

1. (5 Points) In class lecture, we discussed one particular equation of state (EOS), the van der Waals EOS, attempting to describe non-ideal (real) gases. The form of the van der Waals EOS we considered is:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

What is the order of this polynomial equation with respect to molar volume for a single component species? Please derive an explicit functional form to support your answer.

Solution:

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

$$P(\bar{V} - b)(\bar{V}^2) = RT\bar{V}^2 - a(\bar{V} - b)$$

$$P\bar{V}^3 - Pb\bar{V}^2 = RT\bar{V}^2 - a(\bar{V} - b)$$

$$P\bar{V}^3 - (Pb + RT)\bar{V}^2 + a\bar{V} - ab = 0$$

Third order

cubic

2. (5 Points) A mixture of 2.50×10^{-3} grams of O_2 , 3.51×10^{-3} moles of N_2 , and 4.67×10^{20} molecules of CO are placed in a vessel of volume 4.65 Liters at 15.4 Celsius. What is the total pressure in the vessel at this temperature and composition?

Solution:

$$N_{Total} = N_{O_2} + N_{N_2} + N_{CO}$$

$$N_{Total} = (0.00250 \text{ gr } O_2) \left(\frac{1 \text{ mol}}{(2)(15.9994) \text{ gr}} \right) + 0.00351 + \left(\frac{4.67 \times 10^{20}}{6.023 \times 10^{23}} \right)$$

$$N_{Total} = 0.000078129 + 0.00351 + 0.000775361$$

$$N_{Total} = 0.004363490 \text{ moles}$$

$$P_{Total} = \left(\frac{N_{Total} RT}{V} \right) = \left(\frac{(0.004363490)(0.08206 \text{ L atm mol}^{-1} \text{K}^{-1})(15.4 + 273.15)}{(4.65 \text{ L})} \right)$$

$$P_{Total} = 0.0217 \text{ atm}$$

1. (5 Points) Derive an expression for the *reversible*, isothermal work of expansion of a van der Waals gas from volume V_1 to volume V_2 .

$$\begin{aligned} w_{rev} &= - \int_{V_1}^{V_2} p \, dV \\ &= - \int_{V_1}^{V_2} \left(\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right) dV \\ &= -RT \ln \left(\frac{\bar{V}_2 - b}{\bar{V}_1 - b} \right) + a \left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}_1} \right) \end{aligned}$$

1a. (5 Points) What happens in the case where the van der Waals parameters a and b become 0?

In this case, we recover the ideal gas result for reversible isothermal work. Consider the same integral above but with the ideal gas Equation of State (EOS):

$$\begin{aligned} w_{rev} &= - \int_{V_1}^{V_2} p_{ideal \, gas} \, dV \\ &= - \int_{V_1}^{V_2} \left(\frac{RT}{\bar{V}} \right) dV \\ &= -RT \ln \left(\frac{\bar{V}_2}{\bar{V}_1} \right) \end{aligned}$$

2. (2 Points Bonus) Consider an adiabatic expansion process in a piston-cylinder assembly in which a gas initially in equilibrium at (T_1, P_1, V_1) proceeds to a final equilibrium state (T_2, P_2, V_2) . The process occurs under zero external pressure. Using your knowledge of the First Law, determine how much work is done? What is the change in internal energy?

Adiabatic, thus $q=0$.

Since the external pressure is 0, the work is zero: $w = - \int p_{ext} \, dV = 0$

The first law relates the internal energy, heat, and work. We also know that internal energy is a state function. Thus, we need more information to quantitatively determine

the internal energy change. Nevertheless, the change in internal energy is not zero due to temperature change.

Quiz 3

1. (5 Points) Because $(\partial H / \partial P)_T = -C_p \mu_{J-T}$, the change in enthalpy of a gas expanded at constant temperature can be calculated. To do so, the functional dependence of μ_{J-T} on P must be known.

1a. Treating Ar as a van der Waals gas, calculate ΔH when 1 mol of Ar is expanded from 325 bar to 1.75 bar at 375K. Assume that μ_{J-T} is independent of pressure and is given by $\mu_{J-T} = [2a/(RT) - b]/C_{P,m}$ and $C_{P,m} = 5R/2$ for Ar. $C_{P,m}$ is the molar constant pressure heat capacity.

Solution:

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = C_P dT - C_P \mu_{JT} dP$$

At constant temperature, $dT = 0$, thus we can write the change in molar enthalpy as:

$$dH_m = -C_{P,m} \mu_{JT} dP = -C_{P,m} [2a/(RT) - b]/C_{P,m} dP = -[2a/(RT) - b] dP$$

$$dH_m = -[2a/(RT) - b] dP$$

Thus, we now integrate assuming that a and b do not depend on pressure

$$\Delta H_m = H_{m,final} - H_{m,initial} = \int_{P=325 \text{ bar}}^{P=1.75 \text{ bar}} -[2a/(RT) - b] dP = -[2a/(RT) - b] (P_{final} - P_{initial})$$

Plugging in the numbers and making sure of consistency of units, we obtain:

$$a = 1.355 \text{ L}^2 \text{ bar/mol}^2 \quad b = 0.032013 \text{ (parameters from Table 4.1)}$$

$$\Delta H_m = H_{m,final} - H_{m,initial} = \int_{P=325 \text{ bar}}^{P=1.75 \text{ bar}} -[2a/(RT) - b] dP = -[2a/(RT) - b] (P_{final} - P_{initial})$$

$$\begin{aligned} \Delta H_m &= H_{m,final} - H_{m,initial} = -[2a/(RT) - b] (P_{final} - P_{initial}) \\ &= - \left[\frac{2(1.355 \text{ L}^2 \text{ bar/mol}^2)}{(8.314472 \times 10^{-2} \text{ Lbar/Kmol})(375 \text{ K})} - 0.032013 \text{ L/mol} \right] (1.75 - 325) \text{ bar} \\ &= -(0.0869167238 \text{ L/mol} - 0.032013 \text{ L/mol})(-323.25 \text{ bar}) \\ &= 17.747628 \text{ Lbar/mol} = 1774.7628 \text{ J/mol} = 1.77 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Since we are considering 1 mol Ar, the enthalpy change is 1.77 kJ

1b. What value would ΔH have if the gas exhibited ideal gas behavior?

Solution: Because the enthalpy of an ideal gas depends only on temperature, an isothermal process will not lead to a change in enthalpy. Thus, enthalpy change = 0.

2 (5 Points) In class, you discussed that a special property of state functions of several variables, such as : $f(x, y)$ pertains to the relationship between the partial derivatives of the function $\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x$. Using your knowledge of this relation, determine whether the following functions are state functions, or exact functions.

2a. $f(x, y) = x^5y^4 - 3x^2y^3 + 2x^2$

Solution:

$$f(x, y) = x^5y^4 - 3x^2y^3 + 2x^2$$

$$\left(\frac{\partial f}{\partial x}\right)_y = f_x = 5x^4y^4 - 6xy^3 + 4x ; \quad \left(\frac{\partial f_x}{\partial y}\right)_x = f_{xy} = 20x^4y^3 - 18xy^2$$

$$\left(\frac{\partial f}{\partial y}\right)_x = f_y = 4x^5y^3 - 9x^2y^2 ; \quad \left(\frac{\partial f_y}{\partial x}\right)_y = f_{yx} = 20x^4y^3 - 18xy^2$$

Because $f_{xy} = f_{yx}$, the original function is a state function.

2b. $f(x, y) = \ln\sqrt{x^2 + y^2}$

Solution:

$$f(x, y) = \ln\sqrt{x^2 + y^2}$$

$$\left(\frac{\partial f}{\partial x}\right)_y = f_x = \frac{1}{\sqrt{x^2 + y^2}} \left(\frac{1}{2}(x^2 + y^2)^{-1/2}\right)(2x) = \frac{x}{(x^2 + y^2)} ; \quad \left(\frac{\partial f_x}{\partial y}\right)_x = f_{xy} = \frac{-2xy}{(x^2 + y^2)^2}$$

$$\left(\frac{\partial f}{\partial y}\right)_x = f_y = \frac{1}{\sqrt{x^2 + y^2}} \left(\frac{1}{2}(x^2 + y^2)^{-1/2}\right)(2y) = \frac{y}{(x^2 + y^2)} ; \quad \left(\frac{\partial f_y}{\partial x}\right)_y = f_{yx} = \frac{-2xy}{(x^2 + y^2)^2}$$

Because $f_{xy} = f_{yx}$, the original function is a state function.

Quiz 4

1. (5 Points) For the given reactions, calculate the standard enthalpy of reaction at $T=298.15\text{K}$ and $P=1$ bar. Information found on pages 5-7 through 5-10 of your Equations Handbook may be useful in answering questions 1a and 1b.



Solution:

$$\Delta H_{rx}(T = 298.15\text{K}) = \sum_{\text{products},i} \nu_i \Delta H_{f,i}^{\circ} - \sum_{\text{react},j} \nu_j \Delta H_{f,j}^{\circ}$$

$$= 6\Delta H_{f,\text{H}_2\text{O}}^{\circ} + 5\Delta H_{f,\text{N}_2}^{\circ} - 4\Delta H_{f,\text{NH}_3}^{\circ} - 6\Delta H_{f,\text{NO}}^{\circ}$$

Plugging in the numbers, one obtains (with formation enthalpies from the handbook):

$$\Delta H_{rx}(T = 298.15\text{K}) = (5 \text{ mol N}_2)(0.0\text{kJ/mol}) + (6 \text{ mol H}_2\text{O})(-241.8 \text{ kJ/mol}) - (4 \text{ mol NH}_3)(-45.9 \text{ kJ/mol}) - (6 \text{ mol NO})(91.3 \text{ kJ/mol})$$

$$= -1815\text{kJ}$$

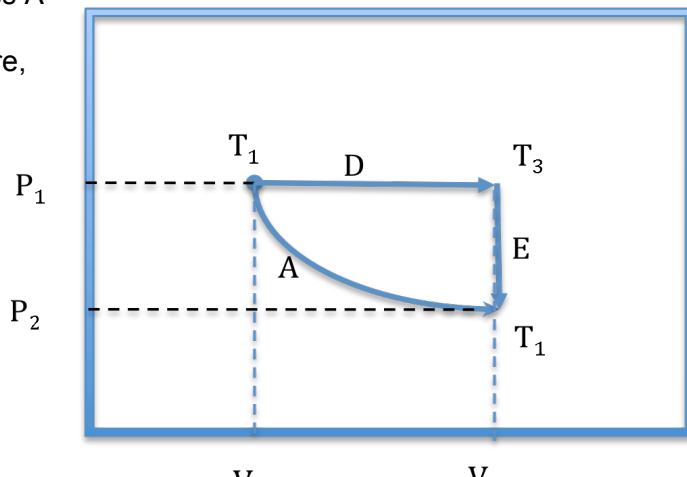
1b. (2 Points) For the reaction in part 1a, how would you calculate the standard enthalpy of reaction at $T = 350\text{K}$ and $P = 1$ bar; provide a specific protocol including the appropriate equations and assumptions you think appropriate.

Solution: Use the relation between enthalpy changes at constant pressure with temperature to determine the enthalpy (heat) of reaction at the required temperature. One might assume constant heat capacities, no phase changes (since we are dealing with gases initially).

$$\Delta H_{rx}(T = 350\text{K}) = \Delta H_{rx}(T = 298.15\text{K}) + \int_{298.15}^{350} \Delta C_p dT$$

$$\Delta C_p dT = \sum_{\text{products},i} \nu_i C_{p,i} - \sum_{\text{reactants},j} \nu_j C_{p,j}$$

2. (5 Points) Consider the process A, D, and E shown on this (p,V) diagram for an ideal gas fluid. Process A is reversible and isothermal, constant pressure, is constant. Calculate for processes A, D, and E. ΔU , ΔH , q , w A, D, and E.



is reversible process D is and process E volume. ΔU , ΔH , q , w A, D, and E.

$$\Delta U_A = 0 ; \quad \Delta H_A = 0 \text{ (ideal gas; isothermal)}$$

$$w_A = -RT_1 \ln\left(\frac{V_2}{V_1}\right); \quad q_A = RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta U_D = C_V(T_3 - T_1); \quad \Delta H_D = C_P(T_3 - T_1) \text{ (ideal gas)}$$

$$w_D = -R(T_3 - T_1); \quad q_D = C_P(T_3 - T_1)$$

$$\Delta U_E = C_V(T_1 - T_3); \quad \Delta H_E = C_P(T_1 - T_3) \text{ (ideal gas)}$$

$$w_E = 0; \quad q_E = C_V(T_1 - T_3)$$

Quiz 5

1. (10 Points) The mean solar flux at the Earth's surface is about $2.0 \text{ J cm}^{-2} \text{ min}^{-1}$. In a nonfocusing solar collector, the temperature can reach a value of 85°C . A heat engine is operated using the collector as the hot reservoir and a cold reservoir at 298K . Calculate the area of the collector needed to produce one horsepower ($1 \text{ hp} = 746 \text{ watts}$). Assume the engine operates at the maximum Carnot efficiency.

$$\varepsilon = 1 - \frac{T_C}{T_H} = \frac{-w}{q_{hot}}$$

$$w = (-q_{hot})(\varepsilon) = (-q_{hot})\left(1 - \frac{T_C}{T_H}\right) = (q_{hot})\left(\frac{T_C}{T_H} - 1\right)$$

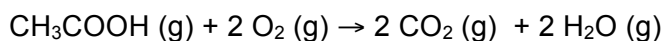
On a per unit time basis,

$$\dot{w} = (\dot{q}_{hot})\left(\frac{T_C}{T_H} - 1\right)$$

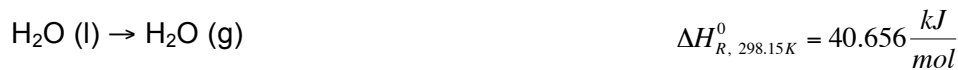
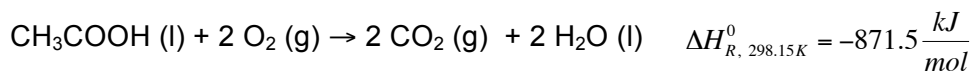
$$746 \frac{\text{J}}{\text{sec}} = \left(\frac{-2 \text{ J}}{\text{cm}^2 \text{ min}}\right)\left(\frac{1 \text{ min}}{60 \text{ sec}}\right)\left(\frac{298\text{K}}{358\text{K}} - 1\right)A$$

$$A = 133534 \text{ cm}^2 = 13.35 \text{ m}^2$$

2. (5 Extra Credit Points) Estimate the standard enthalpy of reaction, $\Delta H_{R, 391.4\text{K}}^0$, for the following reaction:



The following data may be helpful:



Substance	CH ₃ COOH (l)	O ₂ (g)	CO ₂ (g)	H ₂ O (l)	H ₂ O (g)
C _{p,m} /R	14.9	3.53	4.46	9.055	4.038

Solution:

Convert the individual reactions to the appropriate temperature:

$$\Delta H_{R,391.4}^0(\text{reaction \#1}) = -871.5 \frac{\text{kJ}}{\text{mol}} + \int_{298.15}^{391.4} R \Delta C_p(T) dT$$

$$\begin{aligned} \Delta C_p(T) &= \sum_{\text{products}} \nu_i \frac{C_{p,m}^i(T)}{R} + \sum_{\text{reactants}} \nu_j \frac{C_{p,m}^j(T)}{R} \\ &= (2)(4.46) + (2)(9.055) + (-1)(14.9) + (-2)(3.53) \\ &= 5.070 \end{aligned}$$

Thus

$$\begin{aligned} \Delta H_{R,391.4}^0(\text{reaction \#1}) &= -871.5 \frac{\text{kJ}}{\text{mol}} + \int_{298.15}^{391.4} (5.070)(R) dT = -871.5 \frac{\text{kJ}}{\text{mol}} + (391.4\text{K} - 298.15\text{K})(5.070)(0.0083144 \frac{\text{kJ}}{\text{mol K}}) \\ &= -871.5 \frac{\text{kJ}}{\text{mol}} + (3.93086 \frac{\text{kJ}}{\text{mol}}) = -867.56914 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Likewise for reaction #2

$$\Delta H_{R,391.4}^0(\text{reaction \#2}) = 40.656 \frac{\text{kJ}}{\text{mol}} + \int_{298.15}^{391.4} R \Delta C_p(T) dT$$

$$\begin{aligned} \Delta C_p(T) &= \sum_{\text{products}} \nu_i \frac{C_{p,m}^i(T)}{R} + \sum_{\text{reactants}} \nu_j \frac{C_{p,m}^j(T)}{R} \\ &= (1)(4.038) + (-1)(9.055) \\ &= -5.017 \end{aligned}$$

Thus

$$\begin{aligned} \Delta H_{R,391.4}^0(\text{reaction \#2}) &= 40.656 \frac{\text{kJ}}{\text{mol}} + \int_{298.15}^{391.4} (-5.017)(R) dT = 40.656 \frac{\text{kJ}}{\text{mol}} + (391.4\text{K} - 298.15\text{K})(-5.017)(0.0083144 \frac{\text{kJ}}{\text{mol K}}) \\ &= 40.656 \frac{\text{kJ}}{\text{mol}} + (3.93086 \frac{\text{kJ}}{\text{mol}}) = 40.656 \frac{\text{kJ}}{\text{mol}} - 3.88977 \frac{\text{kJ}}{\text{mol}} = 36.76623 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Reaction #3 remains the same.

Thus, the overall enthalpy of reaction at 391.4K is:

$$\begin{aligned} \Delta H_{R,391.4}^0 &= -24.4 \frac{\text{kJ}}{\text{mol}} + (2)(36.76623 \frac{\text{kJ}}{\text{mol}}) + (1)(-867.56914 \frac{\text{kJ}}{\text{mol}}) \\ &= -818.44 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Section 10

1. (10 Points) Show that $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$. It may be helpful to think about what variables are being differentiated with respect to in order to solve this problem. Please state any assumptions you make and present your solution in as explicit a manner as possible.

Solution:

S and V are the variables. They are natural variables for internal energy. $U=U(S,V)$ for a single component system. Thus we may be able to make use of the state function property of U. For state functions:

$$\left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S$$

$$\left[\frac{\partial}{\partial S}\left(\frac{\partial[TdS - PdV]}{\partial V}\right)_S\right]_V = \left[\frac{\partial}{\partial V}\left(\frac{\partial[TdS - PdV]}{\partial S}\right)_V\right]_S$$

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

Quiz 7

1. (5 Points) In class, we have shown that the entropy of mixing for a mixture of “L” ideal gases is:

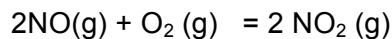
$$\Delta S_{\text{mixing}} = -nR \left[\sum_{i=1}^L X_i \ln X_i \right]$$

Using your knowledge of thermodynamics, derive a relation for the Gibbs free energy of mixing, ΔG_{mixing} , for this same mixture.

$$\Delta S_{\text{mixing}} = -nR \left[\sum_{i=1}^L X_i \ln X_i \right]$$

$$\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}} = 0 + nRT \left[\sum_{i=1}^L X_i \ln X_i \right]$$

2 (5 Points) For the following reaction, the equilibrium constant is $K_p = 1.8$. At a particular instant of time, the partial pressures of all species are 0.5 atmospheres. Is the reaction at equilibrium? If not, in which direction will it proceed, towards products or reactants?



$$Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{O}_2} P_{\text{NO}}^2} = \frac{0.5^2}{(0.5)(0.5^2)} = 2$$

taking standard state pressure to be 1atm

Since Q_p is greater than $K_p=1.8$, the reaction proceeds towards reactants.

Quiz 8

1. **(10 Points) A).** Using the following data, estimate the vaporization enthalpy of ethanol. State any approximations you use. **B).** Compare your result to the heat of vaporization at the normal boiling point of ethanol. Data in Table 6.1 of your Handbook may be helpful.

P (mm Hg)	40	100	400	760	1520	3800	7600	15200	30400	45600
T °C	19.0	34.9	63.5	78.4	97.5	126.0	151.8	183.0	218.0	242.0

Table data obtained from CRC Handbook of Chemistry and Physics 44th ed.

Solution:

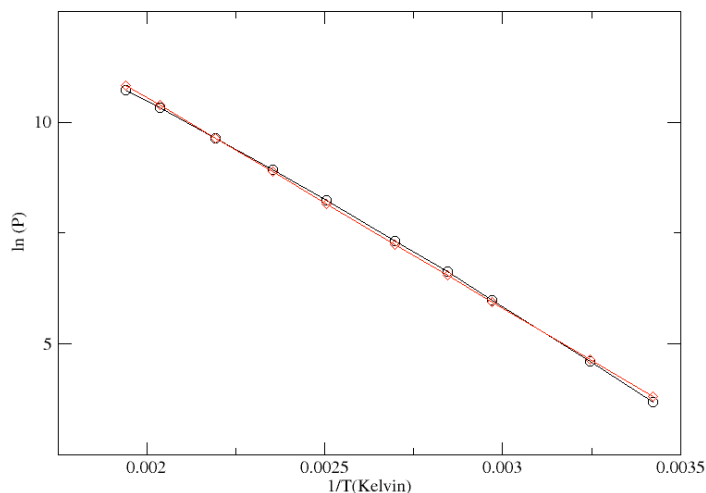
Using the Clausius-Clapeyron equation with the assumption that the vapor is ideal gas and the vaporization enthalpy is constant over the temperature range given in the data set:

$$d(\ln P) = \frac{\Delta H_v}{R} \frac{dT}{T^2}$$

$$\ln P + C_1 = -\frac{\Delta H_v}{RT} + C_2$$

$$\ln P = -\left(\frac{\Delta H_v}{R}\right)\frac{1}{T} + b$$

Thus, plot $\ln(P)$ versus $(1/T)$. The slope multiplied by $-R$ is the vaporization enthalpy (red diamonds are the fit to the experimental data shown as black circles)



Number of observations	= 10
Mean of independent variable	= 0.00262101
Mean of dependent variable	= 7.610287
Standard dev. of ind. variable	= 0.0005038954
Standard dev. of dep. variable	= 2.389071
Correlation coefficient	= -0.9994531
Regression coefficient (SLOPE)	= -4738.612
Standard error of coefficient	= 55.42907
t - value for coefficient	= -85.48964
Regression constant (INTERCEPT)	= 20.03024
Standard error of constant	= 0.1476768
t - value for constant	= 135.6357

Analysis of variance

Source	d.f	Sum of squares	Mean Square	F
Regression	1	51.31278	51.31278	7308.478
Residual	8	0.05616795	0.007020994	
Total	9	51.36895		

$$y = 20.03 - 4738.6 * x$$

$$H_{vap} = -4738.6 * -8.314 \text{ J / (mol K)} = 39.4 \text{ kJ/mol}$$

This value is in remarkably good agreement with the experimentally measured value of 38.56 kJ/mol quoted in your book. Considering uncertainties in the experimental data and regression, these numbers are quite close.

1. **(10 Points)** An ideal solution of 5.0 moles of benzene and 3.25 moles of toluene is placed in a piston and cylinder assembly. At 298K, the vapor pressure of the pure substances are $P^{\text{sat}}(\text{benzene})=96.4 \text{ Torr}$ and $P^{\text{sat}}(\text{toluene})=28.9 \text{ Torr}$.

A. The system is initially at pressure of 760 Torr (temperature = 298K). The pressure is reduced. At what pressure does the vapor phase first appear?

B. What is the composition of the vapor phase at the point discussed in part A?

Solution:

$$P_{\text{total}} = x_{\text{benzene}} P_{\text{benzene}}^{\text{saturation}} + x_{\text{toluene}} P_{\text{toluene}}^{\text{saturation}}$$

$$A. = (0.606)(96.4\text{Torr}) + (0.394)(28.9\text{Torr})$$

$$= 69.8\text{Torr}$$

Thus, need to reduce to 69.8 Torr to form first bubble of vapor.

B. Use Raoult's relation:

$$y_{\text{benzene}} P_{\text{Total}} = x_{\text{benzene}} P_{\text{benzene}}^{\text{saturation}}$$

$$y_{\text{benzene}} = \frac{x_{\text{benzene}} P_{\text{benzene}}^{\text{saturation}}}{P_{\text{Total}}}$$

$$= \frac{(0.606)(96.4\text{Torr})}{(69.8\text{Torr})}$$

$$= 0.837$$