

10.40 Thermodynamics

Fall 2003

Final Exam

Problem 1

1. (20 points) Rocky and Rochelle Jones are having one of their heated arguments on thermodynamics. This time they are trying to reconcile the theoretical and empirical underpinnings of the so-called K factor charts or nomographs that were used during the last century, before computers were readily available, to characterize equilibrium phase partitioning in multicomponent distillation of hydrocarbons. K is defined as the equilibrium ratio of a particular component y_i in the vapor phase to x_i in the liquid phase. A typical nomograph is shown below for a set of light alkane and alkene hydrocarbons – C-1 (methane) through C-9 (nonane),

Rocky claims that the K factors do a reasonable job of capturing important non-idealities over a wide range of conditions. In fact, Rocky notes that you only need the temperature and pressure to specify the vapor liquid equilibrium state as indicated by the nomograph. By connecting a straight line to a specific T and P , the intersection of that line with curve for each compound yields the $K = y_i/x_i$.

Rochelle adamantly maintains that the K 's are only based on single component information and that they fail to include intermolecular interactions.

We need your help to settle this argument.

(a) (10 points) Derive a general relationship for K in an n -component system vapor-liquid mixture at equilibrium. Clearly indicate the functional dependence of all derived parameters on measurable properties and state what type of constitutive property relationships are needed to evaluate K for each component.

(b) (10 points) For the P and T conditions given in the nomograph, who do you think is correct, Rocky or Rochelle? Explain.

(Image removed due to copyright considerations.)

K-values for systems of light hydrocarbons

Solution:

(a)

For a system comprised of an n-component vapor-liquid mixture at equilibrium, the temperature (T) and pressure (P) in the two phases are equal. For vapor-liquid equilibrium, the chemical potential (and hence, fugacity) of each component across phases is also equal:

$$\mu_i^L = \mu_i^V \quad \text{or} \quad \hat{f}_i^L = \hat{f}_i^V$$

For components in the vapor phase, the expression for fugacity can be expanded using the fugacity coefficient:

$$\hat{f}_i^V = \hat{\phi}_i^V y_i P$$

$$\text{where: } \hat{\phi}_i^V = f(T, P, x_j)$$

For components in the liquid phase, we do not want to use the fugacity coefficient, since evaluating $\hat{\phi}_i^L$ will require a $PVTN$ EOS, and these are normally not accurate for condensed phases. Instead, the expression for fugacity can be expanded using the activity coefficient:

$$\hat{f}_i^L = \gamma_i^L x_i \hat{f}_i^+$$

$$\text{where: } \begin{aligned} \gamma_i^L &= f(T, P, x_j) \\ \hat{f}_i^+ &= f(T, P, x_j) \quad \text{ref. state fugacity} \end{aligned}$$

Taking the conventional reference state for \hat{f}_i^+ of a pure component at the temperature, pressure, and state of aggregation as the mixture, we see that $\hat{f}_i^+ = f_i^L(T, P)$. This pure component fugacity can be expressed in terms of pure liquid i in equilibrium with its pure vapor. Using the fugacity coefficient expression used above and a Poynting correction factor, we eventually can express the liquid phase fugacity of component i as:

$$\hat{f}_i^L = \gamma_i^L x_i \phi_i^V(T, P_{VP,i}) P_{VP,i} e^{\int_{P_{VP,i}}^P V_i^L dP}$$

where $\phi_i^V = f(T, P_{VP,i})$ is the fugacity coefficient of pure vapor i in equilibrium with pure liquid i at a temperature T . At these conditions, the pressure would be the vapor pressure, $P_{VP,i}$.

Equating the fugacities and re-arranging, we finally find that:

$$K = \frac{y_i}{x_i} = \frac{\gamma_i^L(T, P, x_j) \phi_i^V(T, P_{VP,i}) P_{VP,i} e^{\int_{P_{VP,i}}^P V_i^L dP}}{\hat{\phi}_i^V(T, P, x_j) P}$$

The functional dependence of all derived parameters on measurable properties and the type of constitutive property relationships needed to evaluate K for each component are as follows:

i. $\gamma_i^L = f(T, P, x_j)$, and can be evaluated using Equation (9-180): $\overline{\Delta G_i^{EX}} = RT \ln \gamma_i$

ii. $\hat{\phi}_i^V = f(T, P, x_j)$, and can be evaluated using Equation (9-142):

$$RT \ln \hat{\phi}_i = - \int_{\infty}^V \left[\left(\frac{\partial P}{\partial N_i} \right)_{T, \underline{V}, N_{j[i]}} - \frac{RT}{\underline{V}} \right] d\underline{V} - RT \ln Z, \text{ and some sort of } P\underline{V}TN \text{ EOS in order to}$$

evaluate the derivatives. Some mixing rules must be specified in order to evaluate the $P\underline{V}TN$ EOS for the mixture.

iii. $\phi_i^V = f(T, P_{VP,i})$, meaning that the fugacity coefficient of pure component i is a function of temperature only, and once this temperature is specified the vapor pressure will be set by the equilibrium condition. The pure component fugacity coefficient is evaluated via

$$\text{Equation (9-143): } RT \ln \hat{\phi}_i = - \int_{\infty}^V \left[\left(\frac{\partial P}{\partial N} \right)_{T, \underline{V}} - \frac{RT}{\underline{V}} \right] d\underline{V} - RT \ln Z.$$

Once again some sort of $P\underline{V}TN$ EOS is needed.

iv. $P_{VP,i} = f(T)$, and is a property of the pure component. Its value can come directly from experimental data, or can be approximated using the Antoine or Clausius-Clapeyron equation to correlate some data.

v. $e^{\int_{P_{VP,i}}^P V_i^L dP} = f(T, P)$, since the liquid volume varies with T and P , and can be evaluated using experimental liquid density data.

(b)

Since the nomograph does not make any assumptions about the composition of the system, but merely gives the K values of each component as a function of temperature and pressure, it is apparent that only pure component properties were used in constructing the chart. However, the chart should look familiar to students from their undergrad classes, or one should realize that not many people would spend their time making such an elaborate chart only to say that it is not useful, so the chart must be accurate at least under some conditions. The pressure and temperature ranges are such that an ideal gas assumption is not valid for the vapor phase at all conditions. However, we could assume **ideal solution** behavior in **both** the liquid and vapor

phases. In this case, both phases follow the Lewis and Randall rule, so that the symmetrically normalized activity coefficients are all unity and:

$$\hat{f}_i^L = x_i f_i^L \quad \hat{f}_i^V = y_i f_i^V$$

The expression for K then reduces to:

$$K = \frac{y_i}{x_i} = \frac{\phi_i^V(T, P_{VP,i}) P_{VP,i} e^{\int_{P_{VP,i}}^P \frac{V_i^L}{RT} dP}}{\phi_i^V(T, P) P}$$

Note that all the parameters are only functions of pure property information. Therefore, even though this new expression for K only considers pure component properties and is not concerned with intermolecular interactions of unlike species, it is obvious that it can still capture many non-idealities.

At low pressures, the Poynting correction factor is small enough that it can be ignored, and the vapor phase approaches ideal gas behavior, so that the fugacity coefficients approach a value of unity, and:

$$\lim_{P \rightarrow 0} K = \frac{P_{VP,i}}{P}$$

The same conclusion is reached if it is assumed that the liquid phase is an ideal solution and the vapor phase is an ideal gas mixture.

In the end, it turns out that both Rocky and Rochelle are correct, to a certain extent. Rochelle is correct because the nomograph is based off of pure component properties and does not account for molecular interactions. A failure to count for these interactions will lead to some error in the resulting data, with the error increasing the more non-ideal the solution becomes. So Rochelle is correct in her assertion that the K values in the chart fail to include intermolecular interactions.

However, these hydrocarbons are very similar in structure, so that we would expect the components to have similar properties. Therefore, ideal solution ($\gamma_i = 0$) behavior is a reasonable assumption, and the resulting nomograph would give fairly accurate values of K for mixtures of the given components. The ideal gas assumption is fairly accurate as well for many of the pressures given in the chart. Since it is very likely that the nomograph is based off of experimental data, even at higher pressures, the chart should capture many of the non-idealities introduced by the breakdown of the ideal gas assumption and the Poynting correction factor, as long as ideal solution behavior holds. For systems of components of dissimilar molecular structures, we could expect non-ideal effects to be large though.