Plant Notebook

AN EQUATION TO RELATE K-FACTORS TO PRESSURE AND TEMPERATURE

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Multicomponent flash and distillation computations often require much time, particularly if many components are present. The design or simulation of a multicomponent distillation tower may require a digital computer.

These calculations must allow for variations in the distribution coefficients (K factors) with temperature and pressure.* However, while correlations for these variations are available in chart and nomograph form, we have not been able to find the corresponding equations in the common public literature.

The following equation correlates K with temperature and pressure. It is in a form chosen to produce results accurate enough for chemical engineering courses in

*Also for changes in the concentration when these effects are significant.

colleges and universities, but it usually gives results suitable for industrial application as well.

The general form of the regression equation is:

$$\ln (K) = a_{T_1}\left(\frac{1}{T^2}\right) + a_{T_2}\left(\frac{1}{T}\right) + a_{T_3}(\ln T) + a_{T_4} T$$
$$+ a_{T_5} T^2 + a_{T_6} + a_{P_1} [\ln P] + a_{P_2}\left(\frac{1}{P^2}\right) + a_{P_3}\left(\frac{1}{P}\right)$$
$$+ a_{P_4} (\ln P)^2 + a_{P_5} (\ln P)^3 + a_{P_6} (P)$$

where P is pressure, psia.; and T is temperature, °R.

A stepwise multiple linear regression technique implemented in a new statistical programming system[1] was used to determine the coefficients in this equation. Data were entered into this digital computer program. A value of 0.001—representing the proportion of the sum of

Values of the Coefficients Used

Compound	a_{T_1}	a_{T_2}	a_{T_3}	a_{T_4}	a_{T_5}	a_{T_6}
Methane	−292860.	0	0	0	0	8.24450
Ethylene	−600076.875	0	0	0	0	7.90595
Ethane	−687248.25	0	0	0	0	7.90699
Propylene	−923484.6875	0	0	0	0	7.71725
Propylene$_a$	0	−4630.24609	0	−0.00409	0	15.32456
Propane	−970688.5625	0	0	0	0	7.15059
Propane$_a$	−1095349.0	402.79321	0	0	0	6.83885
Isobutane	−1166846.0	0	0	0	0	7.72668
Isobutane$_a$	−1162432.0	0	0	0.00014	0	7.66712
Isobutane$_b$	−1126074.0	0	0	0	0	7.32168
n-Butane	−1280557.0	0	0	0	0	7.94986
n-Butane$_a$	0	0	19.65479	−0.02024	0	−109.11067
n-Butane$_b$	−1227406.0	0	0	0	0	7.44621
Isopentane	−1481583.0	0	0	0	0	7.58071
Isopentane$_a$	0	−8974.08954	−6.13344	0	0	58.70558
Isopentane$_b$	−1435771.0	0	0	0	0	7.18972
n-Pentane	−1524891.0	0	0	0	0	7.33129
n-Pentane$_a$	−1644864.0	0	0	0	0	8.32880
n-Pentane$_b$	−1478683.0	0	0	0	0	6.95724
n-Hexane	−1778901.0	0	0	0	0	6.96783
n-Hexane$_a$	0	0	0	0.04476	−0.0000233488	−15.52781
n-Hexane$_b$	−1740492.0	0	0	0	0	6.67291
n-Heptane	−2013803.0	0	0	0	0	6.52914
n-Heptane$_b$	−1984315.0	0	0	0	0	6.29305
n-Octane	0	−7646.81641	0	0	0	12.48457
n-Octane$_b$	−838108.375	−4686.72266	0	0	0	9.92379
n-Nonane	−255104.0	0	0	0	0	5.69313
n-Decane	0	−9760.45703	0	0	0	13.80354

Values of the Coefficients Used For Standard Compounds—Table II

Range	a_{T_1}	a_{T_2}	a_{T_3}	a_{T_5}	a_{T_6}	a_{P_1}	a_{P_4}	a_{P_6}	Mean Error	%-5	%-10	Number of Data Values
I	-1.36607	-2.22168	0	0	3.45273	-0.9078	0	0	9.53	35.1	81.8	225
Ia	-1.86662	0	1.23998	0	1.57230	-0.95053	0	0	5.96	49.1	86.1	173
Ib	-2.2935	0	0	-0.97288	2.63478	-0.87608	0	0.59618	2.84	86.5	100	52
II	-1.84423	0	0	0	2.06556	0	0	0	3.09	72.5	100	51

squares of the residuals reduced by a particular form of the equation—was used to limit the number of coefficients in the correlation.

A preliminary statistical analysis was performed on the resulting correlation equation to check on the accuracy of the approximation. A mean-percent absolute error was computed for K-values greater than 0.01. Accumulative percentages showing the fraction of the estimated K-values lying within 5% and 10% of the correct values were also tabulated, and these are designated in the tables as %-5 and %-10, respectively.

It should be noted that when many of the K-values of a certain compound are less than 10^{-2}, the percent errors may be rather high, causing a high mean percent error not indicative of the true accuracy of the correlation, as applied to the solution of real problems.

The first correlation predicts the value of K for 14 light hydrocarbons. Data were taken from DePriester's nomographs.[2] Values of the regression coefficients are shown in Table I. It was found that smaller errors resulted when the data were analyzed in two sections—one containing values of K greater than 1, and the other containing K-values less than 1. These results are given in the rows subscribed a and b, respectively. These correlations are

...Used for Light Hydrocarbons—Table I

	a_{P_1}	a_{P_2}	a_{P_3}	a_{P_4}	a_{P_5}	Mean Error	%-5	%-10	Number of Data Values
24450	-0.89510	59.8465	0	0	0	1.66	96.3	100	135
0595	-0.84677	42.94594	0	0	0	2.65	88.1	97.8	135
0699	-0.88600	49.02654	0	0	0	1.95	94.1	100	135
1725	-0.87871	47.67624	0	0	0	1.90	93.3	100	135
2456	-0.88084	48.14787	0	0	0	1.34	96.0	100	126
5059	-0.76984	0	6.90224	0	0	2.35	93.3	100	135
3885	-0.77212	0	6.90804	0	0	2.08	96.7	100	122
2668	-0.92213	0	0	0	0	2.52	88.1	100	135
3712	-0.93307	0	0	0	0	2.42	96.1	100	102
2168	-0.86415	0	0	0	0	1.73	100	100	33
1986	-0.96455	0	0	0	0	3.61	73.3	97.0	135
067	-0.99838	0	0	0	0	2.82	79.6	100	93
621	-0.89063	0	0	0	0	2.04	95.2	100	42
071	-0.93159	0	0	0	0	4.56	68.1	91.9	135
558	-1.49632	0	0	0.06708	0	1.48	98.5	100	66
972	-0.87511	0	0	0	0	3.14	79.7	100	69
129	-0.89143	0	0	0	0	4.30	71.1	90.4	135
880	-1.17078	0	0	0	0.00523	1.43	98.4	100	61
724	-0.83977	0	0	0	0	3.10	82.4	95.9	74
783	-0.84634	0	0	0	0	4.90	60.0	91.5	130
781	-1.23197	0	0	0	0.00718	1.38	96.9	100	32
291	-0.80600	0	0	0	0	3.12	83.7	98.0	98
14	-0.79543	0	0	0	0	6.34	46.6	84.7	118
05	-0.76124	0	0	0	0	4.89	55.7	97.2	106
57	-0.73152	0	0	0	0	7.58	40.6	69.3	101
79	-0.72922	0	0	0	0	6.15	53.1	81.2	96
13	-0.67818	0	0	0	0	9.40	24.1	59.0	83
54	-0.71470	0	0	0	0	5.69	54.0	77.8	63

valid for $460 < T < 760$ R. and $14.7 < P < 120$ psia.

For other compounds, data for the generalized ideal-solution K-values were taken from Hougen, others.[3] The restrictions and assumptions concerning the use and development of these K-values are given in this reference. These data were correlated with the reduced temperature and pressure in the general equation and for $z_c = 0.27$.

The results of the regression analysis are given in Table II. The ranges $0.90 \le T_r \le 2.00$, $P_r \le 2.0$ and $0.60 \le T_r \le 0.90$, $0.01 \le P_r \le 0.5$ are denoted in this table as I; and the range $0.60 \le T_r \le 0.90$, $0.5 \le P_r \le 2.0$ is denoted as II. As before, more-accurate predictions were found to result if the data were divided into two sections containing values of K above and below 1.0. These cases are shown as rows subscribed with a and b in Table II.

Finally, to correct the value of K given by the equation and Table II for substances having a value of z_c other than 0.27, the following equation may be used to make corrections.[3]

$$\frac{Kz_c}{K_{0.27}} = 10^{D(z_c - 0.27)}$$

where D was found to be correlated with T_r and independent of P_r in the following form:

$$D = 427.1181 - 1723.142\ T_r + 2922.283\ T_r^2$$
$$- 2659.991\ T_r^3 + 1363.795\ T_r^4 - 372.0939\ T_r^5$$
$$+ 42.09153\ T_r^6 \quad \blacksquare$$

References

1. Padgett, L. R., "Statistical Organizer System," West Virginia University Computer Center, Morgantown, W. Va. (1972).
2. McCabe, W. L., and Smith, J. C., "Unit Operations of Chemical Engineering," McGraw-Hill, 1967, pp. 992–3.
3. Hougen, O. A., Watson, K. M., and Ragatz, R. A., "Chemical Process Principles; Part II," John Wiley & Sons Inc., 1959, Chapter 22.