X_{SO_2} = fractional conversion of inlet SO_2
θ = contact time, based on inlet reactor conditions and total catalyst volume, sec

Literature Cited

Baker, R. A., Doerr, R. C., *Ind. Eng. Chem., Process Des. Develop.*, **4**, 188 (1965).
Bartok, W., Crawford, A. R., Skopp, A., *Chem. Eng. Progr.*, **67**, 64 (1971).
Bird, R. B., Stewart, W. E., Lightfoot, E. N., "Transport Phenomena," Wiley, New York, N.Y., 1960.
Chilton, T. H., *Chem. Eng. Progr.*, **67**, 69 (1971).
Khalafalla, S. E., Haas, L. A., *J. Catal.*, **24**, 121 (1972).
Khalafalla, S. E., Foerster, E. F., Haas, L. A., *Ind. Eng. Chem., Prod. Res. Develop.*, **10**, 133 (1971).
Klimisch, R. L., Barnes, G. J., *Environ. Sci. Technol.*, **6**, 543 (1972).
Meguerian, G. H., Lang, C. R., *SAE (Soc. Automot. Eng.) J.*, IIEC SP-361 (1971).
Okay, V. C., Short, W. L., *Ind. Eng. Chem., Process Des. Develop.*, **12**, 291 (1973).
Querido, R., University of Massachusetts, Ph.D. Thesis, 1971.
Querido, R., Short, W. L., *Ind. Eng. Chem., Proc. Des. Develop.*, **12**, 10 (1973).
Quinlan, C. W., University of Massachusetts, M.S. Thesis, 1972.
Quinlan, C. W., Okay, V. C., Kittrell, J. R., *Ind. Eng. Chem., Proc. Des. Develop.*, **12**, 107 (1973).
Ryason, P. T., Harkins, J., *J. Air Pollut. Contr. Ass.*, **17**, 796 (1967).
Shelef, M., Kummer, J. T., *Chem. Eng. Progr., Symp. Ser.*, **67**, 117, 74 (1971).
Shelef, M., Otto, K., Gandhi, H., *J. Catal.*, **12**, 4 (1968).
White, W. B., *et al.*, *J. Chem. Phys.*, **28**, 751 (1958).

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Acentric Factor. A Valuable Correlating Parameter for the Properties of Hydrocarbons

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Revised acentric factors, based on the original defining equation of Pitzer, have been determined for 192 hydrocarbons. Critical property and vapor pressure data were collected, evaluated, and then used to obtain new values for the acentric factors. These values are recommended for use in most available correlations. Correlators are urged to use values for the acentric factor based on the literal definition rather than values determined by requiring optimum agreement with their final equations.

Presently the most useful tool in the prediction of physical properties of hydrocarbons is the theory of corresponding states. This theory hypothesizes that fluids behave similarly when they are compared at the same reduced temperature (T/T_c) and reduced pressure (P/P_c). Through statistical mechanics a third parameter, in addition to the critical temperature and pressure, has been introduced, which has greatly improved the accuracy of corresponding state predictions. The parameter was developed by Pitzer (1955*a*,*b*) and termed the acentric factor, ω. It is defined in terms of the vapor pressure behavior of the material.

$$\omega = -\log (P_r')_{T_r = 0.7} - 1.00 \quad (1)$$

where P_r' is the reduced vapor pressure (P'/P_c). The vapor pressure used is the value at a reduced temperature of 0.7. The definition of ω was chosen so as to make $\omega = 0$ for the heavier rare gases Ar, Kr, and Xe, *i.e.*, the simple spherical molecules. Extensive tables for correlating physical properties were developed by Curl and Pitzer (1958) in the following form

$$G = G^{(0)}(T_r,P_r) + \omega G^{(1)}(T_r,P_r) \quad (2)$$

where G is the particular property being correlated and $G^{(0)}$ and $G^{(1)}$ are tabular functions of the reduced temperature and reduced pressure. The $G^{(0)}$ tables were developed for fluids obeying the simple two-parameter law of corresponding states. The $G^{(1)}$ tables were developed to account for deviations from the two-parameter law of corresponding states caused by molecular size and shape (acentricity). These tables are intended for use with normal fluids (essentially nonpolar materials) which were defined in terms of reduced surface tension by Curl and Pitzer (1958).

It is clear the value of ω as defined by eq 1 will depend on the accuracy of available values for the vapor pressure, critical temperature, and critical pressure. As more accurate values have become available for these physical properties the accepted acentric factor values have changed.

Since the work of Curl and Pitzer (1958), the acentric factor has also been used in many other correlations which do not take the form of eq 2 (Edmister, *et al.* (1968), Fisher and Leland (1970), Johnson and Colver (1970), Lee and Edmister (1971), Starling and Han (1972)). Some of these efforts, in fact, have resulted in the workers backing out of their correlations "modified acentric factors," *i.e.*, empirical values which best fit their correlations. Such an approach tends to lead to a proliferation of ω values and increased confusion.

A comprehensive list of hydrocarbon acentric factors was presented in 1966 in the API "Technical Data Book—Petro-

Table I. Revised Acentric Factors

Compound	Critical temp, °F	Critical pressure, psia	Acentric factor
Paraffins			
Methane	−116.63	667.8	0.0072
Ethane	90.09	707.8	0.0908
Propane	206.01	616.3	0.1454
n-Butane	305.65	550.7	0.1928
2-Methylpropane	274.98	529.1	0.1756
n-Pentane	385.7	488.6	0.2510
2-Methylbutane	369.10	490.4	0.2273
2,2-Dimethylpropane	321.13	464.0	0.1970
n-Hexane	453.7	436.9	0.2957
2-Methylpentane	435.83	436.6	0.2791
3-Methylpentane	448.3	453.1	0.2750
2,2-Dimethylbutane	420.13	446.8	0.2310
2,3-Dimethylbutane	440.29	453.5	0.2473
n-Heptane	512.8	396.8	0.3506
2-Methylhexane	495.00	396.5	0.3298
3-Methylhexane	503.78	408.1	0.3240
3-Ethylpentane	513.48	419.3	0.3101
2,2-Dimethylpentane	477.23	402.2	0.2886
2,3-Dimethylpentane	507.56	421.8	0.2986
2,4-Dimethylpentane	475.95	396.9	0.3059
3,3-Dimethylpentane	505.85	427.2	0.2697
2,2,3-Trimethylbutane	496.44	428.4	0.2510
n-Octane	564.22	360.6	0.3942
2-Methylheptane	547.68	360.3	0.3776
3-Methylheptane	554.94	369.3	0.3694
4-Methylheptane	551.46	368.7	0.3687
3-Ethylhexane	558.21	378.3	0.3605
2,2-Dimethylhexane	530.10	366.8	0.3376
2,3-Dimethylhexane	554.61	381.2	0.3463
2,4-Dimethylhexane	536.67	370.8	0.3430
2,5-Dimethylhexane	530.44	360.6	0.3519
3,3-Dimethylhexane	551.97	384.9	0.3206
3,4-Dimethylhexane	564.26	390.5	0.3384
2-Methyl-3-ethylpentane	561.09	391.6	0.3298
3-Methyl-3-ethylpentane	578.17	407.2	0.3037
2,2,3-Trimethylpentane	554.63	395.9	0.2975
2,2,4-Trimethylpentane	519.46	372.4	0.3033
2,3,3-Trimethylpentane	572.74	409.0	0.2901
2,3,4-Trimethylpentane	559.87	395.9	0.3165
n-Nonane	610.68	332	0.4437
2,2,3-Trimethylhexane	598.8	362	0.3321
2,2,4-Trimethylhexane	572.9	345	0.3211
2,2,5-Trimethylhexane	562.8	338	0.3571
3,3-Diethylpentane	638.4	388	0.3379
2,2,3,3-Tetramethylpentane	639.9	397	0.2793
2,2,3,4-Tetramethylpentane	606.2	372	0.3108
2,2,4,4-Tetramethylpentane	568.8	342	0.3150
2,3,3,4-Tetramethylpentane	636.6	391	0.2994
n-Decane	652.1	304	0.4902
n-Undecane	690.04	285	0.5349
n-Dodecane	725.2	264	0.5622
n-Tridecane	756.7	250	0.6231
n-Tetradecane	785.7	235	0.6797
n-Pentadecane	812.5	220	0.7060
n-Hexadecane	837.3	206	0.7418
n-Heptadecane	860.4	191	0.7699
n-Octadecane	881.8	176	0.7895
n-Nonadecane	901	162	0.8271
n-Eicosane	921	162	0.9065
Naphthenes			
Cyclopropane	256.39	797.0	0.2645
Cyclobutane	368.2	723	0.2089
Cyclopentane	461.5	653.8	0.1923
Methylcyclopentane	499.35	548.9	0.2395
Ethylcyclopentane	565.47	492.8	0.2826
1,1-Dimethylcyclopentane	525	500	0.2727
cis-1,2-Dimethylcyclopentane	557	500	0.2692
trans-1,2-Dimethylcyclopentane	536	500	0.2692
cis-1,3-Dimethylcyclopentane	532	514	0.2975
trans-1,3-Dimethylcyclopentane	536	500	0.2584
n-Propylcyclopentane	626	435.0	0.3350
Isopropylcyclopentane	622	435.0	0.2400
1-Methyl-1-ethylcyclopentane	606	433.5	0.2503
Methyl-*cis*-2-ethylcyclopentane	613	433.5	0.2940
1,1,2-Trimethylcyclopentane	583.5	426.2	0.2516
1,1,3-Trimethylcyclopentane	565.5	410.0	0.2106
cis,cis,trans-1,2,4-Trimethylcyclopentane	583	417.4	0.2771
cis,trans,cis-1,2,4-Trimethylcyclopentane	568	407.8	0.2459
n-Hexylcyclopentane	728.6	310	0.4764
n-Heptylcyclopentane	762.4	283	0.5146
n-Octylcyclopentane	790.3	260	0.5639
n-Nonylcyclopentane	819.3	240	0.6101
n-Decylcyclopentane	843.1	221	0.6538
n-Undecylcyclopentane	869.4	204	0.6740
n-Dodecylcyclopentane	890.1	188	0.7193
n-Tridecylcyclopentane	910.8	175	0.7546
n-Tetradecylcyclopentane	930.6	164	0.7893
n-Pentadecylcyclopentane	945.0	149	0.8333
n-Hexadecylcyclopentane	963.5	141	0.8607
Cyclohexane	536.7	591	0.2144
Methylcyclohexane	570.27	503.5	0.2333
Ethylcyclohexane	637	440	0.2426
1,1-Dimethylcyclohexane	604	430	0.2376
cis-1,2-Dimethylcyclohexane	631	430	0.2363
trans-1,2-Dimethylcyclohexane	613	430	0.2416
cis-1,3-Dimethylcyclohexane	604	430	0.2237
trans-1,3-Dimethylcyclohexane	617	430	0.1886
cis-1,4-Dimethylcyclohexane	617	430	0.2338
trans-1,4-Dimethylcyclohexane	602	430	0.2419
n-Propylcyclohexane	691	407.1	0.2577
Isopropylcyclohexane	692	411.5	0.2370
1,1,3-Trimethylcyclohexane	642	390.9	0.1810
n-Butylcyclohexane	741	457.0	0.3618
Isobutylcyclohexane	726	452.6	0.3189
sec-Butylcyclohexane	744	388.0	0.2643
tert-Butylcyclohexane	727	387.2	0.2520
n-Decylcyclohexane	891	197	0.5825
Cycloheptane	601	540	0.3359
Cyclooctane	653	500	0.4412
Olefins			
Ethene (ethylene)	48.58	729.8	0.0856
Propene	196.9	669	0.1477
1-Butene	295.6	583	0.1874
cis-2-Butene	324.37	610	0.2044
trans-2-Butene	311.86	595	0.2138
2-Methylpropene (isobutylene)	292.55	580	0.1898
1-Pentene	376.93	590	0.2450
cis-2-Pentene	397	530	0.2403
trans-2-Pentene	396	530	0.2372
2-Methyl-1-butene	378	500	0.2321
3-Methyl-1-butene	351	510	0.2285
2-Methyl-2-butene	387	500	0.2837
1-Hexene	447.58	460	0.2848
cis-2-Hexene	472	476.1	0.2555

Table I (*continued*)

Compound	Critical temp, °F	Critical pressure, psia	Acentric factor
trans-2-Hexene	470	474.1	0.2421
cis-3-Hexene	471	476.1	0.2254
trans-3-Hexene	476.1	472	0.2273
2-Methyl-2-pentene	472	476.1	0.2294
3-Methyl-*cis*-2-pentene	472	476.1	0.2694
3-Methyl-*trans*-2-pentene	479	477.6	0.2072
2,3-Dimethyl-1-butene	442	470.3	0.2215
3,3-Dimethyl-1-butene	423	457.0	0.1207
2,3-Dimethyl-2-butene	484	487.9	0.2389
1-Heptene	500.25	410	0.3580
4,4-Dimethyl-1-pentene	488	414.4	0.1715
2,3,3-Trimethyl-1-butene	499	420.3	0.1919
1-Octene	560.3	380	0.3858
trans-2-Octene	585	401.2	0.3500
1-Nonene	606	340	0.4299
1-Decene	647	320	0.4912
1-Undecene	687	289	0.5180
1-Dodecene	723	269	0.5575
1-Tridecene	754	247	0.5981
1-Tetradecene	781	227	0.6441
1-Pentadecene	808	211	0.6822
1-Hexadecene	831	194	0.7213
1-Octadecene	871	166	0.8066
Diolefins			
Propadiene	248	793	0.3125
1,2-Butadiene	339	653	0.3394
1,3-Butadiene	306	628	0.1814
1,2-Pentadiene	446	590.8	0.1725
1-*cis*-3-Pentadiene	438	582	0.1834
1-*trans*-3-Pentadiene	434	579	0.1754
1,4-Pentadiene	400	549.6	0.1038
2-Methyl-1,3-butadiene	412	558.4	0.1642
3-Methyl-1,2-butadiene	434	579	0.1595
Acetylenes			
Ethyne (acetylene)	95.31	890.4	0.1841
Propyne	264.63	816.2	0.2176
1-Butyne	375.0	683.4	0.0501
Aromatics			
Benzene	552.22	710.4	0.2100
Methylbenzene (toluene)	605.55	595.9	0.2566
Ethylbenzene	651.24	523.5	0.3011
1,2-Dimethylbenzene (*o*-xylene)	675.0	541.4	0.3136
1,3-Dimethylbenzene (*m*-xylene)	651.02	513.6	0.3311
1,4-Dimethylbenzene (*p*-xylene)	649.6	509.2	0.3243
n-Propylbenzene	689.41	464.1	0.3444
Isopropylbenzene	676.4	465.4	0.3353
1-Methyl-2-ethylbenzene	712	440.9	0.2937
1-Methyl-3-ethylbenzene	687	411.5	0.3598
1-Methyl-4-ethylbenzene	693	426.2	0.3219
1,2,3-Trimethylbenzene	736.48	501.0	0.3934
1,2,4-Trimethylbenzene	708.76	468.8	0.3964
1,3,5-Trimethylbenzene	687.58	453.5	0.3980
n-Butylbenzene	729.3	418.7	0.3923
Isobutylbenzene	711	440	0.3782
sec-Butylbenzene	736.5	428.0	0.2736
tert-Butylbenzene	728	430.0	0.2647
1-Methyl-2-isopropylbenzene	746	420.0	0.2769
1-Methyl-3-isopropylbenzene	739.5	426.2	0.2792
1-Methyl-4-isopropylbenzene	716	410	0.3714
1,4-Diethylbenzene	724.66	406.5	0.4031
1,2,4,5-Tetramethylbenzene	756	430	0.4255
Biphenyl	961	558	0.3643
Diphenylmethane	921.9	432.51	0.4710
Vinylbenzene	706.0	580	0.2572
1-Methyl-2-ethenylbenzene	763	529	0.3755
1-Methyl-3-ethenylbenzene	755	516	0.3415
1-Methyl-4-ethenylbenzene	757	514	0.3128
Naphthalene	887.50	587.5	0.3024
1-Methylnaphthalene	930	517.6	0.3337
2-Methylnaphthalene	910	508.1	0.3815
1,2,3,4-Tetrahydronaphthalene	835	509.80	0.3028
cis-Decahydronaphthalene	809.8	457	0.2321
trans-Decahydronaphthalene	776.8	457	0.2738

leum Refining" (1966). Since that time, additional vapor pressure data and extensive new data for the critical properties of these hydrocarbons have become available. Updated critical properties have recently been tabulated in the second edition of the API "Technical Data Book" (1971). With this revised data, and an extensive review of the current vapor pressure data, an effort has been made to calculate the best possible values for the acentric factors based on the literal definition of Pitzer (eq 1).

Method of Calculating the Best Acentric Factors

In the selection of the best values for the acentric factors three methods of calculation were used. First, a vapor pressure data set of over 10,000 points for 190 compounds was assembled. If an accurate value of the vapor pressure at a reduced temperature of 0.7 was available, this value was used. Unfortunately, these vapor pressure values are rarely available, and therefore interpolations had to be performed. If the data set contained values which closely bracketed the reduced temperature of 0.7, a value was determined from

$$\log P'_{T_r=0.7} = \frac{\left[\frac{1}{T_{0.7}} - \frac{1}{T_1}\right](\log P_2' - \log P_1')}{\left[\frac{1}{T_2} - \frac{1}{T_1}\right]} + \log P_1' \quad (3)$$

where P_1' and P_2' are the vapor pressure values bracketing the reduced temperature at 0.7 and T_1 and T_2 are the corresponding temperatures.

In some cases, compounds with data from more than one reference produced acentric factors which did not agree. Instead of averaging the values obtained from each reference, all of the data were used in a multiple linear regression analysis to determine the optimum coefficients of the Frost and Kalkwarf (1953) vapor pressure equation. This equation (eq 4) has been demonstrated to be one of the most accurate vapor pressure correlations by Holmes, *et al.* (1966).

$$\ln P' = A + B/T + C \ln T + DP'/T^2 \quad (4)$$

Here A, B, C, and D are derived empirical coefficients. For those compounds for which there were sufficient data, these coefficients were used to predict vapor pressure values at a reduced temperature of 0.7, and acentric factors were calculated.

Another equation frequently used to correlate vapor pressure data is the Antione equation

$$\log P' = A - \frac{B}{C + T}$$

Again A, B, and C are empirically derived constants. Coefficients for this equation have been published by the API

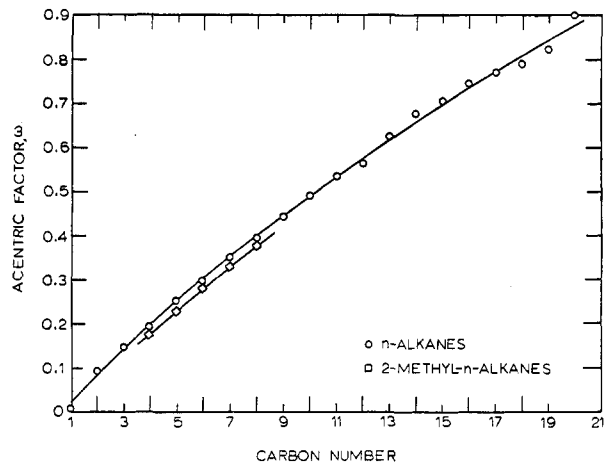

Figure 1. Acentric factors for *n*-alkanes and 2-methyl-*n*-alkanes

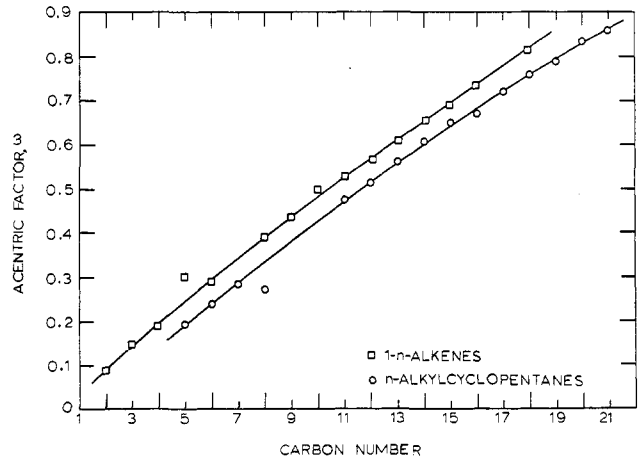

Figure 2. Acentric factors for 1-*n*-alkenes and *n*-alkylcyclopentanes

Research Project 44 (1971) workers. Using these coefficients, another set of vapor pressure values were calculated at a reduced temperature of 0.7 along with the corresponding acentric factors.

The procedure thus produced at least three values for the acentric factors for most compounds. The "best" values for the acentric factors, as presented in Table I, were then determined according to the following hierachy: (1) directly from the vapor pressure data, when accurate data were available at $T_r = 0.7$; (2) from the Frost–Kalkwarf equation (eq 4), if this value was in close agreement with both the interpolated value and that obtained from the Antoine equation; (3) from interpolating the data with eq 3 for those compounds where the Frost–Kalkwarf equation gave values which did not agree well with the interpolated data or with the Antione equation; (4) from the Antione equation, if there was insufficient data to fit the Frost–Kalkwarf equation and/or the data did not bracket a reduced temperature of 0.7.

To check on the consistency of the values determined, the acentric factors were plotted as a function of carbon number for certain homologous series. The results for four such series are shown in Figures 1 and 2. The values in general exhibit an excellent degree of internal consistency. However, two exceptions are to be noted. In Figure 2 the value for 1-pentene appears too high while the value for *n*-propylcyclopentane is low. These values were adjusted to conform to their respective lines. The final values of ω for all the compounds studied are listed in Table I.

Conclusions and Recommendations

An extensive effort has been made to determine the best values for the acentric factors of hydrocarbons, according to the definition originally provided by Pitzer (eq 1). There is no guarantee that these values are the optimum valves to use in a particular correlation, not even the Curl and Pitzer (1958) tables. The authors have determined, however, that for a large number of compounds, the enthalpy deviations predicted by the Curl and Pitzer tables with the cited acentric factors are quite good. The acentric factors cited in Table I are recommended for use in generalized correlations which do not specify a particular set of acentric factors.

For nonpolar materials, the acentric factor has certainly proved to be a valuable correlating parameter. Many workers are involved in developing new methods of predicting properties which employ acentric factors. If confusion is to be avoided and these efforts are to be generally useful, the acentric factors used in these correlations should be those defined by eq 1 and not some empirical values regressed from the correlation itself. If a parameter is backed out of a correlation, the correlation can not be considered completely generalized and the parameter should be given some other name than acentric factor. Only in this way can the uniqueness of the acentric factor value be preserved.

Nomenclature

A, B, C, D } derived coefficients for vapor pressure equations
G = a thermodynamic property
P' = vapor pressure, atm
P_c = critical pressure, atm
P_r' = reduced vapor pressure (P'/P_c)
T = temperature, °R
T_c = critical temperature, °R
T_r = reduced temperature (T/T_c)
ω = acentric factor

Literature Cited

API Research Project 44, "Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds," Thermodynamics Research Center, Department of Chemistry, Texas A & M University, College Station, Tex., 1971.
"Technical Data Book—Petroleum Refining," 1st ed, American Petroleum Institute, Washington, D.C., 1966, Chapter 2.
"Technical Data Book—Petroleum Refining," 2nd ed, American Petroleum Institute, Washington, D.C., 1971, Chapter 1.
Curl, R. F., Pitzer, K. S., *Ind. Eng. Chem.*, **50**, 265 (1958).
Edmister, W. C., Vairogs, J., Klekers, A. J., *AIChE J.*, **14**, 479 (1968).
Fisher, G. D., Leland, T. W., *Ind. Eng. Chem., Fundam.*, **9**, 537 (1970).
Frost, A. A., Kalkwarf, D. R., *J. Chem. Phys.*, **21**, 264 (1953).
Holmes, A. S., Bosler, W. H., Thompson, W. H., Braun, W. G., Fenske, M. R., "Documentation of the Basis for Selection of the Contents of Chapter 5—Vapor Pressure," American Petroleum Institute, Washington, D. C., Mar 1966.
Johnson, D. W., Colver, C. P., *Proc. 49th Ann. Conv. N.G.P.A.*, 19 (1970).
Lee, B., Edmister, W. C., *AIChE J.*, **17**, 1412 (1971).
Pitzer, K. S., *J. Amer. Chem. Soc.*, **77**, 3427 (1955a).
Pitzer, K. S., *J. Amer. Chem. Soc.*, **77**, 3433 (1955b).
Starling, K. E., Han, M. S., *Hydrocarbon Process.*, **51**, 129 (1972).

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