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APPENDIX I

Recommended Van der Waals Radii and Volumes

The calculation of V_w requires knowledge of the van der Waals radii and of the appropriate covalent bond distances between two bonded atoms in a molecule. A recent reevaluation of r_w data from X-ray diffraction patterns of crystals together with crystal density data at O°K, gas kinetic collision radii of small molecules, and critical densities,* has yielded the radii shown in Table 3.

The van der Waals volume and the molecular surface area are calculated by combination of r_w with the covalent bond distance (data for which can be found in most chemistry text books) according to the model shown in Figure 8. The results are presented in the form of V_w and A_w group increments in Table 4. Special effects due to bond contraction or expansion in cases of double-bond conjugation or hyperconjugation can be found in the footnotes to the table.

APPENDIX II

Energy of Vaporization Data

The reducing parameter for temperature proposed in this paper is $E°/R$, where $E°$ is defined as $\Delta E_v = \Delta H_v - RT$ at the temperature where $V^* = 1.70$. This temperature and the appropriate heat of vaporization have been calculated from density and low-temperature vapor-pressure data for a large number of hydrocarbons. Tables 5, 6, and 7 contain the information necessary to estimate the energy of vaporization of a number of different hydrocarbons. The same scheme is being developed for nonhydrocarbon substances.

* It is noteworthy that for 100 out of 124 substances tried, $V_c = 5.3 \pm 0.3\ V_w$. Details of this correlation will be published elsewhere.

Concurrent Gas Absorption Mass Transfer

W. S. DODDS, L. F. STUTZMAN, B. J. SOLLAMI, and R. J. McCARTER

General Food Corporation, Tarrytown, New York

Concurrent flow in gas absorption may be used to practical advantage when liquid partial pressure is minor. The higher transfer coefficients of this operation are reported and analyzed in reference to pertinent variables.

Gas absorption in packed towers with countercurrent flow of gas and liquid has been studied extensively. Several investigators (*1*, *2*, *4* to *9*, *11* to *15*) have reported on the materials of this study; however mass transfer in concurrent flow systems has received little attention.

The general preference for counter-

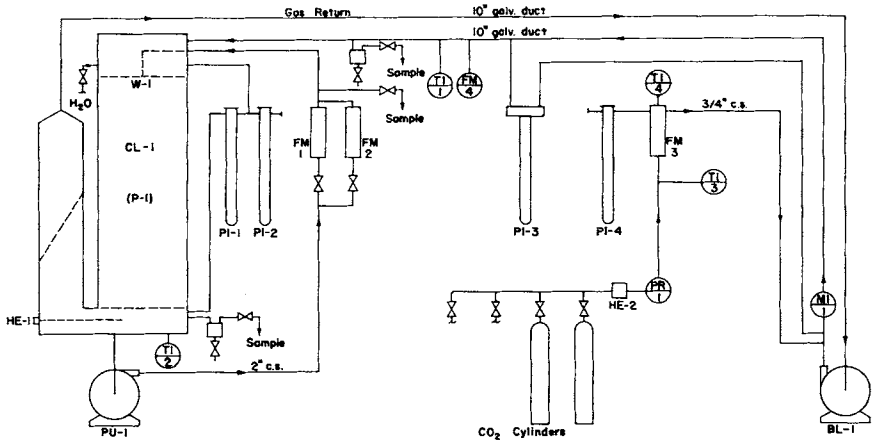

Fig. 3. Mass transfer coefficients.

current flow is apparent from inspection of the simplified equation for gas absorption:

$$N_L = K_g a\, V (\Delta p)_m$$

For a given system and conditions the amount of material transferred is proportional to the potential gradient or driving force, $(\Delta p)_m$, or its equivalent, $P_T\ (\Delta y)_m$. A more efficient operation results from the greater driving force of countercurrent flow (Figure 1*a*) than that of concurrent flow (Figure 1*b*) with the same terminal conditions when the liquid partial pressure varies with concentration. However when the liquid partial pressure is constant or negligible, this advantage ceases, and the driving force and transfer of the two systems tend to be equivalent (Figures 1*c* and *d*).

Such a system was used in this study, with carbon dioxide being absorbed in caustic solutions. Thus it was possible to exploit without disadvantage the higher transfer coefficients that may be attained with concurrent flow. The flow rates in countercurrent operation are limited by the flooding point and probably cannot practically exceed the loading point. But in concurrent operation the flow rates are limited only by the feasible amount of power to be expended in pressure-drop losses. Thus high flow rates under stable operating conditions may be attained and used to yield high transfer coefficients. A wider range for design is in this way obtained, within which to optimize equipment and lower costs.

SCOPE OF INVESTIGATION

High flow rates were selected for this study at levels where countercurrent operation would be impossible and where the greater utility of concurrent flow could be attained. It was anticipated that the data would provide valuable design information in this higher range and be useful in improving over-all correlations. The range of these rates is generally higher than the flooding curves for countercurrent operation, according to the correlation of Lobo (*10*), and hence appreciably higher than the loading curves representing the practical limit in countercurrent operation.

The variables that were investigated were

Temperature (T) = 80° and 130°F.
Packing (P) = Berl saddles 1 and 1½ in., Intalox saddles 1 and 1½ in., and steel rings 2 in.
Liquid flow rate (L) = 17 and 59.4 gal./min./sq. ft. (9,330 and 32,600 lb./(hr.)(sq. ft.) of 2.5N sodium hydroxide
Gas flow rate (G) = 22.7 and 56.6 lb. moles/(hr.)(sq.ft.)
Sodium normality (N) = 2.0, 2.5, 3.0, 3.5, and 4.0
Percentage of conversion (C) of hydroxyl to carbonate in entering solution = 0 to 100%
Material = sodium and potassium

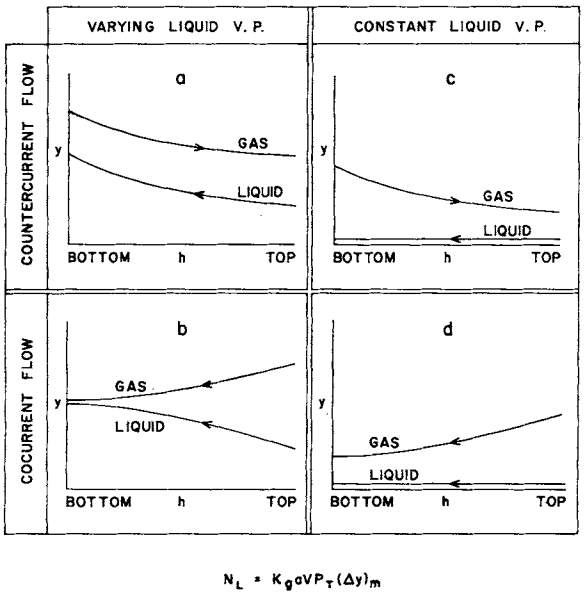

Fig. 1. Driving force.

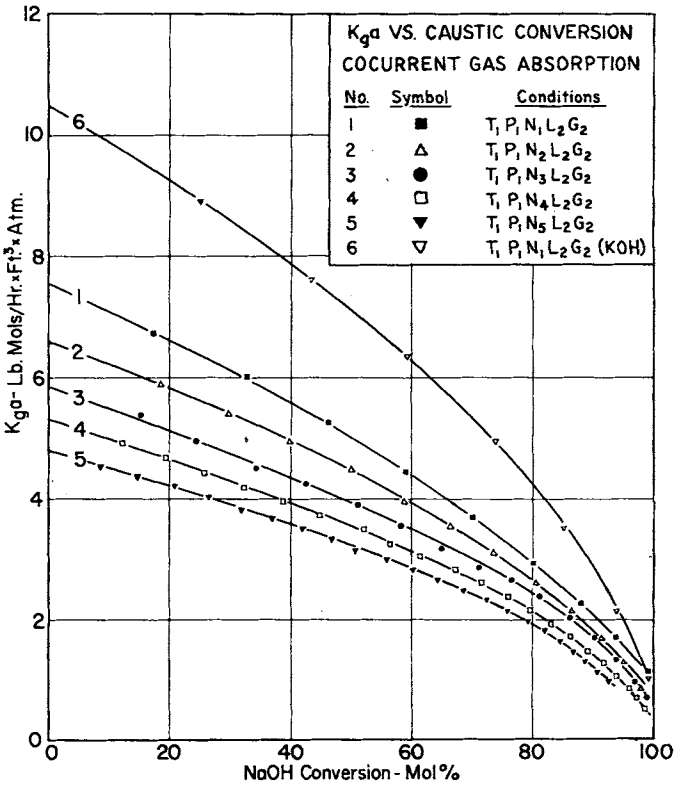

Fig. 2. Flow sheet for concurrent flow.

hydroxides

EQUIPMENT

The equipment used in this study is described in Figure 2.

EXPERIMENTAL PROCEDURE

The caustic solution was used to depletion in each run, so that transfer values were determined for the full range of caustic composition at a fixed concentration of sodium ions. The tower sump was first filled with a predetermined volume of caustic solution of the desired strength, which was maintained constant by the addition of water to replace evaporation losses. Liquid and gas streams were run until the packing was saturated and flow patterns were stabilized. Carbon dioxide was then introduced into the gas stream to constitute about 1 mole % concentration. During each run conversion of base to carbonate gradually progressed to completion, while all other conditions were maintained constant.

Recorded data included temperatures and flow rates of the liquid and gas streams. The liquid temperature varied less than 1°F. through the system because of the high flow rates. The temperature of the exit gas stream was within 1°F. of the liquid temperature. The recorded pressures included barometric pressure (mm.Hg), inlet gas-stream gauge pressure (mm.Hg), and pressure differential across the tower (inches of 0.827-gravity red oil). The carbon dioxide analyses of gas samples were obtained by measuring the weight increase resulting from absorption in Ascarite and anhydrone. As the gas stream was recirculated during the runs at the 130°F. temperature level, it was necessary to adjust the injection of replacement carbon dioxide as the run progressed and the rate of absorption decreased.

The transfer rate was calculated from the liquid analyses and liquid rates and was plotted against the mean of the time interval for sample collection. The smoothed values of N_L obtained from these curves were used for subsequent calculations. The carbon dioxide absorbed per hour also was calculated from the gas analyses and gas rates and the material balance afforded by comparison of N_L and N_G usually varied between 90 and 110% agreement. Deviations outside this range usually occurred when gas composition changed only slightly in transit through the tower and the accuracy of N_G was correspondingly low. The values of N_L were considered more reliable than those of N_G and were used to calculate $K_g a$ from the equation

$$N_L = K_g a \, V P_T (\Delta y)$$

An outlet gas composition was calculated from the liquid analyses and was used, rather than the analyzed composition, to obtain more consistent results.

The calculated values of $K_g a$ were plotted against the percentage conversion of hydroxide to carbonate, as exemplified by Figures 3 and 4. These figures summarize the runs involving solution normality, packing, and type of caustic as

TABLE 1. $K_g a$ VALUES DERIVED FROM DATA CURVES

			% Conversion OH^- to $CO_3^=$	0%		20%		40%		60%		80%	
				T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
P_1	N_1	L_1	G_1	3.9	8.4	3.6	7.3	3.1	6.1	2.5	4.9	1.7	3.4
			G_2	4.4	8.8	3.9	7.7	3.3	6.6	2.7	5.2	1.9	3.6
		L_2	G_1	5.8	8.3	5.2	7.6	4.5	6.8	3.7	5.8	2.7	4.3
			G_2	7.6	12.7	6.6	11.2	5.6	9.6	4.4	7.7	2.9	5.3
	N_2	L_1	G_1	4.2	6.9	3.8	6.3	3.2	5.7	2.5	4.7	1.6	3.2
			G_2	4.4	9.5	3.8	8.2	3.3	6.8	2.6	5.4	1.8	3.7
		L_2	G_1	6.2	10.7	5.5	9.4	4.8	8.0	3.8	6.3	2.7	4.4
			G_2	6.6	11.9	5.8	10.7	5.0	9.3	3.9	7.6	2.6	5.3
P_2	N_1	L_1	G_1	3.7	8.7	3.2	7.4	2.8	6.1	2.2	4.7	1.5	3.1
			G_2	3.8	7.0	3.4	6.3	2.9	5.6	2.3	4.6	1.5	3.2
		L_2	G_1	4.9	9.7	4.4	8.4	3.8	7.0	3.1	5.5	2.2	3.8
			G_2	5.1	10.8	4.6	9.6	3.9	8.2	3.1	6.6	2.1	4.6
	N_2	L_1	G_1	3.6	6.7	3.1	5.9	2.7	5.1	2.1	4.1	1.4	3.0
			G_2	3.6	7.3	3.2	6.4	2.8	5.5	2.2	4.3	1.5	3.0
		L_2	G_1	4.6	9.7	4.1	8.6	3.6	7.3	2.9	5.9	2.1	4.1
			G_2	5.1	10.8	4.6	9.5	4.0	8.2	3.2	6.6	2.2	4.7

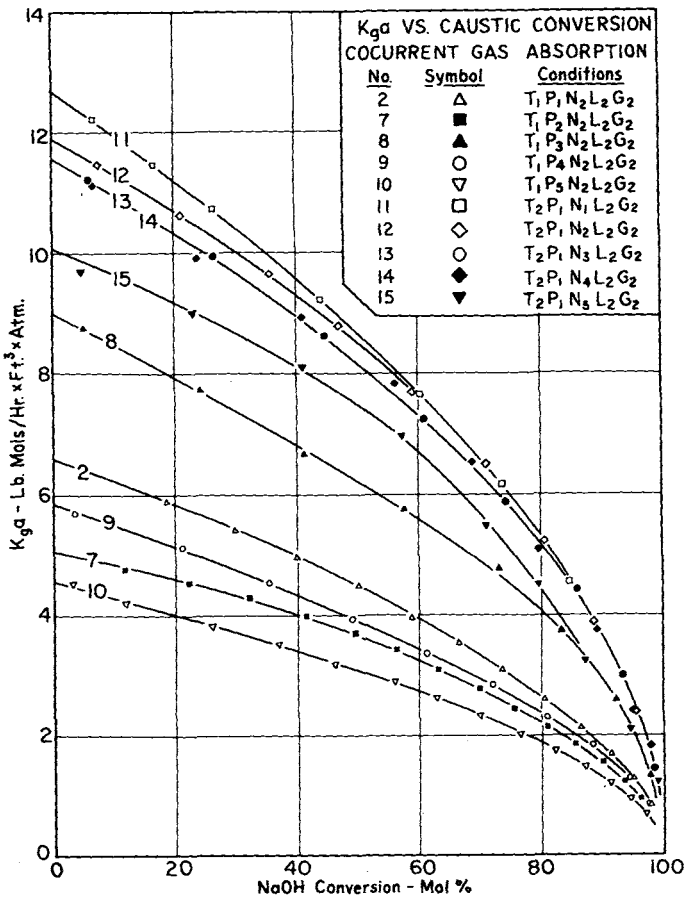

Fig. 4. Mass transfer coefficients.

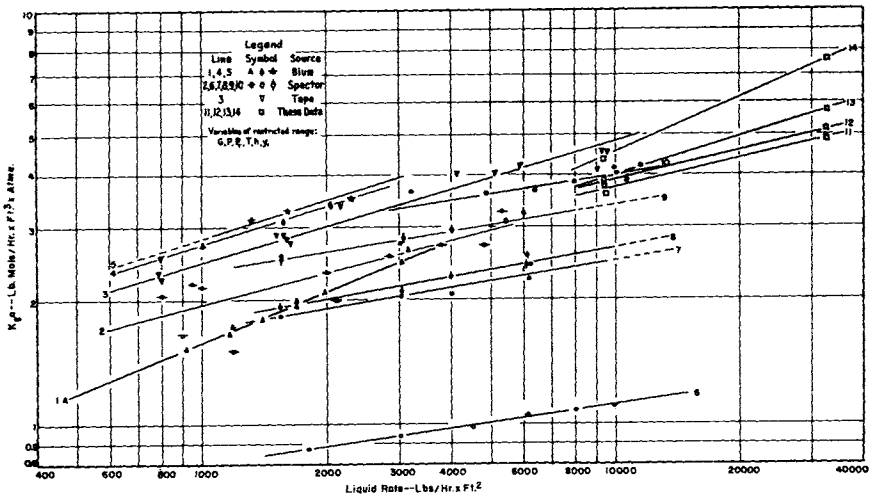

Fig. 5. Carbon dioxide absorption with sodium hydroxide solutions, liquid-rate effect.

individual variants. Similar curves were employed to derive the values of K_ga presented in Table 1, which summarizes the rest of the results.* These runs form various factorial designs. The configuration of Table 1 evidences one such design with five variables at two levels and one variable at additional levels.

DISCUSSION

The simpler effects of the variables are apparent from inspection of Figures 3 and 4 and Table 1 and do not warrant discussion.

The data were compiled in factorial designs as a means toward extracting the most information per study and to facilitate statistical evaluation of the data. Various statistics could be used. The first treatment used was direct analysis of variance of the transfer coefficient. The procedure for such analysis is explained in Brownlee (3) and other texts on statistics. Against this additive model [$K_ga = f(T) + f(P) + f(N) + \ldots$.] numerous interactions of the variables were tested and found to be significant, but the results were unfortunately complex. As a next step the natural logarithm of the transfer coefficient was analyzed for variance. Against this multiplicative model [$\log K_ga = \log f(T) + \log f(P) + \log f(N) + \ldots$.] a simpler picture emerged. Results of a typical analysis are summarized in Table 2. In this set of data significance was indicated for the effects of temperature, packing, liquid rate, and gas rate, and for first-order interactions between temperature and packing and between liquid and gas rates. (In this case normality was not significant but would become so at higher values, as indicated by the data of Figures 3 and 4.) Although this process serves to identify effects of consequence and something of the nature of the relationship, it does not necessarily disclose the specific functions that may best relate the effects. It appears that additional data at more levels will be needed to delineate

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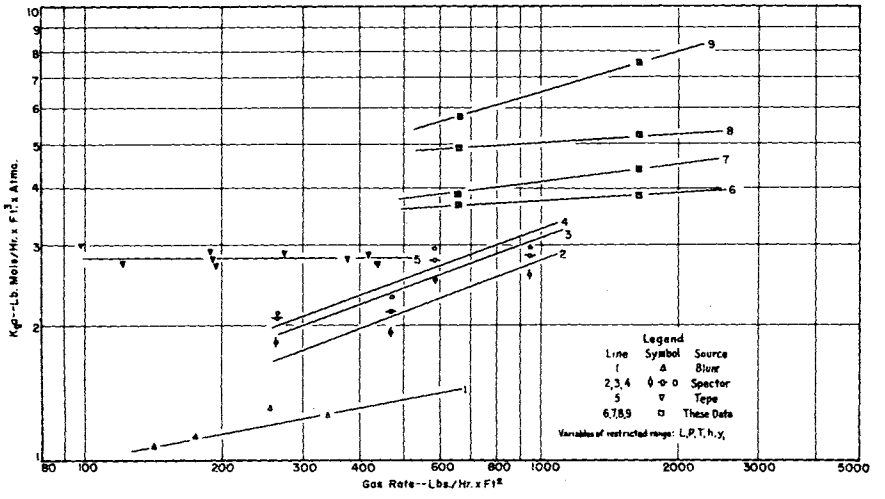

Fig. 6. Carbon dioxide absorption with sodium hydroxide solutions, gas-rate effect.

TABLE 2. STATISTICAL EXAMPLE
Dependent Variable: Natural Log of K_ga at 50% Conversion of Na Ion

				T_1	T_2
P_1	N_1	L_1	G_1	1.06	1.70
			G_2	1.10	1.77
		L_2	G_1	1.41	1.84
			G_2	1.61	2.16
	N_2	L_1	G_1	1.06	1.65
			G_2	1.10	1.81
		L_2	G_1	1.46	1.97
			G_2	1.50	2.14
P_2	N_1	L_1	G_1	0.92	1.69
			G_2	0.96	1.63
		L_2	G_1	1.25	1.84
			G_2	1.25	2.00
	N_2	L_1	G_1	0.88	1.55
			G_2	0.96	1.59
		L_2	G_1	1.19	1.89
			G_2	1.28	2.00

Summary of Analysis of Variance of Dependent Variable

Source of variance	Uncoded mean	Degrees of freedom	Sums of squares	Probability of significant effect %
T	0.320	1	32,768.0	99.9
L	0.168	1	8,978.0	99.9
P	—0.077	1	1,891.1	99.9
G	0.047	1	703.1	99.9
N	—0.005	1	8.0	
TP	0.024	1	180.5	95
LG	0.021	1	144.5	95
PG	—0.018	1	105.1	
TL	—0.014	1	66.1	
TG	0.014	1	60.5	
PL	—0.010	1	32.0	
NL	0.009	1	28.1	
PN	—0.008	1	18.0	
TN	0.003	1	3.1	
NG	—0.001	1	0.5	
TPL	0.016	1	78.1	
NLG	—0.016	1	78.1	
Other 2nd. Order		8	228.9	
Residual		6	82.8	
Total		31	45,454.5	

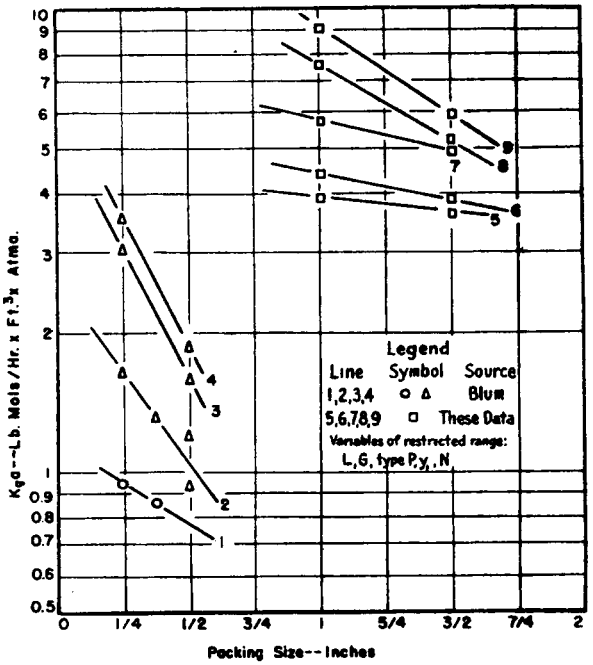

Fig. 7. Carbon dioxide absorption with sodium hydroxide, packing-size effect.

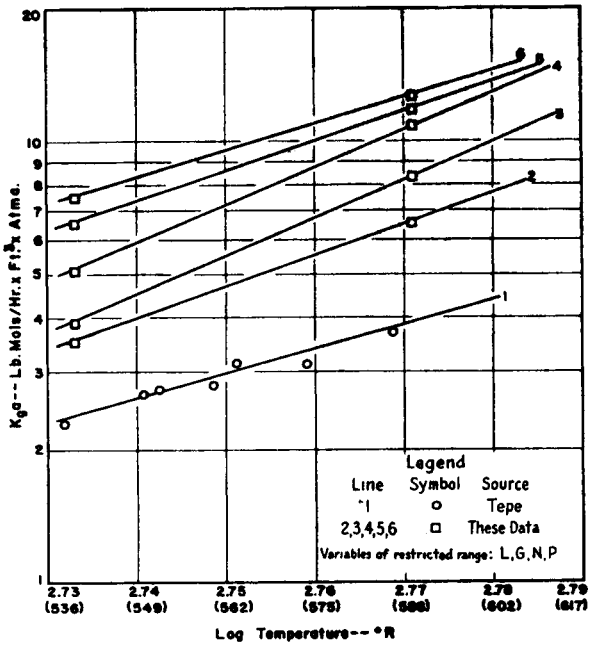

Fig. 8. Carbon dioxide absorption with sodium hydroxide solutions, temperature effect.

with confidence the best equation for the identified effects. Thus this work is a step toward a general correlation.

The data obtained in this study may be compared with other data of the field in the graphs of Figures 5 to 8. It was attempted to plot, against each of the major variables, values of K_ga obtained under otherwise nearly similar conditions; the data were not entirely sufficient for this. Some ranges in the conditions had to be included, and lines, rather than points, are used in the graphs. Discrepancies within this variety of data make further resolution of effects difficult. The graphs respectively concern the effect of liquid rate, gas rate, packing size, and temperature.

CONCLUSIONS

High transfer coefficients were attained in this study of concurrent gas absorption, a demonstration that under some conditions this type of operation is advantageous. The data will be useful for design purposes. Reference ground is provided for a general correlation.

NOTATION

G = gas flow rate, lb. moles/(hr.)(sq. ft.)
G_1 = gas flow rate of 40 lb moles/hr.
G_2 = gas flow rate of 100 lb. moles/hr.
h = height of packing, ft.
K_ga = over-all gas transfer coefficient, lb. moles/(hr.)(cu. ft.)(atm.)
L = liquid flow rate, lb. moles/hr. sq. ft.
L_1 = liquid flow rate of 30 gal./min.
L_2 = liquid flow rate of 105 gal./min.
N = normality of sodium ion
N_1 = normality of sodium ion of 2.0
N_2 = normality of sodium ion of 2.5
N_3 = normality of sodium ion of 3.0
N_4 = normality of sodium ion of 3.5
N_5 = normality of sodium ion of 4.0
N_G = carbon dioxide transfer rate based on gas composition, lb. moles/hr.
N_L = carbon dioxide transfer rate based on liquid composition, (smoothed values), lb. moles/hr.
N_L' = carbon dioxide transfer rate based on liquid composition (original experimental data), lb. moles/hr.
P = packing as a parameter
P_1 = packing type, 1 in. Berl saddles
P_2 = packing type, 1½ in. Berl saddles
P_3 = packing type, 1 in. Intalox saddles
P_4 = packing type, 1½ in. Intalox saddles
P_5 = packing type, 2 in. steel rings
P_T = pressure, total, in atm.
p = partial pressure of transferring component
T = temperature, °R.
T_1 = temperature of 80°F.
T_2 = temperature of 130°F.
V = volume of packing in tower, cu. ft.
y = composition of transferring component, carbon dioxide, in gas stream
Δ = difference between two quantities

Subscripts

m = log mean average of two quantities
1 = inlet condition
2 = outlet condition
3 = calculated outlet condition based on material balance

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