

Azeotropic composition for cyclohexane and ethanol from gas chromatographic data

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Goal: The composition of a binary solution with lowest Gibbs free energy of mixing corresponds to the azeotrope. Gas chromatography data is used to calculate the Gibbs free energy of mixing for various cyclohexane and ethanol solutions. Based on the uncertainty of all the measurements and using error propagation techniques, the property is calculated with its associated uncertainty. This exercise is adequate for the undergraduate physical chemistry curriculum.

Prerequisites: Introductory thermodynamics, phase behavior.

Resources you will need: EXCEL or similar software package

Background:

The molar Gibbs free energy of mixing (ΔG_{mix}) for a binary solution is given by:

$$\begin{aligned}\Delta G_{\text{mix}} &= RT (x_1 \ln a_1 + x_2 \ln a_2) = RT (x_1 \ln g_1 x_1 + x_2 \ln g_2 x_2) \\ &= RT (x_1 \ln g_1 + x_2 \ln g_2) + RT (x_1 \ln x_1 + x_2 \ln x_2)\end{aligned}\quad [1]$$

where R is the ideal gas constant, T the absolute temperature, x_i the molar fraction of the i^{th} components, a_i its activity, and g_i its activity coefficient. The ideal molar Gibbs free energy of mixing ($\Delta G_{\text{mix}}^{\text{ideal}}$) and the excess molar Gibbs free energy of mixing ($\Delta G_{\text{mix}}^{\text{excess}}$) are then defined as:

$$\Delta G_{\text{mix}}^{\text{ideal}} = RT (x_1 \ln x_1 + x_2 \ln x_2) \quad [2]$$

$$\Delta G_{\text{mix}}^{\text{excess}} = RT (x_1 \ln g_1 + x_2 \ln g_2) \quad [3]$$

The regular solution model assumes that the molar entropy of mixing ΔS_{mix} corresponds to an ideal solution, assumption that is reasonable for small molecules of similar size:

$$\Delta S_{\text{mix}} = -R (x_1 \ln x_1 + x_2 \ln x_2). \quad [4]$$

Since:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad [5]$$

then, the molar heat of mixing ΔH_{mix} for a real solution is given by:

$$\Delta H_{\text{mix}} = RT (x_1 \ln g_1 + x_2 \ln g_2) = \Delta G_{\text{mix}}^{\text{excess}} \quad [6]$$

The composition with the lowest Gibbs free energy of mixing (see equation [1]) corresponds to the azeotrope. The mole fractions (x_i) can be calculated from the composition of the binary solution. The activity coefficients (g_i) can be derived from an analysis of the composition of the distillate of the binary solution, using Raoult's and Dalton's laws.

Considering the vapor pressure of the i^{th} component above the binary solution (P_i), Raoult's law convention states that:

$$P_i = a_i P_i^0 = g_i x_i P_i^0 \quad [7]$$

where P_i^0 is the vapor pressure of the i^{th} pure component. If the vapor phase above the solution can be assumed to be ideal, Dalton's law states that:

$$P_i = y_i P_{\text{total}} \quad [8]$$

where y_i is the mole fraction for the i^{th} component in the vapor phase and P_{total} is the total pressure. If P_{total} , P_i^0 , x_i and y_i are known, then the activity coefficients in the liquid phase (g_i) can be calculated by equating [7] and [8]:

$$y_i P_{\text{total}} = g_i x_i P_i^0 \quad [9]$$

Experimental Data:

A series of binary solutions of cyclohexane and ethanol were prepared.

1. The mole fractions of the solutions (x_i) can be calculated from the composition of the binary solutions, knowing the density of the components and their molar mass.

The solutions were analyzed with a gas chromatograph (GC) and the peak heights were recorded (h_i) for the two components.

2. The peak height functions (H_i) may be calculated, as follows:

$$H_i = \frac{h_i}{h_i + h_i} \quad [10]$$

The solutions were boiled, the distillates were collected and analyzed using the GC under the same conditions, and the peak heights were recorded (h'_i) for the two components.

3. The peak height functions for the distillate (H'_i) may be calculated following equation [10].

In order to calculate the molar fraction in the gas phase (y_i), standard curves are constructed for the two components of the binary solutions, using mole fractions (x_i) and peak height functions (H_i) from the liquid phase.

4. The standard curves consist of polynomial fits of the mole fractions (x_i) as a function of peak height functions (H_i). The mole fractions of the distillates (y_i) are determined using the standard curves, when the peak height functions of the distillates (H'_i) are used as the independent variables.

The barometric pressure and the room temperature were measured. The reported value of barometric pressure includes a temperature correction.

5. Since the vapors from the solution displace the air in the apparatus, P_{total} in equation [9] is equal to the barometric pressure and to the sum of the vapor pressures of the two components.

6. The vapor pressure of the pure components (P_i^0) at the boiling temperature of the binary solutions are estimated using Antoine's equation and available parameters A and B for cyclohexane and ethanol:

$$\ln P = A + \frac{B}{T} \quad [11]$$

The molar Gibbs free energy of mixing (ΔG_{mix}) for the various solutions is calculated from equation [1]. Other

thermodynamic terms ($\Delta G_{\text{mix}}^{\text{ideal}}$, $\Delta G_{\text{mix}}^{\text{excess}}$, ΔS_{mix} , ΔH_{mix}) are also obtained. All values are calculated with their associated uncertainty, based on the uncertainty in the data.

Experimental Conditions - further information that will be needed:

room temperature	22.3°C
atmospheric pressure	740.0±0.05 torr ^{*1}
cyclohexane normal bp	80.7°C ^{*2}
ethanol normal bp	78.5°C ^{*2}
cyclohexane vapor pressure function	$\ln P_{\text{cy}}^{\circ} = 17.338 - (3789/T)^{\text{*3}}$
ethanol vapor pressure function	$\ln P_{\text{et}}^{\circ} = 20.62 - (4915/T)^{\text{*4}}$
density of cyclohexane at 20°C (r_{cy})	0.7786 ^{*2} ± 0.00005 ^{*5} g ml ⁻¹
density of ethanol at 20°C (r_{cy})	0.7893 ^{*2} ± 0.00005 ^{*5} g ml ⁻¹
molar mass of cyclohexane (M_{cy})	84.16 ^{*2} ± 0.005 ^{*5} g mol ⁻¹
molar mass of ethanol (M_{et})	46.07 ^{*2} ± 0.005 ^{*5} g mol ⁻¹
cyclohexane standard heat vaporization	29.957 kJ mol ⁻¹ ^{*6}
ethanol standard heat vaporization	38.744 kJ mol ⁻¹ ^{*6}

Composition of the solutions^{*7}:

Sample	mL cyclohexane	mL ethanol	boiling point (°C)
1	0	75 ± 0.4 ^{*8}	77.5 ± 0.05
2	10 ± 0.1	65 ± 0.4	68.0 ± 0.05
3	25 ± 0.2	50 ± 0.3	65.0 ± 0.05
4	35 ± 0.2	40 ± 0.2	64.5 ± 0.05
5	40 ± 0.2	35 ± 0.2	64.2 ± 0.05
6	50 ± 0.3	25 ± 0.2	64.2 ± 0.05
7	65 ± 0.4	10 ± 0.1	64.5 ± 0.05
8	75 ± 0.4	0	79.0 ± 0.05

GC peak heights for the solutions (cm):

Sample	cyclohexane	ethanol
1	0.00	7.95
2	0.94	8.25
3	2.19	6.44
4	2.86	5.00
5	3.96	6.02
6	5.29	4.62
7	7.00	2.29
8	5.72	0.00

GC peak heights for the distillates (cm):

Sample	cyclohexane	ethanol
1	0	7.95
2	4.40	6.75
3	4.31	4.79
4	4.45	4.75
5	5.11	4.60
6	4.25	3.22
7	3.81	2.65
8	5.72	0.00

Exercise:

(Note: See Sample Calculations below)

- Calculate the mole fractions for the solutions (x_i), and their uncertainties. Remember that the error of sums or subtractions is the sum of the errors of the individual terms and that the relative error of products or divisions is the sum of the relative errors of the individual terms.
- Calculate the peak height functions for the solutions (H_i), as well as for the distillates (H'_i).
- Obtain third-order polynomial fits of x_i vs H_i for cyclohexane and for ethanol.
- Using the third-order polynomial functions, calculate the mole fractions in the distillates (y_{cy} and y_{et}) as a function of the peak height function of the distillates (H'_{cy} and H'_{et}). Assume that the associated uncertainty for the y values is the standard error of the y estimates.
- Using the corresponding Antoine equation, calculate the vapor pressure of pure cyclohexane and ethanol (P_i^0) at the boiling temperatures. Calculate the uncertainty for the vapor pressures of the pure compounds, at the boiling temperatures, using the formulas:

$$\Delta \ln P_i^0 = \frac{d(\ln P_i^0)}{dT} \Delta T \quad \text{and} \quad \Delta P_i^0 = P_i^0 \Delta \ln P_i^0$$
- Estimate the activity coefficients for the components (γ_i), and estimate their associated errors.
- Calculate the molar Gibbs free energies of mixing (ΔG_{mix}) at the boiling temperature, with their associated errors. Remember that

$$\Delta \ln x = \frac{\Delta x}{x}$$

8. Calculate ΔH_{mix} (or $\Delta G_{\text{mix}}^{\text{excess}}$) and ΔS_{mix} (or $-\Delta G_{\text{mix}}^{\text{ideal}}/T$) and estimate their associated errors.
9. Plot ΔG_{mix} vs x_i . Fit the data into a third-order polynomial function. Calculate the azeotrope composition by finding the value of x_i at the minimum of the ΔG_{mix} curve.
10. Estimate, by interpolation, the boiling temperature for the azeotrope.

Questions:

1. What assumption is made concerning the vapor phase produced at the boiling point? Is it valid?
2. How do the boiling points of the pure components compare with the literature values?
3. How do activity coefficients vary with mole fraction?
4. Does a boiling point graph (boiling temperature vs mole fractions) give similar azeotrope as the Gibbs free energy calculation?
5. What is the meaning of the signs associated with ΔG_{mix} and ΔH_{mix} ?
6. If one had a mixture corresponding to the azeotropic composition and attempted to distill it, what would take place?
7. If the accepted⁹ value for the azeotrope is 69.5% cyclohexane by mass, and the boiling temperature is 64.9°C, what is the accuracy of the results?

Sample Calculations:

1. Mole fraction for cyclohexane (x_{cy}) in solution 2:

$$\begin{aligned}
 x_{cy} &= \frac{n_{cy}}{n_{cy} + n_e} = \frac{\left(\frac{\rho_{cy} \times V_{cy}}{M_{cy}} \right)}{\left(\frac{\rho_{cy} \times V_{cy}}{M_{cy}} \right) + \left(\frac{\rho_{et} \times V_{et}}{M_{et}} \right)} \\
 &= \frac{\left(\frac{0.7786 \text{ g mL}^{-1} \times 10 \text{ mL}}{84.16 \text{ g mol}^{-1}} \right)}{\left(\frac{0.7786 \text{ g mL}^{-1} \times 10 \text{ mL}}{84.16 \text{ g mol}^{-1}} \right) + \left(\frac{0.7893 \text{ g mL}^{-1} \times 65 \text{ mL}}{46.07 \text{ g mol}^{-1}} \right)} \\
 &= \frac{0.0925}{0.0925 + 1.1136} = 0.0767
 \end{aligned}$$

where n_i is the number of moles, ρ_i is the density, V_i is the volume, and M_i the molar mass of the i^{th} component.

Associated uncertainty for x_{cy} in solution 2 (Δx_{cy}):

$$\begin{aligned}
 \Delta n_{cy} &= n_{cy} \left(\frac{\Delta \rho_{cy}}{\rho_{cy}} + \frac{\Delta V_{cy}}{V_{cy}} + \frac{\Delta M_{cy}}{M_{cy}} \right) = 0.0925 \left(\frac{0.00005}{0.7786} + \frac{0.1}{10} + \frac{0.005}{84.16} \right) \\
 &= 9.364 \times 10^{-4} \text{ mol} \\
 \Delta n_{et} &= n_{et} \left(\frac{\Delta \rho_{et}}{\rho_{et}} + \frac{\Delta V_{et}}{V_{et}} + \frac{\Delta M_{et}}{M_{et}} \right) = 1.1136 \left(\frac{0.00005}{0.7893} + \frac{0.4}{65} + \frac{0.005}{46.07} \right) \\
 &= 7.044 \times 10^{-3} \text{ mol} \\
 \Delta x_{cy} &= x_{cy} \left(\frac{\Delta n_{cy}}{n_{cy}} + \frac{\Delta n_{cy} + \Delta n_{et}}{n_{cy} + n_{et}} \right) \\
 &= 0.0767 \left(\frac{9.364 \times 10^{-4}}{0.0925} + \frac{9.364 \times 10^{-4} + 7.044 \times 10^{-3}}{0.0925 + 1.1136} \right) = 1.284 \times 10^{-3}
 \end{aligned}$$

2. Peak height functions for cyclohexane in solution 2 (H_{cy} and H'_{cy}):

$$H_{cy} = \frac{0.94}{0.94 + 8.25} = 0.102 \quad H'_{cy} = \frac{4.40}{4.40 + 6.75} = 0.395$$

3. Standard curve of x_i vs H_i for cyclohexane: $x = a + b H + c H^2 + d H^3$.

Solution #	x_{cy}	H_{cy}	H_{cy}^2	H_{cy}^3
1	0.000	0.000	0.000	0.000
2	7.670E-02	1.023E-01	1.046E-02	1.070E-03
3				

4				
5				
6				
7				
8				

Using LINEST(known_y's,[known_x's],true,true) {Ctrl-Shift,Enter}

d	c	b	a
± Dd	± Dc	± Db	± Da
0.9996	0.0095		

$$x_{cy} = \mathbf{a} + \mathbf{b} H_{cy} + \mathbf{c} H_{cy}^2 + \mathbf{d} H_{cy}^3$$

Coefficient of determination = 0.9996

Standard error of the y estimates: 0.0095.

4. Mole fraction for cyclohexane in the distillate of solution 2:

$$y_{cy} = \mathbf{a} + \mathbf{b} H'_{cy} + \mathbf{c} H'_{cy}{}^2 + \mathbf{d} H'_{cy}{}^3$$

$$Dy_{cy} = 0.0095$$

5. Vapor pressure for pure cyclohexane in solution 2:

$$\ln P^0_{cy} = 17.338 - \frac{3789}{T} = 17.338 - \frac{3789}{273.15 + 68.0} = 6.231$$

$$\Delta \ln P^0_{cy} = \frac{d \ln P^0_{cy}}{dT} \Delta T = \frac{3789}{T^2} \Delta T = \frac{3789}{(273.15 + 68.0)^2} 0.05 = 1.63 \times 10^{-3} \text{ torr}$$

$$P^0_{cy} = \exp(6.231) = 508.49 \text{ torr}$$

$$\Delta P^0_{cy} = P^0_{cy} \Delta \ln P^0_{cy} = 0.83 \text{ torr}$$

6. Activity coefficient for cyclohexane in solution 2:

$$\gamma_{cy} = \frac{y_{cy} P_{total}}{x_{cy} P_{cy}^0} = \frac{y_{cy} \times 740.0 \text{ torr}}{0.0767 \times 508.49 \text{ torr}}$$

$$\begin{aligned} \Delta\gamma_{cy} &= \gamma_{cy} \left(\frac{\Delta y_{cy}}{y_{cy}} + \frac{\Delta P_{total}}{P_{total}} + \frac{\Delta x_{cy}}{x_{cy}} + \frac{\Delta P_{cy}^0}{P_{cy}^0} \right) \\ &= \gamma_{cy} \left(\frac{0.0095}{y_{cy}} + \frac{0.05}{740.0} + \frac{1.3 \times 10^{-3}}{0.0767} + \frac{0.83}{508.49} \right) \end{aligned}$$

7. Molar Gibbs free energy of mixing (ΔG_{mix}) for solution 2;

$$\Delta G_{mix} = RT(x_{cy} \ln x_{cy} + x_{et} \ln x_{et} + x_{cy} \ln \gamma_{cy} + x_{et} \ln \gamma_{et})$$

$$\begin{aligned} \Delta G_{mix} &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times (68.0 + 273.15) \text{ K} \times \\ &\quad (0.0767 \ln 0.0767 + x_{et} \ln x_{et} + x_{cy} \ln \gamma_{cy} + x_{et} \ln \gamma_{et}) \text{ J mol}^{-1} \end{aligned}$$

Associated uncertainty in solution 2 [$\Delta(\Delta G_{mix})$]:

$$\begin{aligned} \Delta(x_{cy} \ln x_{cy}) &= x_{cy} \ln x_{cy} \left(\frac{\Delta x_{cy}}{x_{cy}} + \frac{\Delta \ln x_{cy}}{\ln x_{cy}} \right) = x_{cy} \ln x_{cy} \left(\frac{\Delta x_{cy}}{x_{cy}} + \frac{\Delta x_{cy}}{x_{cy} \ln x_{cy}} \right) \\ &= (\ln x_{cy} + 1) \Delta x_{cy} = \text{abs} [(-2.5678 + 1) 0.00128] = 0.0020 \end{aligned}$$

$$\begin{aligned} \Delta(x_{cy} \ln \gamma_{cy}) &= x_{cy} \ln \gamma_{cy} \left(\frac{\Delta x_{cy}}{x_{cy}} + \frac{\Delta \ln \gamma_{cy}}{\ln \gamma_{cy}} \right) = x_{cy} \ln \gamma_{cy} \left(\frac{\Delta x_{cy}}{x_{cy}} + \frac{\Delta \gamma_{cy}}{\gamma_{cy} \ln \gamma_{cy}} \right) \\ &= \ln \gamma_{cy} (0.00128) + \frac{0.0767}{\gamma_{cy}} \Delta \gamma_{cy} \end{aligned}$$

$$\Delta(\Delta G_{mix}) = \Delta G_{mix} \left[\frac{\Delta T}{T} + \frac{0.0020 + \Delta(x_{cy} \ln \gamma_{cy}) + \Delta(x_{et} \ln x_{et}) + \Delta(x_{et} \ln \gamma_{et})}{-0.1970 + x_{cy} \ln \gamma_{cy} + x_{et} \ln x_{et} + x_{et} \ln \gamma_{et}} \right]$$

8. Other thermodynamic properties:

Similarly to ΔG_{mix} , selecting only certain terms.

9. Location of the azeotrope:

Use LINEST to obtain the polynomial fit $\Delta G_{mix} = \mathbf{a} + \mathbf{b} x_{cy} + \mathbf{c} x_{cy}^2 + \mathbf{d} x_{cy}^3$.

Minimize the function with respect to x_{cy} .

$$(\mathbf{d} \Delta G_{mix} / \mathbf{d} x_{cy}) = \mathbf{b} + (2 \mathbf{c}) x_{cy, \min} + (3 \mathbf{d}) x_{cy, \min}^2 = 0$$

Solve for $x_{cy,min}$.

10. Given that $x_{cy,min}$ is between $x_{cy,j}$ and $x_{cy,k}$, with boiling temperatures T_j and T_k :

Solve for T_{min} .

$$\frac{T_j - T_k}{x_{cy,j} - x_{cy,k}} = \frac{T_{min} - T_k}{x_{cy,min} - x_{cy,k}}$$

Notes and references:

*1 Includes a barometer temperature correction of -2.7 torr based on Lange's Handbook of Chemistry, Editor John A. Dean, Copyright 1973 by McGraw-Hill, Inc., page 2-30.

*2 http://organicdivision.org/organic_solvents.html; last accessed 02/01/2008.

*3 Based on data from B.E. Poling, J. M. Prausnitz, J. P. O'Connell, "The Properties of Gases and Liquids", 5th Edition, McGraw-Hill, 2001, fitted between 60° and 85°C. Pressure in torr; temperature in K.

*4 Based on data from R.C. Reid, J. M. Prausnitz, B. E. Poling, "The Properties of Gases and Liquids", 4th Edition, McGraw-Hill, 1987, fitted between 60° and 85°C. Pressure in torr; temperature in K.

*5 The uncertainty is estimated from the unreported decimal place.

*6 Chemical Engineering Research Information Center; <http://www.cheric.org/research/kdb/hcprop/cmprch.php>; last accessed 02/15/2008.

*7 Experiment performed 3/26/1989 by Beatriz H. Cardelino using a GOW-MAC 350 gas chromatograph, with thermal conductivity detector, Chromosorb (nonpolar) column, helium as a carrier gas, and column and inlet temperatures set to 83°C. Setup similar to D. P. Shoemaker, C. W. Garland, J. W. Nibler, Experiments in Physical Chemistry, 5th edition, Copyright 1989 by McGraw-Hill, Inc., page 236.

*8 Accuracy of pipettes: 5mL = 1%; 10mL = 0.8%; in 20mL = 0.5%.

*9 CRC Handbook of Chemistry and Physics, 59th Edition, 1978-1979.

Suggestions for improving this web site are welcome. You are also encouraged to submit your own data-driven exercise to this web archive. All inquiries should be directed to the curator: Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University, DeLand, FL 32720.

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