

## Quantitative prediction of K values

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## Critical remarks on approaches from chemical engineering

In the field of chemical engineering some other approaches have long been used to predict partitioning:

**Hildebrand's Solubility Parameters:** These parameters describe the cohesive energy and used to scale the solvent strength of different solvents. While this approach covers the cavity energy contribution to the partition process it ignores the energy contributions that come from H-bonding. In order to correct for this obvious shortcoming, **Hansen's three dimensional solubility parameters** were introduced. However, Hansen's method does not describe the H-bond interactions correctly as shown by Fowkes and Mostafa (*Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 3–7. [Journal link](#) [Download pdf](#) ). It ignores that compounds which do not have H-bonds within their own pure phase might still form (strong) H-bonds when entering other phases.

According to the Hansen approach, no organic compound should show a higher affinity to any other organic phase than to its own pure phase. However, this statement is only correct if all interactions are solely of the van der Waals type. It often fails if H-bonds play a role as shown by the first two examples in the Table below.

Besides, the model also fails at the other end of the scale, i.e. in predicting high activity coefficients as is demonstrated by the last two examples in Table 1.

**Table 1** Experimental and calculated (according to the Hansen approach equation 18 from reference (1)) activity coefficients,  $\gamma$ , at infinite dilution.

Solute	Solvent	$\gamma_{\text{(exper.)}}$	$\gamma_{\text{(calc.)}}$
1,4 dioxane	chloroform	0.21	1.06
butylacetate	phenol	0.18	1.83
octane	anilin	37	5.10
octane	nitromethan	111	4.96

(1) Jang, M.; Kamens, R.M.; Leach, K.B.; Strommen, M.R. *Environ. Sci. Technol.* **1997**, *31*, 2805–2811. [Journal link](#) [Download pdf](#) )

**UNIFAQ and UNIQUAC:** This is a fragment method in which not only the solute but also the molecular structure of the phases is broken down into fragments. Energy increments for the mutual interaction between all fragments have been derived from existing partition data. New partition data can be calculated for any new combination of fragments that already exist in the database. It appears that quite often the fragments needed for environmental applications do not exist in the data base.

