Greek Letters

β = cell constant defined by Equation (7) and applicable to Equations (4) and (5)
β^* = cell constant determined experimentally by using Equation (6)
λ = ratio of diaphragm volume to cell compartment volume

Subscripts

B = bottom compartment
D = diaphragm
T = top compartment

Superscript

o = zero time

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On the Correlation of Critical Properties of Mixtures

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New experimental measurements of critical temperatures and critical pressures have been reported by Kay and Hissong (*2*) for twenty-two binary hydrocarbon mixtures. We have reduced these data within the framework of the correlation recently presented by Chueh (*1*).

Chueh fits experimental critical temperatures and critical volumes to quadratic functions of the surface fraction θ:

$$T_c = \theta_1 T_{c1} + \theta_2 T_{c2} + 2\ \tau_{12}\theta_1\theta_2$$

$$v_c = \theta_1 v_{c1} + \theta_2 v_{c2} + 2\ \nu_{12}\theta_1\theta_2$$

where τ_{12} and ν_{12} are binary parameters characterizing the 1-2 interaction. As shown by Chueh, reduced values of τ_{12} and ν_{12} follow definite trends within a chemical family. Critical pressures are found from critical temperatures and critical volumes by using a modified Redlich-Kwong equation (*1*).

TABLE 1. AVERAGE DEVIATIONS IN CRITICAL TEMPERATURES AND PRESSURES FOR 22 BINARY SYSTEMS

System	$\dfrac{2\tau_{12}}{T_{c1}+T_{c2}}$	Average deviation, % T_c	P_c
n-octane–*n*-heptane	0.0018	0.01	0.4
n-hexane–*n*-heptane	0.0027	0.01	1.5
n-hexane–*n*-octane	0.0086	0.02	1.1
o-xylene–benzene	0.0069	0.04	1.5
o-xylene–toluene	0.0008	0.02	0.3
o-xylene–ethylbenzene	—0.0002	0.02	0.5
toluene–benzene	0.0031	0.02	1.7
toluene–ethylbenzene	0.0018	0.02	3.9
ethylbenzene–benzene	0.0065	0.03	2.1
cyclopentane–methylcyclohexane	0.0742	0.61	4.6
cyclopentane–methylcyclopentane	0.0012	0.02	1.3
cyclopentane–cyclohexane	0.0066	0.03	0.1
cyclohexane–methylcyclohexane	0.0032	0.05	6.9
methylcyclopentane–methylcyclohexane	0.0035	0.01	5.5
methylcyclopentane–cyclohexane	0.0030	0.04	0.7
methylcyclopentane–*n*-hexane	0.0005	0.02	0.5
benzene–cyclopentane	—0.0062	0.01	0.7
benzene–methylcyclopentane	—0.0113	0.02	0.1
benzene–*n*-hexane	—0.0127	0.03	0.9
benzene–*n*-heptane	—0.0153	0.02	0.4
benzene–*n*-octane	—0.0124	0.05	2.0
benzene–*n*-nonane	—0.0056	0.09	4.0

Table 1 lists τ_{12} for the systems studied by Kay and Hissong. The temperature parameters τ_{12} shown for the first 16 systems in Table 1 are in good agreement with those calculated from Chueh's Figure 2 for paraffin-paraffin systems. Also shown are the average percent deviations between calculated and measured critical temperatures and critical pressures.

Since critical volumes were not measured for these systems, for each system we calculated critical pressures for various values of the unknown parameter ν_{12}. In all cases the optimum ν_{12} parameter was small, close to or equal to zero. We found that best results for the critical pressure were obtained as indicated:

1. For paraffin-paraffin systems use the ν_{12} curve presented by Chueh for such systems.
2. For aromatic-aromatic systems use $\nu_{12} = 0$.
3. For hydrocarbon systems containing at least one cycloparaffin use $\nu_{12} = 0$.
4. For systems containing one aromatic and one paraffin, use 83% of the ν_{12} values given by Chueh's curve for paraffin-aromatic systems.

Average deviations in critical pressure reported in Table 1 were obtained by following the procedure given above.

Extension of this method of correlation to systems containing more than two components is straightforward as discussed previously (*1*).

Values for k_{12} in the modified Redlich-Kwong equation were taken as zero except for the last six systems for which $k_{12} = 0.01$.

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