Review of Chemical Equilibrium — Introduction

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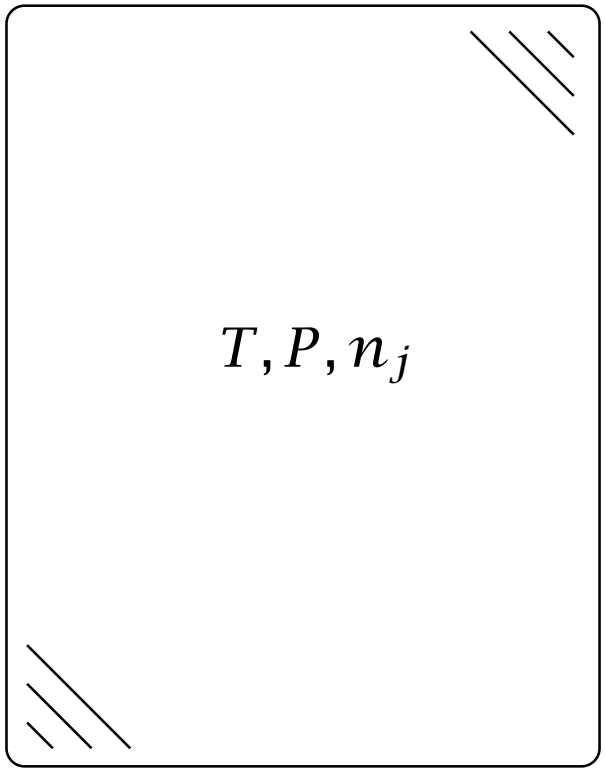
- This chapter is a review of the equilibrium state of a system that can undergo chemical reaction
- Operating reactors are *not* at chemical equilibrium, so why study this?
- Find limits of reactor performance
- Find operations or design changes that allow these restrictions to be changed and reactor performance improved

Thermodynamic system



Variables: temperature, T, pressure, P, the number of moles of each component, n_j, $j = 1, \ldots, n_s$.

Specifying the temperature, pressure, and number of moles of each component then completely specifies the equilibrium state of the system.

Gibbs Energy

- The **Gibbs energy** of the system, G, is the convenient energy function of these state variables

- The difference in Gibbs energy between two different states

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

S is the system entropy,

V is the system volume and

μ_j is the **chemical potential** of component j.

Condition for Reaction Equilibrium

Consider a closed system. The n_j can change only by the single chemical reaction,

$$\nu_1 A_1 + \nu_2 A_2 \rightleftharpoons \nu_3 A_3 + \nu_4 A_4 \qquad \sum_j \nu_j A_j = 0$$

Reaction extent.

$$dn_j = \nu_j d\varepsilon$$

Gibbs energy.

$$dG = -SdT + VdP + \sum_j \left(\nu_j \mu_j\right) d\varepsilon \tag{1}$$

For the closed system, G is only a function of T, P and ε.

Partial derivatives

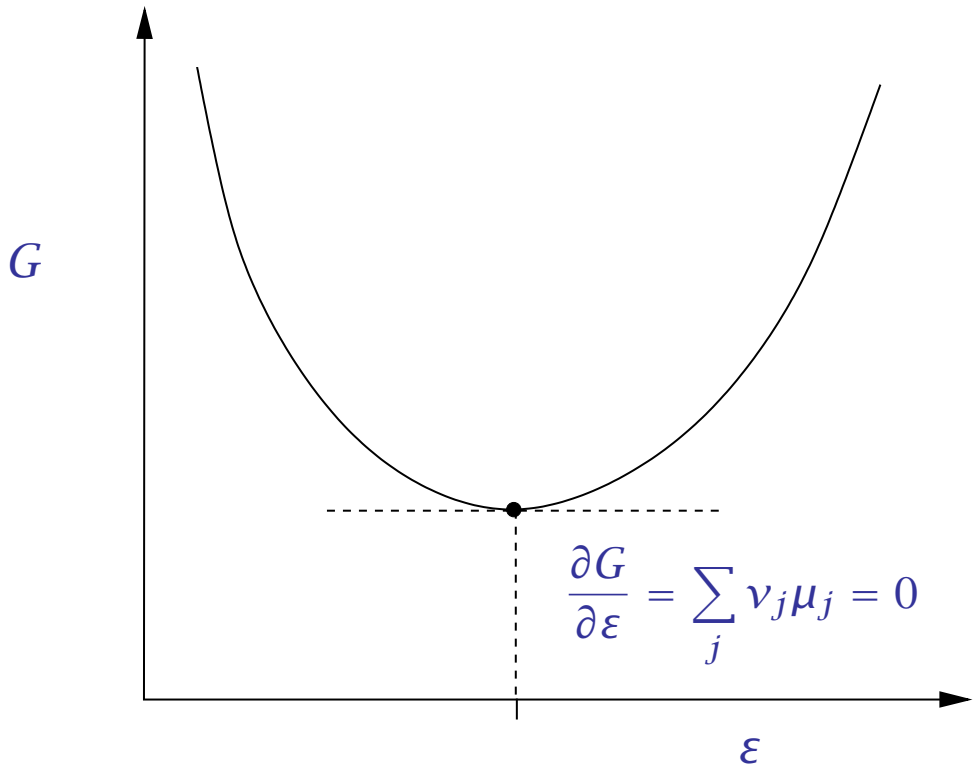
$$dG = -SdT + VdP + \sum_j \left(\nu_j \mu_j\right) d\varepsilon$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\varepsilon} \tag{2}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,\varepsilon} \tag{3}$$

$$\sum_j \nu_j \mu_j = \left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P} \tag{4}$$

G versus the reaction extent



A necessary condition for the Gibbs energy to be a minimum

$$\boxed{\sum_j \nu_j \mu_j = 0} \qquad (5)$$

Other forms: activity, fugacity

$$\mu_j = G_j^\circ + RT \ln a_j$$

- a_j is the activity of component j in the mixture referenced to some standard state
- G_j° is the Gibbs energy of component j in the same standard state.
- The activity and fugacity of component j are related by

$$a_j = f_j / f_j^\circ$$

f_j is the fugacity of component j
f_j° is the fugacity of component j in the standard state.

The Standard State

- The standard state is: pure component j at 1.0 atm pressure and the system temperature.
- G_j° and f_j° are therefore *not* functions of the system pressure or composition
- G_j° and f_j° are strong functions of the system temperature

Gibbs energy change of reaction

$$\mu_j = G_j^\circ + RT \ln a_j$$

$$\sum_j \nu_j \mu_j = \sum_j \nu_j G_j^\circ + RT \sum_j \nu_j \ln a_j \tag{6}$$

The term $\sum_j \nu_j G_j^\circ$ is known as the standard Gibbs energy change for the reaction, ΔG°.

$$\Delta G^\circ + RT \ln \prod_j a_j^{\nu_j} = 0 \tag{7}$$

Equilibrium constant

$$K = e^{-\Delta G^\circ / RT} \tag{8}$$

Another condition for chemical equilibrium

$$K = \prod_j a_j^{\nu_j} \tag{9}$$

K also is a function of the system temperature, but not a function of the system pressure or composition.

Ideal gas equilibrium

The reaction of isobutane and linear butenes to branched C_8 hydrocarbons is used to synthesize high octane fuel additives.

$$\text{isobutane} + 1\text{-butene} \rightleftharpoons 2,2,3\text{-trimethylpentane}$$
$$\text{I} \quad + \quad \text{B} \quad \rightleftharpoons \quad \text{P}$$

Determine the equilibrium composition for this system at a pressure of 2.5 atm and temperature of 400K. The standard Gibbs energy change for this reaction at 400K is -3.72 kcal/mol [5].

Solution

The fugacity of a component in an ideal-gas mixture is equal to its partial pressure,

$$f_j = P_j = y_j P \tag{10}$$

$f_j^\circ = 1.0$ atm because the partial pressure of a pure component j at 1.0 atm total pressure is 1.0 atm. The activity of component j is then simply

$$a_j = \frac{P_j}{1 \text{ atm}} \tag{11}$$

$$K = \frac{a_\mathrm{P}}{a_\mathrm{I} a_\mathrm{B}} \tag{12}$$

Solution (cont.)

$$K = e^{-\Delta G^\circ / RT}$$

$$K = 108$$

$$K = \frac{P_\mathrm{P}}{P_\mathrm{I} P_\mathrm{B}} = \frac{y_\mathrm{P}}{y_\mathrm{I} y_\mathrm{B} P}$$

in which P is 2.5 atm. Three unknowns, one equation,

$$\sum_j y_j = 1$$

Three unknowns, two equations. What went wrong?

Ideal-gas equilibrium, revisited

Additional information. The gas is contained in a closed vessel that is initially charged with an equimolar mixture of isobutane and butene.

Let n_{j0} represent the unknown initial number of moles

$$\begin{aligned} n_{\mathrm{I}} &= n_{\mathrm{I0}} - \varepsilon \\ n_{\mathrm{B}} &= n_{\mathrm{B0}} - \varepsilon \\ n_{\mathrm{P}} &= n_{\mathrm{P0}} + \varepsilon \end{aligned} \tag{13}$$

Summing Equations 13 produces

$$n_T = n_{T0} - \varepsilon$$

in which n_T is the total number of moles in the vessel.

Moles to mole fractions

The total number of moles decreases with reaction extent because more moles are consumed than produced by the reaction. Dividing both sides of Equations 13 by n_T produces equations for the mole fractions in terms of the reaction extent,

$$y_{\mathrm{I}} = \frac{n_{\mathrm{I0}} - \varepsilon}{n_{T0} - \varepsilon} \qquad y_{\mathrm{B}} = \frac{n_{\mathrm{B0}} - \varepsilon}{n_{T0} - \varepsilon} \qquad y_{\mathrm{P}} = \frac{n_{\mathrm{P0}} + \varepsilon}{n_{T0} - \varepsilon}$$

Dividing top and bottom of the right-hand side of the previous equations by n_{T0} yields,

$$y_{\mathrm{I}} = \frac{y_{\mathrm{I0}} - \varepsilon'}{1 - \varepsilon'} \qquad y_{\mathrm{B}} = \frac{y_{\mathrm{B0}} - \varepsilon'}{1 - \varepsilon'} \qquad y_{\mathrm{P}} = \frac{y_{\mathrm{P0}} + \varepsilon'}{1 - \varepsilon'}$$

in which $\varepsilon' = \varepsilon / n_{T0}$ is a *dimensionless* reaction extent that is scaled by the initial total number of moles.

One equation and one unknown

$$K = \frac{(y_{\mathrm{P0}} + \varepsilon')(1 - \varepsilon')}{(y_{\mathrm{B0}} - \varepsilon')(y_{\mathrm{I0}} - \varepsilon')P}$$

$$(y_{\mathrm{B0}} - \varepsilon')(y_{\mathrm{I0}} - \varepsilon')KP - (y_{\mathrm{P0}} + \varepsilon')(1 - \varepsilon') = 0$$

Quadratic in ε'. Using the initial composition, $y_{\mathrm{P0}} = 0, y_{\mathrm{B0}} = y_{\mathrm{I0}} = 1/2$ gives

$$\varepsilon'^2(1 + KP) - \varepsilon'(1 + KP) + (1/4)KP = 0$$

The *two* solutions are

$$\varepsilon' = \frac{1 \pm \sqrt{1/(1 + KP)}}{2} \tag{14}$$

Choosing the solution

The correct solution is chosen by considering the physical constraints that mole fractions must be positive.

The negative sign is therefore chosen, and the solution is $\varepsilon' = 0.469$.

The equilibrium mole fractions are then computed from Equation giving

$$y_{\mathrm{I}} = 5.73 \times 10^{-2}$$

$$y_{\mathrm{B}} = 5.73 \times 10^{-2}$$

$$y_{\mathrm{P}} = 0.885$$

The equilibrium at 400K favors the product trimethylpentane.

Second derivative of G.

Please read the book for this discussion.

I will skip over this in lecture.

Evaluation of G.

Let's calculate directly $G(T, P, \varepsilon')$ and see what it looks like.

$$G = \sum_j \mu_j n_j \tag{15}$$

$$\mu_j = G_j^\circ + RT\left[\ln \gamma_j + \ln P\right]$$

$$G = \sum_j n_j G_j^\circ + RT \sum_j n_j \left[\ln \gamma_j + \ln P\right] \tag{16}$$

For this single reaction case, $n_j = n_{j0} + \nu_j \varepsilon$, which gives

$$\sum_j n_j G_j^\circ = \sum_j n_{j0} G_j^\circ + \varepsilon \Delta G^\circ \tag{17}$$

Modified Gibbs energy

$$\widetilde{G}(T,P,\varepsilon') = \frac{G - \sum_j n_{j0} G_j^\circ}{n_{T0} RT} \tag{18}$$

Substituting Equations 16 and 17 into Equation 18 gives

$$\widetilde{G} = \varepsilon' \frac{\Delta G^\circ}{RT} + \sum_j \frac{n_j}{n_{T0}} \left[\ln \gamma_j + \ln P \right] \tag{19}$$

Expressing the mole fractions in terms of reaction extent gives

$$\widetilde{G} = -\varepsilon' \ln K + \sum_j (\gamma_{j0} + \nu_j \varepsilon') \left[\ln \left(\frac{(\gamma_{j0} + \nu_j \varepsilon')}{1 + \bar{\nu} \varepsilon'} \right) + \ln P \right]$$

Final expression for the modified Gibbs Energy

$$\widetilde{G} = -\varepsilon' \ln K + (1 + \bar{\nu}\varepsilon') \ln P + \sum_j (\gamma_{j0} + \nu_j \varepsilon') \ln \left(\frac{\gamma_{j0} + \nu_j \varepsilon'}{1 + \bar{\nu}\varepsilon'} \right) \qquad (20)$$

- T and P are known values, so $\widetilde{G}$ is simply a shift of the G function up or down by a constant and then rescaling by the positive constant $1/(n_{T0}RT)$.
- The shape of the function $\widetilde{G}$ is the same as G
- The minimum with respect to ε' is at the same value of ε' for the two functions.

Minimum in G for an ideal gas

Goal: plot $\widetilde{G}$ for the example and find the minimum with respect to ε'

$$\mathrm{I} + \mathrm{B} \rightleftharpoons \mathrm{P} \tag{21}$$

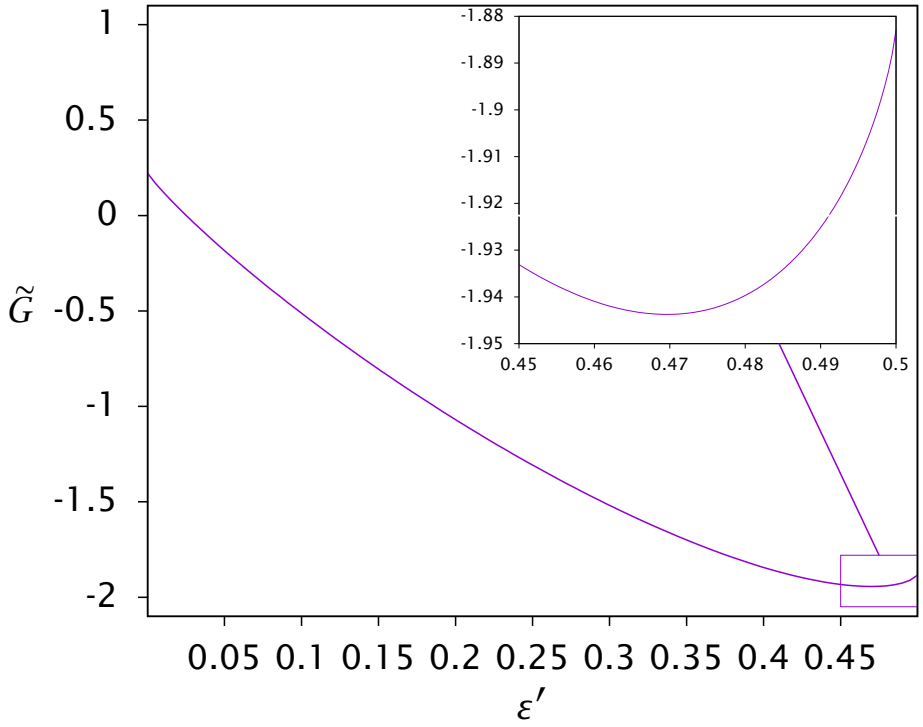
For this stoichiometry: $\sum_j \nu_j = \bar{\nu} = -1$.
Equimolar starting mixture: $y_{P0} = 0, y_{I0} = y_{B0} = 0.5$

$$\widetilde{G}(T,P,\varepsilon') = -\varepsilon' \ln K(T) + (1-\varepsilon') \ln P + \varepsilon' \ln(\varepsilon') + 2(0.5-\varepsilon') \ln(0.5-\varepsilon') - (1-\varepsilon') \ln(1-\varepsilon') \tag{22}$$

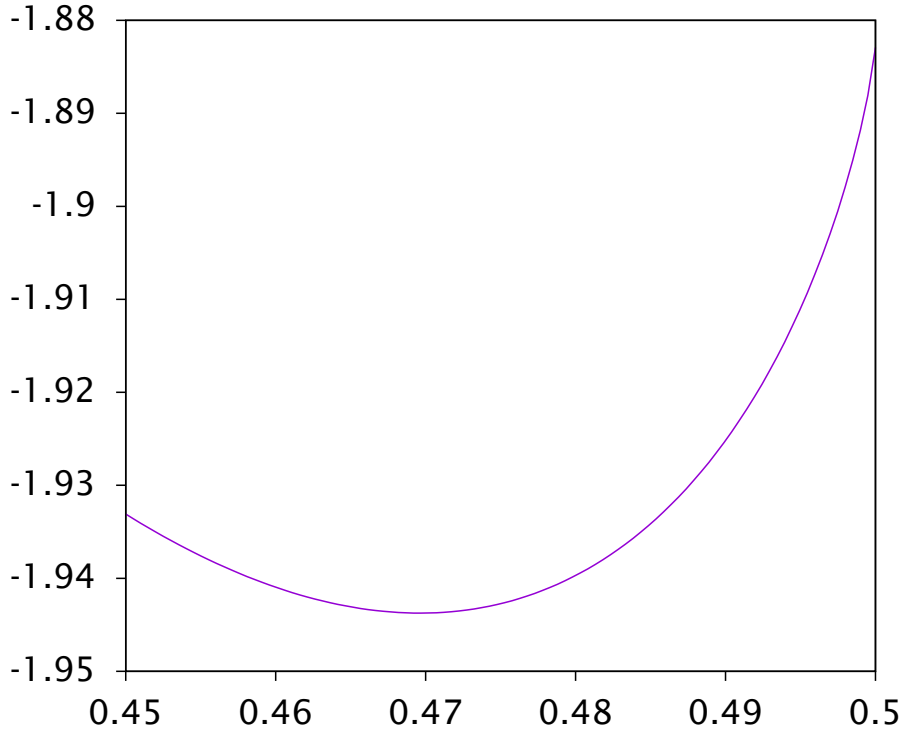
A picture is worth 1000 words

Recall that the range of physically significant ε' values is $0 \leq \varepsilon' \leq 0.5$

and what do we see...



A closer look



Good agreement with the calculated value 0.469

The solution is a minimum, and the minimum is unique.

Effect of pressure

- From Equation 20, for an ideal gas, the pressure enters directly in the Gibbs energy with the $\ln P$ term.
- Remake the plot for $P = 2.0$.
- Remake the plot for $P = 1.5$.
- How does the equilibrium composition change.
- Does this agree with Le Chatelier's principle?
- For single liquid-phase or solid-phase systems, the effect of pressure on equilibrium is usually small, because the chemical potential of a component in a liquid-phase or solid-phase solution is usually a weak function of pressure.

Effect of temperature

- The temperature effect on the Gibbs energy is contained in the $\ln K(T)$ term.
- This term often gives rise to a large effect of temperature on equilibrium.
- We turn our attention to the evaluation of this important temperature effect in the next section.

Evaluation of the Gibbs Energy Change of Reaction

We usually calculate the standard Gibbs energy change for the reaction, ΔG°, by using the Gibbs energy of formation of the species.

The standard state for the elements are usually the pure elements in their common form at 25°C and 1.0 atm.

$$G^\circ_{\mathrm{H_2O}f} = G^\circ_{\mathrm{H_2O}} - G^\circ_{\mathrm{H_2}} - \frac{1}{2}G^\circ_{\mathrm{O_2}} \tag{23}$$

This gives the Gibbs energy change for the reaction at 25°C

$$\boxed{\Delta G^\circ_i = \sum_j \nu_{ij} G^\circ_{jf}} \tag{24}$$

Thermochemical Data — Where is it?

- Finding appropriate thermochemical data remains a significant challenge for solving realistic, industrial problems.
- Vendors offer a variety of commercial thermochemical databases to address this need.
- Many companies also maintain their own private thermochemical databases for compounds of special commercial interest to them.
- Design Institute for Physical Property Data (DIPPR) database. A web-based student version of the database provides students with access to data for 2000 common compounds at no charge: `http://dippr.byu.edu/students/chemsearch.asp`.

Temperature Dependence of the Standard Gibbs Energy

The standard state temperature $25^{\circ}\mathrm{C}$ is often not the system temperature.

To convert to the system temperature, we need the temperature dependence of ΔG°

Recall from Equation 2 that the change of the Gibbs energy with temperature is the negative of the entropy,

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_j} = -S, \qquad \left(\frac{\partial G_j^{\circ}}{\partial T}\right)_{P,n_j} = -S_j^{\circ}$$

Summing with the stoichiometric coefficients gives

$$\sum_j \frac{\partial(\nu_j G_j^\circ)}{\partial T} = \sum_j -\nu_j S_j^\circ$$

Defining the term on the right-hand side to be the standard entropy change of reaction, ΔS° gives

$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ \tag{25}$$

Let H denote the enthalpy and recall its connection to the Gibbs energy,

$$G = H - TS \tag{26}$$

Partial molar properties.

Recall the definition of a partial molar property is

$$\overline{X}_j = \left(\frac{\partial X}{\partial n_j}\right)_{T,P,n_k}$$

in which X is any extensive mixture property (U, H, A, G, V, S, etc.).

$$G_j^\circ = H_j^\circ - TS_j^\circ$$

summing with the stoichiometric coefficient yields

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (27)$$

$$\frac{\partial \Delta G^\circ}{\partial T} = \frac{\Delta G^\circ - \Delta H^\circ}{T}$$

van 't Hoff equation

Rearranging this equation and division by RT gives

$$\frac{1}{RT}\frac{\partial \Delta G^\circ}{\partial T} - \frac{\Delta G^\circ}{RT^2} = -\frac{\Delta H^\circ}{RT^2}$$

Using differentiation formulas, the left-hand side can be rewritten as

$$\frac{\partial \left(\frac{\Delta G^\circ}{RT}\right)}{\partial T} = -\frac{\Delta H^\circ}{RT^2}$$

which finally can be expressed in terms of the equilibrium constant

$$\boxed{\frac{\partial \ln K}{\partial T} = \frac{\Delta H^\circ}{RT^2}} \qquad (28)$$

One further approximation

$$\int_{T_1}^{T_2} \frac{\partial \ln K}{\partial T} dT = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} dT$$

If ΔH° is approximately constant

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{29}$$

Condition for Phase Equilibrium

Consider a multicomponent, multiphase system that is at equilibrium and denote two of the phases as α and β.

T^k and P^k are the temperature and pressure of phase k

n_j^k is the number of moles of component j in phase k.

$\hat{\mu}_j^k$ is the chemical potential of component j in phase k

Phase equilibrium conditions.

$$T^{\alpha} = T^{\beta}$$

$$P^{\alpha} = P^{\beta}$$

$$\hat{\mu}_j^{\alpha} = \hat{\mu}_j^{\beta}, \qquad j = 1, 2, \ldots, n_s \tag{30}$$

$$\hat{\mu}_j = \mu_j^{\circ} + RT \ln \hat{f}_j \tag{31}$$

If we express Equation 31 for two phases α and β and equate their chemical potentials we deduce

$$\hat{f}_j^{\alpha} = \hat{f}_j^{\beta}, \qquad j = 1, 2 \ldots, n_s \tag{32}$$

One can therefore use either the equality of chemical potentials or fugacities as the condition for equilibrium.

Gaseous Solutions

Let f_j^G denote the fugacity of pure component j in the gas phase at the mixture's temperature and pressure.

The simplest mixing rule is the linear mixing rule

$$\hat{f}_j^G = f_j^G y_j \qquad \text{(ideal mixture)} \tag{33}$$

An ideal gas obeys this mixing rule *and* the fugacity of pure j at the mixture's T and P is the system's pressure, $f_j^G = P$.

$$\hat{f}_j^G = P y_j \qquad \text{(ideal gas)}$$

Liquid (and Solid) Solutions

The simplest mixing rule for liquid (and solid) mixtures is that the fugacity of component j in the mixture is the fugacity of pure j at the mixture's temperature and pressure times the mole fraction of j in the mixture.

$$\hat{f}_j^L = f_j^L x_j \tag{34}$$

This approximation is usually valid when the mole fraction of a component is near one.

In a two-component mixture, the Gibbs-Duhem relations imply that if the first component obeys the ideal mixture, then the second component follows **Henry's law**

$$\hat{f}_2^L = k_2 x_2 \tag{35}$$

in which k_2 is the Henry's law constant for the second component.

Is $k_2 = f_2^L$?

Fugacity pressure dependence.

For condensed phases, the fugacity is generally a weak function of pressure. See the notes for this derivation

$$\hat{f}_j\Big|_{P_2} = \hat{f}_j\Big|_{P_1} \exp\left[\frac{\overline{V}_j(P_2 - P_1)}{RT}\right] \tag{36}$$

The exponential term is called the Poynting correction factor.

The Poynting correction may be neglected if the pressure does not vary by a large amount.

Nonideal Mixtures

For gaseous mixtures, we define the fugacity coefficient, $\hat{\phi}_j$

$$\hat{f}_j^G = P y_j \hat{\phi}_j$$

The analogous correcting factor for the liquid phase is the activity coefficient, γ_j.

$$\hat{f}_j^L = f_j^L x_j \gamma_j$$

These coefficients may be available in several forms. Correlations may exist for systems of interest or phase equilibrium data may be available from which the coefficients can be calculated [2, 3, 6, 4, 1].

Equilibrium Composition for Heterogeneous Reactions

We illustrate the calculation of chemical equilibrium when there are *multiple phases* as well as a *chemical reaction* taking place.

Consider the liquid-phase reaction

$$\mathrm{A(l)} + \mathrm{B(l)} \rightleftharpoons \mathrm{C(l)} \tag{37}$$

that occurs in the following three-phase system.
Phase I: nonideal liquid mixture of A and C only. For illustration purposes, assume the activity coefficients are given by the simple Margules equation,

$$\ln \gamma_A = x_C^2 \left[A_{AC} + 2(A_{CA} - A_{AC}) x_A \right]$$
$$\ln \gamma_C = x_A^2 \left[A_{CA} + 2(A_{AC} - A_{CA}) x_C \right]$$

Phase II: pure liquid B.

Phase III: ideal-gas mixture of A, B and C.

Phase and reaction equilibrium

All three phases are in intimate contact and we have the following data:

$$A_{AC} = 1.4$$

$$A_{CA} = 2.0$$

$$P_A^\circ = 0.65 \text{ atm}$$

$$P_B^\circ = 0.50 \text{ atm}$$

$$P_C^\circ = 0.50 \text{ atm}$$

in which P_j° is the vapor pressure of component j at the system temperature.

Phase and reaction equilibrium

1. Plot the partial pressures of A and C versus x_A for a vapor phase that is in equilibrium with only the A–C liquid phase. Compute the Henry's law constants for A and C from the Margules equation. Sketch the meaning of Henry's law on the plot and verify your calculation from the plot.

2. Use Henry's law to calculate the composition of all three phases for $K = 4.7$. What is the equilibrium pressure?

3. Repeat for $K = 0.23$.

4. Assume $K = 1$. Use the Margules equation to calculate the composition of all three phases.

5. Repeat 4 with an ideal mixture assumption and compare the results.

Part 1.

Equate the chemical potential in gas and liquid-phases. Since the gas phase is assumed an ideal-gas mixture:

$$\hat{f}_A^{\mathrm{G}} = P_A \quad \text{gas phase,} \qquad \hat{f}_A^{\mathrm{L}} = f_A^{\mathrm{L}} x_A \gamma_A \quad \text{liquid phase} \tag{38}$$

The fugacity of pure liquid A at the system T and P is not known.

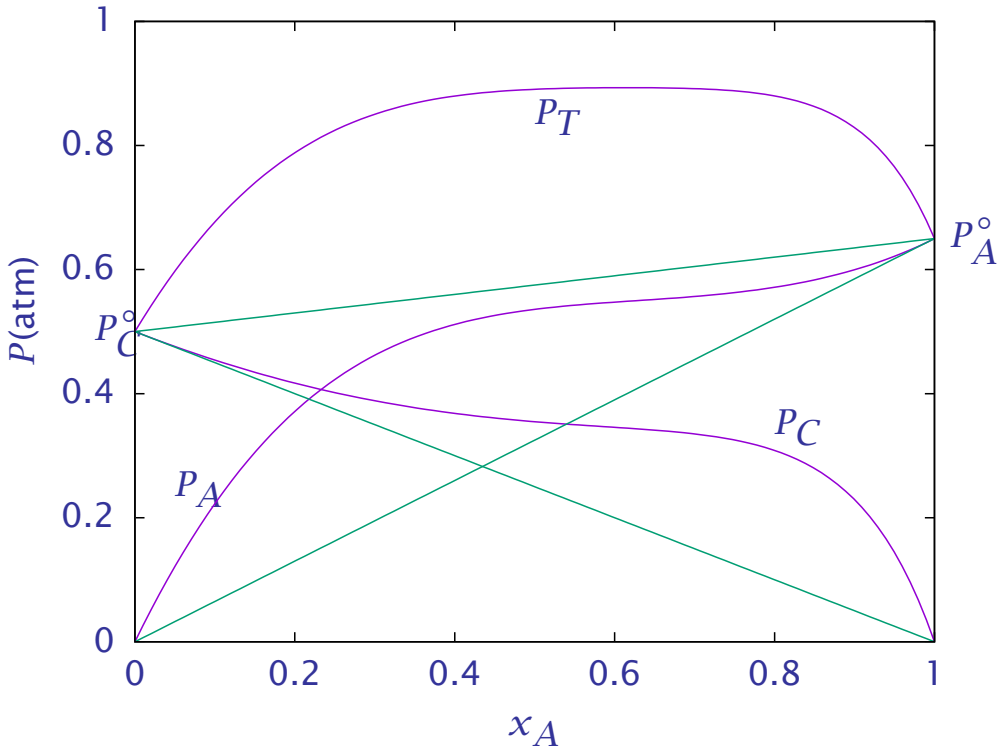
The fugacity of pure liquid A at the system temperature and the *vapor pressure of A at the system temperature is* known; it is simply the vapor pressure, P_A°.

If we neglect Poynting

$$f_A^{\mathrm{L}} = P_A^\circ, \qquad P_A = P_A^\circ x_A \gamma_A \tag{39}$$

The analogous expression is valid for P_C.

Part 1.



Part 1.

Henry's law for component A is

$$\hat{f}_A^L = k_A x_A, \qquad \hat{f}_A^L = f_A^L x_A \gamma_A$$

which is valid for x_A small.

$$k_A = P_A^\circ \gamma_A$$

which is also valid for small x_A. Computing γ_A from the Margules equation for $x_A = 0$ gives

$$\gamma_A(0) = e^{A_{AC}}$$

So the Henry's law constant for component A is

$$k_A = P_A^\circ e^{A_{AC}}$$

Part 1.

The analogous expression holds for component C. Substituting in the values gives

$$k_A = 2.6, \qquad k_C = 3.7$$

The slope of the tangent line to the P_A curve at $x_A = 0$ is equal to k_A.

The negative of the slope of the tangent line to the P_C curve at $x_A = 1$ is equal to k_C.

Part 2.

For $K = 4.7$, one expects a large value of the equilibrium constant to favor the formation of the product, C. We therefore assume that x_A is small and Henry's law is valid for component A.

The unknowns in the problem: x_A and x_C in the A–C mixture, y_A, y_B and y_C in the gas phase, P.

We require six equations for a well-posed problem: equate fugacities of each component in the gas and liquid phases,

the mole fractions sum to one in the gas and A–C liquid phases.

The chemical equilibrium provides the sixth equation.

Part 2.

$$K = \frac{\hat{a}_C}{\hat{a}_A \hat{a}_B}$$

$$\hat{a}_A^L = \frac{\hat{f}_A^L}{f_A^\circ} = \frac{k_A x_A}{f_A^\circ}$$

f_A° is the fugacity of pure liquid A at the system temperature and 1.0 atm. Again, this value is *unknown*, but we do know that P_A° is the fugacity of pure liquid A at the system temperature and the vapor pressure of A at this temperature.

The difference between 0.65 and 1.0 atm is not large, so we assume $f_A^\circ = P_A^\circ$.

x_C is assumed near one, so

$$\hat{a}_C^L = \frac{\hat{f}_C^L}{f_C^\circ} = \frac{f_C^L x_C}{f_C^\circ}$$

Now f_C^L and f_C° are the fugacities of pure liquid C at the system temperature and the system pressure and 1.0 atm, respectively.

If the system pressure turns out to be reasonably small, then it is a good assumption to assume these fugacities are equal giving,

$$\hat{a}_C^L = x_C$$

Since component B is in a pure liquid phase, the same reasoning leads to

$$\hat{a}_B^L = \frac{\hat{f}_B^L}{f_B^\circ} = \frac{f_B^L}{f_B^\circ} = 1$$

Part 2.

Substituting these activities into the reaction equilibrium condition gives

$$K = \frac{x_C}{x_A k_A / P_A^\circ \cdot 1} \tag{40}$$

Solving Equation 40 for x_A yields

$$x_A = \left(1 + \frac{k_A K}{P_A^\circ}\right)^{-1} \qquad x_C = \left(1 + \frac{P_A^\circ}{k_A K}\right)^{-1}$$

Substituting in the provided data gives

$$x_A = 0.05, \qquad x_C = 0.95$$

The assumption of Henry's law for component A is reasonable.

Part 2.

The vapor compositions now are computed from the phase equilibrium conditions.

$$P_A = k_A x_A$$

$$P_B = P_B^\circ$$

$$P_C = P_C^\circ x_C$$

Substituting in the provided data gives

$$P_A = 0.13 \text{ atm}, \qquad P_B = 0.50 \text{ atm}, \qquad P_C = 0.48 \text{ atm}$$

The system pressure is therefore $P = 1.11$ atm.

Finally, the vapor-phase concentrations can be computed from the ratios of partial pressures to total pressure,

$$y_A = 0.12, \qquad y_B = 0.45, \qquad y_C = 0.43$$

Part 3.

For $K = 0.23$ one expects the reactants to be favored so Henry's law is assumed for component C. You are encouraged to work through the preceding development again for this situation. The answers are

$$x_A = 0.97, \qquad x_C = 0.03$$

$$y_A = 0.51, \qquad y_B = 0.40, \qquad y_C = 0.09$$

$$P = 1.24 \text{ atm}$$

Again the assumption of Henry's law is justified and the system pressure is low.

Part 4.

For $K = 1$, we may not use Henry's law for either A or C.

In this case we must solve the reaction equilibrium condition using the Margules equation for the activity coefficients,

$$K = \frac{x_C y_C}{x_A y_A}$$

Using $x_C = 1 - x_A$, we have one equation in one unknown,

$$K = \frac{(1 - x_A) \exp\left[x_A^2 (A_{CA} + 2(A_{AC} - A_{CA})(1 - x_A))\right]}{x_A \exp\left[(1 - x_A)^2 (A_{AC} + 2(A_{CA} - A_{AC}) x_A)\right]} \tag{41}$$

Part 4.

Equation 41 can be solved numerically to give $x_A = 0.35$.

$$P_j = P_j^\circ x_j \gamma_j, \qquad j = A, C$$

The solution is

$$x_A = 0.35, \qquad x_C = 0.65$$

$$y_A = 0.36, \qquad y_B = 0.37, \qquad y_C = 0.28$$

$$P = 1.37 \text{ atm}$$

Part 5.

Finally, if one assumes that the A–C mixture is ideal, the equilibrium condition becomes

$$K = \frac{x_C}{x_A}$$

which can be solved to give $x_A = 1/(1+K)$. For $K = 1$, the solution is

$$x_A = 0.5, \qquad x_C = 0.5$$

$$y_A = 0.30, \qquad y_B = 0.47, \qquad y_C = 0.23$$

$$P = 1.08 \text{ atm}$$

The ideal mixture assumption leads to significant error given the strong deviations from ideality shown in Figure .

Multiple Reactions

We again consider a single-phase system but allow n_r reactions

$$\sum_j \nu_{ij} A_j = 0, \qquad i = 1, 2, \ldots, n_r$$

Let ε_i be the reaction extent for the ith reaction

$$n_j = n_{j0} + \sum_i \nu_{ij} \varepsilon_i \tag{42}$$

We can compute the change in Gibbs energy as before

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

Multiple Reactions

Using $dn_j = \sum_i \nu_{ij} d\varepsilon_i$, gives

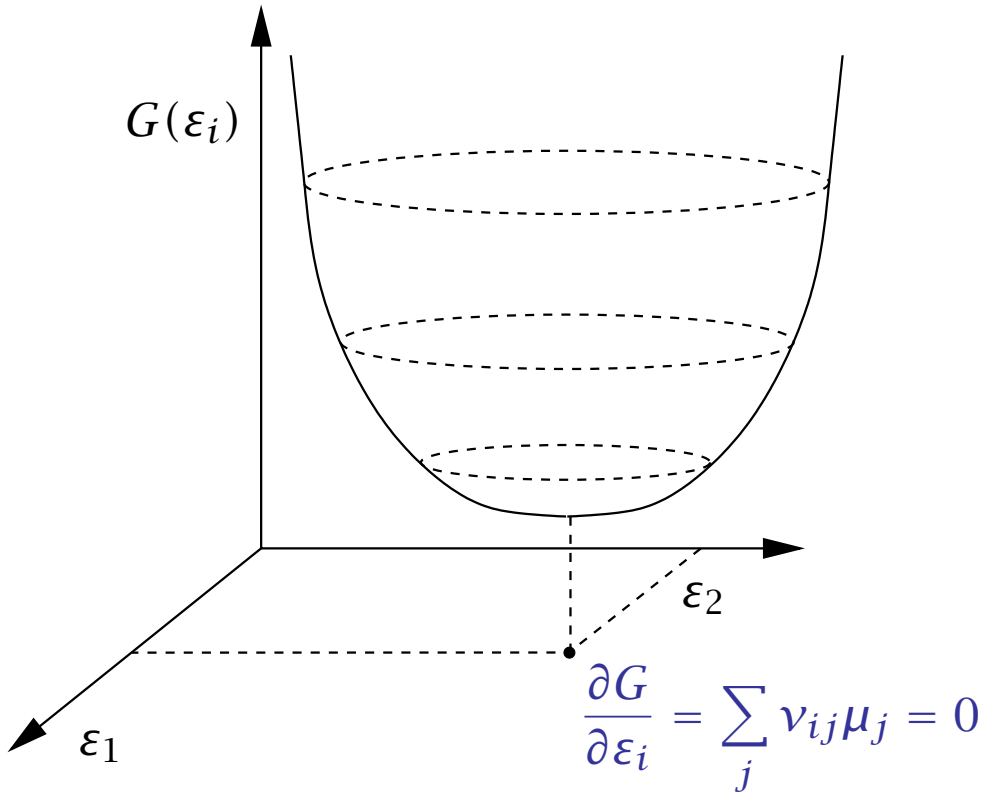
$$dG = -SdT + VdP + \sum_j \mu_j \sum_i \nu_{ij} d\varepsilon_i$$

$$= -SdT + VdP + \sum_i \left(\sum_j \nu_{ij} \mu_j \right) d\varepsilon_i \qquad (43)$$

At constant T and P, G is a minimum as a function of the n_r reaction extents. Necessary conditions are therefore

$$\left(\frac{\partial G}{\partial \varepsilon_i} \right)_{T,P,\varepsilon_{l \neq i}} = 0, \qquad i = 1, 2, \ldots, n_r$$

Multiple Reactions



Evaluating the partial derivatives in Equation 43 gives

$$\sum_j \nu_{ij}\mu_j = 0, \qquad i = 1, 2, \ldots, n_r \tag{44}$$

Multiple Reactions

$$\sum_j \nu_{ij}\mu_j = \sum_j \nu_{ij}G_j^\circ + RT\sum_j \nu_{ij}\ln a_j$$

Defining the standard Gibbs energy change for reaction i, $\Delta G_i^\circ = \sum_j \nu_{ij}G_j^\circ$ gives

$$\sum_j \nu_{ij}\mu_j = \Delta G_i^\circ + RT\sum_j \nu_{ij}\ln a_j$$

Finally, defining the equilibrium constant for reaction i as

$$K_i = e^{-\Delta G_i^\circ/RT} \tag{45}$$

allows one to express the reaction equilibrium condition as

$$K_i = \prod_j a_j^{\nu_{ij}}, \qquad i = 1, 2, \ldots, n_r \tag{46}$$

Equilibrium composition for multiple reactions

In addition to the formation of 2,2,3-trimethylpentane, 2,2,4-trimethylpentane may also form

$$\text{isobutane} + 1\text{–butene} \rightleftharpoons 2,2,4\text{–trimethylpentane} \tag{47}$$

Recalculate the equilibrium composition for this example given that $\Delta G^\circ = -4.49$ kcal/mol for this reaction at 400K.

Let P_1 be 2,2,3 trimethylpentane, and P_2 be 2,2,4-trimethylpentane. From the Gibbs energy changes, we have

$$K_1 = 108, \qquad K_2 = 284$$

Trimethyl pentane example

$$n_I = n_{I0} - \varepsilon_1 - \varepsilon_2 \qquad n_B = n_{B0} - \varepsilon_1 - \varepsilon_2 \qquad n_{P_1} = n_{P_{10}} + \varepsilon_1 \qquad n_{P_2} = n_{P_{20}} + \varepsilon_2$$

The total number of moles is then $n_T = n_{T0} - \varepsilon_1 - \varepsilon_2$. Forming the mole fractions yields

$$y_I = \frac{y_{I0} - \varepsilon_1' - \varepsilon_2'}{1 - \varepsilon_1' - \varepsilon_2'} \qquad y_B = \frac{y_{B0} - \varepsilon_1' - \varepsilon_2'}{1 - \varepsilon_1' - \varepsilon_2'} \qquad y_{P_1} = \frac{y_{P_{10}} + \varepsilon_1'}{1 - \varepsilon_1' - \varepsilon_2'} \qquad y_{P_2} = \frac{y_{P_{20}} + \varepsilon_2'}{1 - \varepsilon_1' - \varepsilon_2'}$$

Applying Equation 46 to the two reactions gives

$$K_1 = \frac{y_{P_1}}{y_I y_B P} \qquad K_2 = \frac{y_{P_2}}{y_I y_B P}$$

Trimethyl pentane example

Substituting in the mole fractions gives two equations for the two unknown reaction extents,

$$PK_1(y_{I0} - \varepsilon_1' - \varepsilon_2')(y_{B0} - \varepsilon_1' - \varepsilon_2') - (y_{P_{10}} + \varepsilon_1')(1 - \varepsilon_1' - \varepsilon_2') = 0$$

$$PK_2(y_{I0} - \varepsilon_1' - \varepsilon_2')(y_{B0} - \varepsilon_1' - \varepsilon_2') - (y_{P_{20}} + \varepsilon_2')(1 - \varepsilon_1' - \varepsilon_2') = 0$$

Initial condition: $y_I = y_B = 0.5, y_{P_1} = y_{P_2} = 0.$

Numerical solution

Using the initial guess: $\varepsilon_1 = 0.469, \varepsilon_2 = 0$, gives the solution

$$\varepsilon_1 = 0.133, \qquad \varepsilon_2 = 0.351$$

$$y_I = 0.031, \qquad y_B = 0.031, \qquad y_{P_1} = 0.258, \qquad y_{P_2} = 0.680$$

Notice we now produce considerably less 2,2,3-trimethylpentane in favor of the 2,2,4 isomer.

It is clear that one cannot allow the system to reach equilibrium and still hope to obtain a high yield of the desired product.

Optimization Approach

The other main approach to finding the reaction equilibrium is to minimize the Gibbs energy function

We start with

$$G = \sum_j \mu_j n_j \tag{48}$$

and express the chemical potential in terms of activity

$$\mu_j = G_j^\circ + RT \ln a_j$$

We again use Equation 42 to track the change in mole numbers due to multiple reactions,

$$n_j = n_{j0} + \sum_i \nu_{ij} \varepsilon_i$$

Expression for Gibbs energy

Using the two previous equations we have

$$\mu_j n_j = n_{j0} G_j^\circ + G_j^\circ \sum_i \nu_{ij} \varepsilon_i + \left[n_{j0} + \sum_i \nu_{ij} \varepsilon_i \right] RT \ln a_j \tag{49}$$

It is convenient to define the same modified Gibbs energy function that we used in Equation 18

$$\widetilde{G}(T, P, \varepsilon_i') = \frac{G - \sum_j n_{j0} G_j^\circ}{n_{T0} RT} \tag{50}$$

in which $\varepsilon_i' = \varepsilon_i / n_{T0}$.

If we sum on j in Equation 49 and introduce this expression into Equations 48

and 50, we obtain

$$\tilde{G} = \sum_i \varepsilon_i' \frac{\Delta G_i^\circ}{RT} + \sum_j \left[y_{j0} + \sum_i \nu_{ij} \varepsilon_i' \right] \ln a_j$$

Expression for $\widetilde{G}$

$$\boxed{\widetilde{G} = -\sum_i \varepsilon'_i \ln K_i + \sum_j \left[\gamma_{j0} + \sum_i \nu_{ij} \varepsilon'_i \right] \ln a_j} \tag{51}$$

We minimize this modified Gibbs energy over the physically meaningful values of the n_r extents.

The main restriction on these extents is, again, that they produce nonnegative mole numbers, or, if we wish to use intensive variables, nonnegative mole fractions. We can express these constraints as

$$\boxed{-\gamma_{j0} - \sum_i \nu_{ij} \varepsilon'_i \leq 0, \qquad j = 1, \ldots, n_s} \tag{52}$$

Optimization problem

Our final statement, therefore, for finding the equilibrium composition for multiple reactions is to solve the optimization problem

$$\boxed{\min_{\varepsilon_i'} \widetilde{G}} \tag{53}$$

subject to Equation 52.

Multiple reactions with optimization

Revisit the two-reaction trimethylpentane example, and find the equilibrium composition by minimizing the Gibbs energy.

$$a_j = \frac{P}{1\ \text{atm}} y_j \qquad \text{(ideal-gas mixture)}$$

Substituting this relation into Equation 51 and rearranging gives

$$\begin{aligned} \tilde{G} \quad = \quad & -\sum_i \varepsilon'_i \ln K_i + \left(1 + \sum_i \bar{\nu}_i \varepsilon'_i\right) \ln P \\ & + \sum_j \left(y_{j0} + \sum_i \nu_{ij} \varepsilon'_i\right) \ln \left[\frac{y_{j0} + \sum_i \nu_{ij} \varepsilon'_i}{1 + \sum_i \bar{\nu}_i \varepsilon'_i}\right] \end{aligned} \tag{54}$$

Constraints

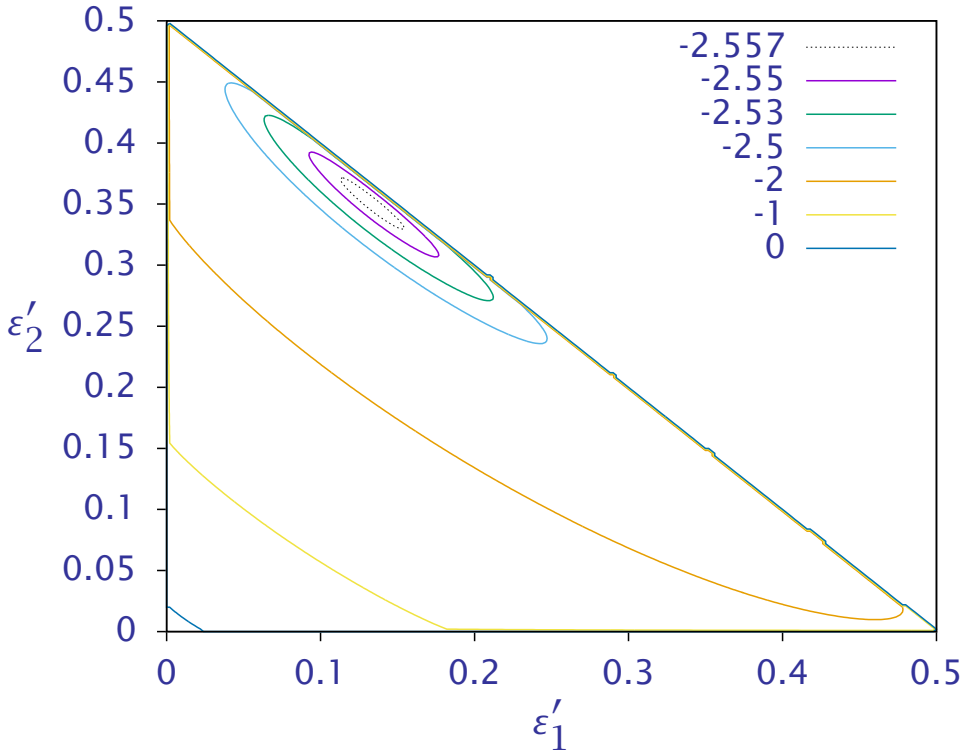
The constraints on the extents are found from Equation 52. For this problem they are

$$-y_{I0} + \varepsilon'_1 + \varepsilon'_2 \le 0 \quad -y_{B0} + \varepsilon'_1 + \varepsilon'_2 \le 0 \quad -y_{P_10} - \varepsilon'_1 \le 0 \quad -y_{P_20} - \varepsilon'_2 \le 0$$

Substituting in the initial conditions gives the constraints

$$\varepsilon'_1 + \varepsilon'_2 \le 0.5, \qquad 0 \le \varepsilon'_1, \qquad 0 \le \varepsilon'_2$$

Solution


0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
ε_2'
0
0.1
0.2
0.3
0.4
0.5
ε_1'
-2.557
-2.55
-2.53
-2.5
-2
-1
0

Solution

We see that the minimum is unique.

The numerical solution of the optimization problem is

$$\varepsilon_1' = 0.133, \qquad \varepsilon_2' = 0.351, \qquad \widetilde{G} = -2.569$$

The solution is in good agreement with the extents computed using the algebraic approach, and the Gibbs energy contours depicted in Figure .

Summary

The Gibbs energy is the convenient function for solving reaction equilibrium problems when the temperature and pressure are specified.

The fundamental equilibrium condition is that the Gibbs energy is minimized. This fundamental condition leads to several conditions for equilibrium such as

For a single reaction

$$\sum_j \nu_j \mu_j = 0$$

$$K = \prod_j a_j^{\nu_j}$$

Summary

For multiple reactions,

$$\sum_j \nu_{ij}\mu_j = 0, \qquad i = 1, \ldots, n_r$$

$$K_i = \prod_j a_j^{\nu_{ij}}, \qquad i = 1, \ldots, n_r$$

in which the equilibrium constant is defined to be

$$K_i = e^{-\Delta G_i^\circ / RT}$$

Summary

You should feel free to use whichever formulation is most convenient for the problem.

The equilibrium "constant" is not so constant, because it depends on temperature via

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

or, if the enthalpy change does not vary with temperature,

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Summary

- The conditions for phase equilibrium were presented: equalities of temperature, pressure and chemical potential of each species in all phases.

- The evaluation of chemical potentials of mixtures was discussed, and the following methods and approximations were presented: ideal mixture, Henry's law, and simple correlations for activity coefficients.

- When more than one reaction is considered, which is the usual situation faced in applications, we require numerical methods to find the equilibrium composition.

- Two approaches to this problem were presented. We either solve a set of nonlinear algebraic equations or solve a nonlinear optimization problem sub-

ject to constraints. If optimization software is available, the optimization approach is more powerful and provides more insight.

Notation

a_j	activity of species j
a_{jl}	formula number for element l in species j
A_j	jth species in the reaction network
$\overline{C}_{Pj}$	partial molar heat capacity of species j
E_l	lth element constituting the species in the reaction network
f_j	fugacity of species j
G	Gibbs energy
$\overline{G}_j$	partial molar Gibbs energy of species j
ΔG_i°	standard Gibbs energy change for reaction i
H	enthalpy
$\overline{H}_j$	partial molar enthalpy of species j
ΔH_i°	standard enthalpy change for reaction i
i	reaction index, $i = 1, 2, \ldots, n_r$

j	species index, $j = 1, 2, \ldots, n_s$
k	phase index, $k = 1, 2, \ldots, n_p$
K	equilibrium constant
K_i	equilibrium constant for reaction i
l	element index, $l = 1, 2, \ldots, n_e$
n_j	moles of species j
n_r	total number of reactions in reaction network
n_s	total number of species in reaction network
P	pressure
P_j	partial pressure of species j
R	gas constant
S	entropy
$\overline{S}_j$	partial molar entropy of species j
T	temperature
V	volume
$\overline{V}_j$	partial molar volume of species j
x_j	mole fraction of liquid-phase species j

y_j	mole fraction of gas-phase species j
z	compressibility factor of the mixture
γ_j	activity coefficient of species j in a mixture
ε	reaction extent
ε_i	reaction extent for reaction i
μ_j	chemical potential of species j
ν_{ij}	stoichiometric number for the jth species in the ith reaction
ν_j	stoichiometric number for the jth species in a single reaction
$\bar{\nu}$	$\sum_j \nu_j$
$\bar{\nu}_i$	$\sum_j \nu_{ij}$
$\hat{\phi}_j$	fugacity coefficient of species j in a mixture

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