A

Whence, on the assumptions before stated, we have: Heat of vaporization per lb. of fatty acid at 24.51 in. vacuum = 315.3–0.46 (433.8–32) = 130.5 B. t. u.

Similarly we find for Test B the values 308.2 B. t. u. and 118.0 B. t. u., but at 25.14 in. vacuum.

9 per cent. This discrepancy can be accounted for in two ways: Firstly, the stock was not the same in both cases. Undoubtedly, there was some difference in the mixtures being distilled, but unfortunately no chemical analyses were made to determine the difference; secondly, the two tests were made at somewhat different pressures and temperatures.

The heat of vaporization differs with temperature. If it did not the vapor pressure curve would be a straight line, and this we know is not the case. Probably the discrepancy is due to a combination of these two factors.

The writer desires to express his appreciation of the assistance rendered in this work by Messrs. S. B. Murdock, J. W. Bodman, and A. D. Whitby, and to thank the N. K. Fairbanks Company, through whose courtesy these figures are published.

NUMERICAL RELATION BETWEEN CELLS AND TREATMENTS IN EXTRACTION PROCESSES

By L. F. Hawley

Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin

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In a previous study of extraction processes[1] conducted at the U. S. Forest Products Laboratory, Madison, Wisconsin, it was found that no definite relation had ever been developed between the number of solvent treatments received by each charge of material and the number of cells or extractors required to furnish this number of treatments. It was also evident that the ideas in regard to such a relation were very much confused, and that the usual conception was the entirely unfounded one that for a certain number of treatments an equal number of cells was required or the same number plus one.[2] After it had been determined how many treatments in series were required for efficient extraction and how much time would be required for boiling, pumping, discharging, charging, etc., there was still no method by which it could be determined how many cells or extractors would be required by the process.

In the development of the numerical relation between the cells and the treatments it will be necessary to consider a general case covering all conditions; and this will require the use of terms and the assumption of conditions that may seem unusual or impractical to operators who have had experience with only one kind of extraction process and have used a peculiar set of terms for describing the various operations. On this account indulgence is requested from the readers who find unusual processes described in unusual terms, and they are asked to overlook these until the general principles become clear.

There is, of course, a definite relation between the number of cells and the number of treatments. It varies with different methods of manipulation, however, and several conditions of treatment must be known accurately before the relation can be developed. It is necessary to know the amount of time required for the operations performed on each charge other than the typical extraction operations, and this time must be known in terms of the typical extraction operations. These latter operations are:

1—The movement of solvent from one charge to another, from the last charge to storage or from the solvent tank to the first charge, which movements will be called "pumping" and designated by p.

2—The period of the actual solution action of the solvent on the charge, whether by standing, boiling, or agitating, which will be called "boiling" and designated by b. These typical operations are necessary parts of every discontinuous extraction process and may vary only in the time required for their fulfillment.[1] While there are only these two kinds of extraction operations, each may take place a variable number of times in a complete cycle of extractions. The non-extraction operations may vary widely in number, kind, and time required, and include charging and discharging the cells, or any preliminary or after-treatment performed on the charge while in the cells.

SIMULTANEOUS PUMPING

The simplest way to determine the relation between the number of treatments and the number of cells in terms of the time required for the various operations seems to be to use cut and try methods under several different sets of conditions and then to find the complete mathematical relation by inspection. This can be readily done by representing a series of extractions graphically. The easiest system to start with is one in which the pumping of all cells in action is done simultaneously. A series of extractions in four cells by this system can be represented as in Fig. 1.

In this method of representation the arrows indicate movement of the solvent or pumping; for instance, the first line of the diagram indicates simultaneous move-

[1] This Journal, 9 (1917), 866.

[2] Kressmann, *Met. & Chem. Eng.*, 15 (1916), 78.

[1] As will be seen later, b may equal zero in some cases.

ment of solvent from cell 2 to cell 3, cell 3 to cell 4, and cell 4 to storage, while line 3 indicates simultaneous application of fresh solvent to cell 3, and movement of solvent from cell 3 to cell 4, and from cell 4 to cell 1. All cells are assumed to contain solvent except those with a double circle. Those indicated in line 2 as containing solvent but without solvent movement show the extraction or boiling period. By following this series of operations we find that a complete cycle has been finished in 16 lines and that line 17 is the same as line 1. During this cycle each cell receives 5 treatments and each batch of solvent is used 5 times. It will be noted that for a period of 3 boilings and 2 pumpings (indicated by braces) each cell stands idle so far as solvent action is concerned; this period is the time available for charging and discharging and for other preliminary or after-treatment of the charge. The relation between this idle period, n, the number of cells, c, and the number of treatments, t, in terms of the boiling period, b, and the pumping period, p, will now be worked out.[1] In the case just shown $n = 3b + 2p$ when $c = 4$ and $t = 5$.

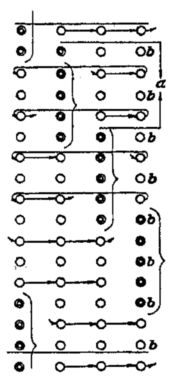

FIG. 1

SIMULTANEOUS PUMPING 4 CELLS 5 TREATMENTS

$n = 3b + 2p$
$a = 2b + 2p$

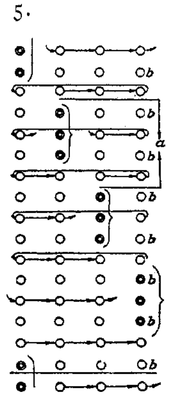

FIG. 2

SIMULTANEOUS PUMPING 4 CELLS 6 TREATMENTS

$n = 2b + p$
$a = 2b + 2p$

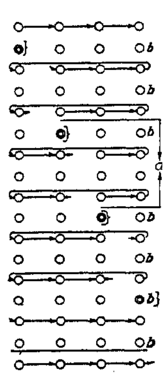

FIG. 3

SIMULTANEOUS PUMPING 4 CELLS 7 TREATMENTS

$n = b$
$a = 2b + 2p$

In Fig. 2 is shown the same number of cells so used as to give each cell one more treatment. This arrangement shortens the idle period n to $2b + 1p$ and our next relation is that when $c = 4$ and $t = 6$, $n = 2b + p$. In the same way when one more treatment is obtained, the maximum possible in 4 cells, the time available for discharging, charging, etc., is reduced to a single boiling period. (See Fig. 3.)

Similar diagrams for various other numbers of cells and treatments were made and from them was prepared Table I in which the general relation between the factors c, t, n, b, and p becomes apparent.

From inspection of the table it is seen that n is composed of boiling periods equal in number to twice the number of cells minus the number of treatments, and of pumping periods always one less than the number of boiling periods, or

$$n = b(2c - t) + p(2c - t - 1) \text{ or } t = 2c - \frac{n + p}{b + p}.$$

It is suggested that more confidence in the table and in the formula derived from it will be produced if the reader will verify a few of the relations shown in the table by preparing diagrams similar to these given, but for different values of c or t. This procedure will also make it possible to follow the further similar developments more readily.

TABLE I—ALL CELLS PUMPED AT ONE TIME

CELLS c	TREATMENTS t	Time Available for Charging, Discharging, etc. n	Time between Discharges a
2	2	$2b + 1p$	$2b + 2p$
2	3	$1b$	$2b + 2p$
3	2	$4b + 3p$	$2b + 2p$
3	3	$3b + 2p$	$2b + 2p$
3	4	$2b + 1p$	$2b + 2p$
3	5	$1b$	$2b + 2p$
4	3	$5b + 4p$	$2b + 2p$
4	4	$4b + 3p$	$2b + 2p$
4	5	$3b + 2p$	$2b + 2p$
4	6	$2b + 1p$	$2b + 2p$
4	7	$1b$	$2b + 2p$
5	3	$7b + 6p$	$2b + 2p$

It should be noted further that in this method of operation, *viz.*, simultaneous pumping of all cells with a boiling period after every pumping period, the time elapsed between any similar operations on successive cells (which is the measure of the output of the system) is always the same, $2b + 2p$, whatever the number of cells or treatments. This period is indicated by a on the diagrams and shows the time elapsed between the beginning discharge of two consecutive cells.

CONTINUOUS EXTRACTION

It should be noticed here that these formulas are applicable also to continuous extraction. Continuous extraction is the same as the system of simultaneous pumping just described in which $b = 0$ and p is the period of time required for moving the liquid contents of one cell to the next or to storage. Under these conditions, $n = p(2c - t - 1)$ or $t = 2c - \frac{n + p}{p}$, and $a = 2p$.

SEPARATE PUMPING

It has been shown[1] that the method of pumping all cells simultaneously gives much less efficient extraction than pumping one cell at a time. It might possibly be thought that the pumping of only one cell at a time would take so much longer that in the case of a large number of cells it would lose more in time than would be gained in efficiency of extraction. Some very interesting comparative figures are obtained by developing the relations between c, t, n, etc., under this method of pumping. The method of representation of the extraction process is the same as in the other case, and the diagram, Fig. 4, shows that in an operation of 6 treatments in 4 cells $n = 2b + 4p$.

In this method there are two other variable time periods which are important and will also be studied; these are the average length of time each charge is boiled with each separate batch of solvent, designated by e, and the time elapsed between successive discharges, designated by a.

In this method of pumping the actual length of time each charge is boiled with each batch of solvent is not always the boiling period b only, but is variable. This is due to the fact that sometimes only one and

[1] The letters used in designating the different variables are all shown either in this sentence or in the headings of Tables I and II.

[1] THIS JOURNAL, *Loc. cit.*

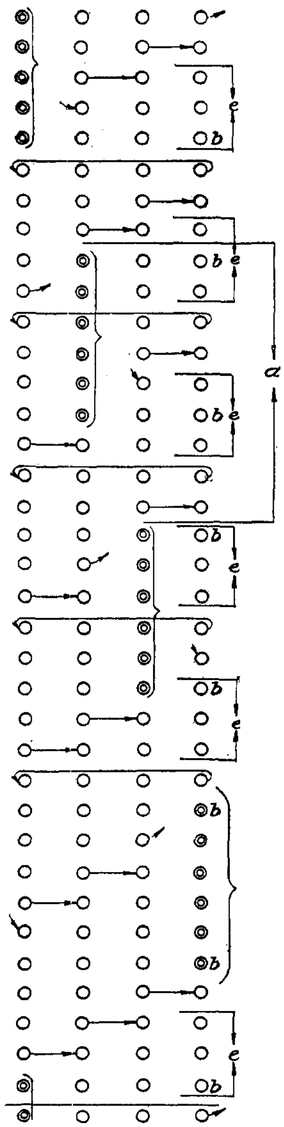

Fig. 4

Separate Pumping
4 Cells 6 Treatments

$n = 2b + 4p$
$a = 2b + 7p$
$e = b + 2p$

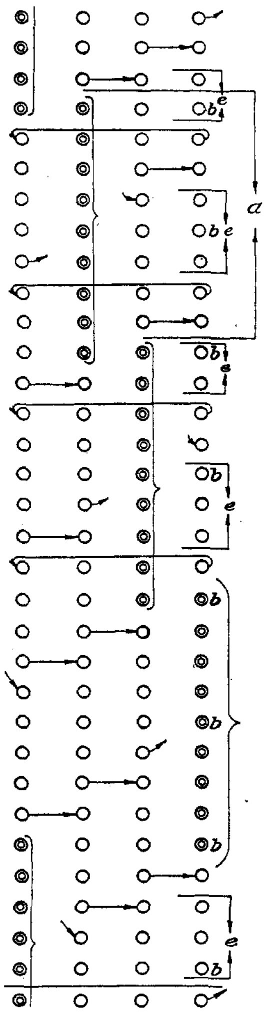

Fig. 5

Separate Pumping
4 Cells 5 Treatments

$n = 3b + 6p$
$a = 2b + 6p$
$e = b + 8/5\,p$

never more than two cells are in the pumping stage at one time, and as soon as one cell is pumped full it can immediately enter the boiling stage while the others are being pumped.

Table II—Each Cell Pumped Separately

Cells c	Treatments t	Time Available for Charging, Discharging, etc. n	Time between Discharges a	Average Single Boiling Period e
2	3	$1b$	$2b + 4p$	$b + 2/3\,p$
2	2	$2b + 2p$	$2b + 3p$	b
3	5	$1b$	$2b + 6p$	$b + 8/5\,p$
3	4	$2b + 3p$	$2b + 5p$	$b + p$
3	3	$3b + 4p$	$2b + 4p$	$b + 2/3\,p$
3	2	$4b + 5p$	$2b + 3p$	$b + 0\,p$
4	7	$1b$	$2b + 8p$	$b + 18/7\,p$
4	6	$2b + 4p$	$2b + 7p$	$b + 2p$
4	5	$3b + 6p$	$2b + 6p$	$b + 8/5\,p$
4	4	$4b + 8p$	$2b + 5p$	$b + p$
4	3		$2b + 4p$	
5	9	$1b$	$2b + 10p$	$b + 32/9\,p$
5	8	$2b + 5p$	$2b + 9p$	$b + 3p$
5	7	$3b + 8p$	$2b + 8p$	$b + 18/7\,p$
5	6	$4b + 11p$	$2b + 7p$	$b + 2p$

In the diagram showing 6 treatments in 4 cells, $e = b + 2p$ and $a = 2b + 7p$. In the next diagram, Fig. 5, showing 5 treatments in 4 cells the time n has increased to $3b + 6p$, $e = b + 8/5\,p$ and $a = 2b + 6p$.

In the same way diagrams have been prepared showing a wide variation in number of cells and number of treatments, and the resulting values for n, a, and e are given in Table II.

From this table the following formulas were developed[1] showing the various relations between c, t, n, a, and e.

Extractions in Which Every Charge Receives Two Treatments with Fresh Solvent

Simultaneous Pumping

$$n = (3c - t)\,b + (3c - t - 1)\,p$$

$$a = 3b + 3p$$

$$e = b$$

Separate Pumping

$$n = bc\,(3c - t - 1) - (3c - t\left(\frac{3c - t - 1}{3}\right)p \text{ when } t \text{ is multiple of } 3$$

$$n = bc\,(3c - t - 1) - \frac{(3c - t - 1)^3 - (3c - t - 1)}{3\,(3c - t)}\,p \text{ when } t \text{ is not multiple of } 3$$

$$a = 3b + (t + 2)\,p$$

$$e = b + (t/3 - 1)\,p \text{ when } t \text{ is multiple of } 3$$

$$e = b + \frac{(t - 1)^3 - (t - 1)}{3t^2}\,p, \text{ when } t \text{ is not multiple of } 3$$

$$n = (2c - t)b + c(2c - t - 5)p + (2t + 4)p \qquad (1)$$

$$a = 2b + (t + 1)p \qquad (2)$$

$$e = b + \frac{(t - 1)^2}{2t}\,p \text{ (when } t \text{ is odd)} \qquad (3)$$

$$e = b + \frac{t - 2}{2}\,p \text{ (when } t \text{ is even)}$$

These formulas are of particular interest in showing that:

1—The extra time available for charging, discharging, etc., n, varies directly with the number of cells and inversely with the number of treatments obtained.

2—The length of time between successive discharges of material, a, which is really the reciprocal of the capacity of the system, is *not* influenced by the number of cells but is increased to a slight extent by an increased number of treatments.

3—The average actual time each charge is exposed to the boiling operation is not affected by the number of cells but varies to a slight extent with the number of treatments.

APPLICATION OF FORMULAS

Suppose for example it had been determined that a certain extraction process would require 6 treatments and that the pumping would take 10 min., the boiling 15 min., and the charging, discharging and solvent recovery 1.5 hrs. How many cells would be required for the process?

[1] The development of similar formulas for extractions in which every charge receives two treatments with fresh solvent (This Journal, *Loc. cit.*) will not be given in detail but following are the formulas for this method of extraction which have been developed by the same method as the foregoing.

$$
\begin{aligned}
n &= b(2c - t) + p(2c - t - 1)\\
90 &= 15(2c - 6) + 10(2c - 6 - 1)\\
&= 30c - 90 + 20c - 70\\
90 &= 50c - 160\\
250 &= 50c\\
c &= 5
\end{aligned}
$$

If, however, n had been 60 min. instead of 90 min. the value of c would have come to 4.4; this would mean that either 5 cells would have to be used with a wait of 30 min. after charging before the first batch of solvent is ready to run on or else the time of boiling or of pumping would have to be lengthened so that 4 cells could do the work. If, for instance, 4 cells are to do the work, the boiling period must be lengthened to 25 min.

$$
\begin{aligned}
60 &= b(8 - 6) + 10(8 - 6 - 1)\\
60 &= 2b + 10\\
b &= 25
\end{aligned}
$$

or the pumping period to 30 min.

$$
\begin{aligned}
60 &= 15(8 - 6) + p(8 - 6 - 1)\\
60 &= 30 + p\\
p &= 30.
\end{aligned}
$$

These examples show the method of using the formula in determining the number of cells required under different conditions of treatment.

COMPARISON OF SIMULTANEOUS AND SEPARATE PUMPING SYSTEMS

The formulas also make it possible to compare the time consumed between discharges when pumping simultaneously with that consumed when pumping separately, other conditions of extraction being the same. If we take, for instance, a series of 6 extractions in 4 cells, $b = 15$ and $p = 5$. With separate pumping n will be $15(8 - 6) + 4(8 - 6 - 5)5 + (12 + 4)5 = 30 - 60 + 80 = 50$

a will be $30 + (6 + 1)5 = 65$, and

e will be $15 + \dfrac{6 - 2}{2}\, p = 25$.

For a comparison it would not be fair to use b with the same value in simultaneous pumping as in separate pumping because in the latter case, in the example just given, although b is 15, the *actual* total boiling time for each charge, e, is 25 min. $(b + 2p)$; in order to have conditions the same in the two systems, therefore, the value of b in simultaneous pumping (which is always the actual total time of the boiling) must be 25 min. With $c = 4$, $t = 6$, $b = 25$, and $p = 5$ in simultaneous pumping

$$
\begin{aligned}
n &= 25(8 - 6) + 5(8 - 6 - 1) = 50 + 5 = 55\\
a &= 2b + 2p = 50 + 10 = 60\\
e &= b = 25.
\end{aligned}
$$

That is, a, the time required between successive discharges of material is a little less in the case of simultaneous pumping.[1] But there is a practical consideration which changes this relation slightly; pumping several cells at the same time is likely to take longer than pumping a single cell, and therefore if p (sim) $= 8$, then a (sim) $= 50 + 16 = 66$ min., and a (sep) $= 30 + 35 = 65$ min., that is, when the pumping time is increased a little to allow for the increased difficulty of pumping several cells instead of one cell, the time required for a complete cycle may be the same or even less in the case of separate pumping.

[1] Although this is only one case it may be shown that the difference between a (sep) and a (sim), with other conditions the same, is always p when t is even and $\frac{t-1}{t}\, p$ when t is odd.

SUMMARY

1—Formulas have been developed which show the relation between the number of cells and number of treatments in terms of various typical extraction operations both for separate and simultaneous pumping of the solvent in the cells. The formulas for simultaneous pumping are also applicable to continuous extraction processes.

2—These formulas make it possible to determine the number of separate cells or extractors required to furnish a certain number of treatments or extractions for each charge when the time required for each of the various operations is known.

3—With the formulas the time relation between simultaneous pumping and separate pumping has been developed, showing no advantage or very slight advantage for the former.

VAPOR COMPOSITION OF ALCOHOL-WATER MIXTURES

By W. K. Lewis

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

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In the field of distillation there is no more important problem than the separation of ethyl alcohol from aqueous solutions. Accuracy in the design of apparatus for this separation is absolutely dependent upon exact data as to the composition of the vapors given off by any specific mixture of the two liquids. The data on this point hitherto available in the literature have been inadequate and unreliable. The figures usually accepted are those recalculated for Maercker[1] by Dönitz from the original experimental results of Gröning. These data check reasonably the results obtained a half century ago by Duclaux.[2] The more recent work of Sorel does not check that of Gröning and is apparently less reliable. The work of Evans[3] is obviously unreliable in view of the fact that he finds the composition of vapor and liquid identical at 92 per cent by weight, whereas a distillate of higher than 95 per cent alcohol can be obtained in commercial practice.

In 1913 Wrewsky[4] published the results of a series of careful determinations of the vapor composition of alcohol-water mixtures, which bear the earmarks of reliability. On the other hand, Wrewsky's work was done, not at constant pressure, but at constant temperature. Furthermore, he operated at only three temperatures, approximately 40°, 55°, and 75° C. His work is, therefore, not directly available for industrial practice because the industrial distillation

[1] "Handbuch der Spiritus Fabrikation," 7th Ed., Berlin (1898), 590.

[2] *Ann. chim. phys.*, **14** (1878), 305.

[3] THIS JOURNAL, **8** (1916), 261.

[4] *Z. phys. Chem.*, **81** (1912), 1.