

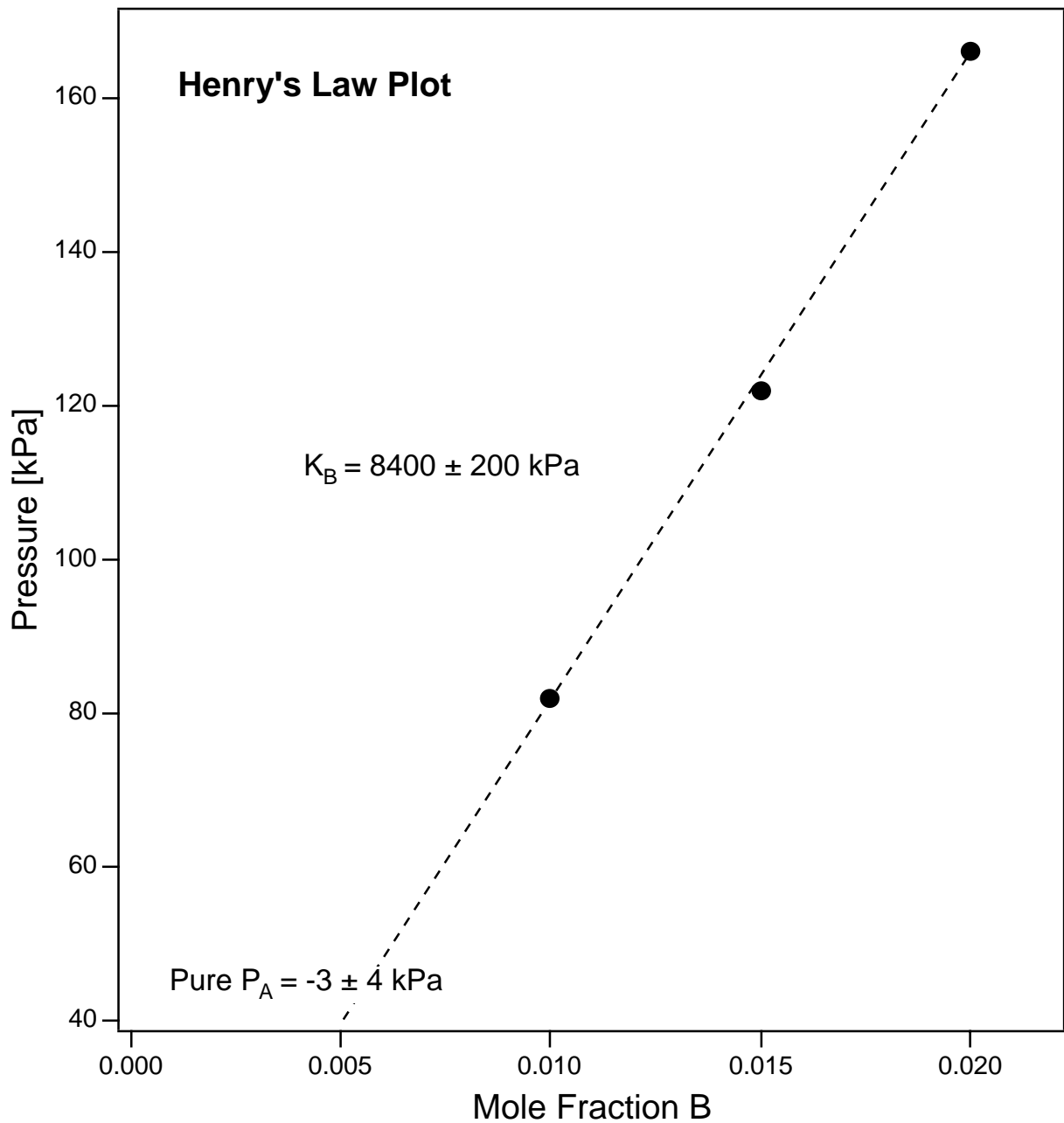
CH 342 S02 Homework 3 Solution 4.Feb.02

> restart:

Problem 1

A graph of the data is shown below. According to the figure, the vapor pressure is linearly dependent on mole fraction over the range given. The Henry's law constant (slope of the data) is 8400 ± 200 kPa.

Interestingly, the vapor pressure of pure A (when $x_B \rightarrow 0$) is found to be -3 ± 4 kPa!



Problem 2

> restart:

part a

Formulation

> with(diffforms):

> eqnGibbsDuhem := 0 = n[A]*D(mu[A]) + n[B]*D(mu[B]);

$$\text{eqnGibbsDuhem} := 0 = n_A D(\mu_A) + n_B D(\mu_B)$$

Substitutions

> mu[A] := muAo + R*T*ln(f[A]): mu[B] := muBo + R*T*ln(f[B]):

> n[A] := n*x[A]: n[B] := n*x[B]:

> eqnGibbsDuhem;

$$0 = n x_A (D(\mu_{Ao}) + D(R) T \ln(f_A) + R D(T) \ln(f_A) + R T D(\ln(f_A))) \\ + n x_B (D(\mu_{Bo}) + D(R) T \ln(f_B) + R D(T) \ln(f_B) + R T D(\ln(f_B)))$$

Assumptions

> assume(R,constant): assume(T,constant):

assume(muAo,constant): assume(muBo,constant):

eqnGibbsDuhem;

$$0 = n x_A R T D(\ln(f_A)) + n x_B R T D(\ln(f_B))$$

Solution

Divide out the constants.

> eqnGDMtemp := 0 = simplify(rhs(eqnGibbsDuhem)/(n*R*T));

$$\text{eqnGDMtemp} := 0 = x_A D(\ln(f_A)) + x_B D(\ln(f_B))$$

Define the relationships for the mole fractions and their derivatives.

> x[A] := Dx[A]/D(lnx[A]): x[B] := Dx[B]/D(lnx[B]): Dx[A] := -Dx[B]:

> eqnGDM := expand((eqnGDMtemp/Dx[A]));

$$\text{eqnGDM} := 0 = \frac{D(\ln(f_A))}{D(\ln x_A)} - \frac{D(\ln(f_B))}{D(\ln x_B)}$$

QED

part b

Substitutions

> f[A] := xA*Po[A]: f[B] := p[B]: eqnGDM;

$$0 = \frac{D(\ln(x_A P_{oA}))}{D(\ln x_A)} - \frac{D(\ln(p_B))}{D(\ln x_B)}$$

This becomes equal to

> eqnProof := 0 = 1 + 0 - D(ln(pB))/D(lnxB);

$$eqnProof := 0 = 1 - \frac{D(\ln(pB))}{D(\ln xB)}$$

or after integration ...

> eqnProof := ln(pB) = ln(xB) + c;

$$eqnProof := \ln(pB) = \ln(xB) + c$$

> expand(solve(eqnProof,pB));

$$e^c xB$$

This means, the pressure of B must be a constant time the mole fraction of B. This constant can be the Raoult's law constant PoB or the Henry's law constant KB.

If one component follows Raoult's law,
the other **must** follow **either** Raoult 's **or** Henry's law.

Problem 3

> restart:

Formulations

> eqnMoleFraction := xB = nB/nT;

$$eqnMoleFraction := xB = \frac{nB}{nT}$$

Solution

Basis: 1 kG Solvent A

> nB := 0.25; nA := 1e3/74.1; nT := nA + nB;

$$nA := 13.49527665$$

$$nT := 13.74527665$$

> eqnMoleFraction;

$$xB = .01818806608$$

> pB := rhs(eqnMoleFraction)*8400; dpB := pB*200/8400;

$$pB := 152.7797551$$

$$dpB := 3.637613217$$

pressure is 153 ± 4 kPa

[-] Problem 4

> restart:

Formulations

Assume Raoult's law applies to benzene.

> eqnPvap := pBz = (1-xC)*PoBz;

$$\text{eqnPvap} := p_{Bz} = (1 - x_C) P_{oBz}$$

> pBz := 386: PoBz := 400:

> xCs := evalf[3](solve(eqnPvap,xC));

$$x_{Cs} := .0350$$

> readmylib(atomicmasses):

MBz := 6*(AM[C] + AM[H]);

$$M_{Bz} := 78.1134$$

> nBz := 500/MBz;

$$n_{Bz} := 6.400950415$$

> eqnMoles := xCs = nC/(nC + nBz): nC := 19/MC: eqnMoles;

$$.0350 = 19 \frac{1}{MC \left(19 \frac{1}{MC} + 6.400950415 \right)}$$

> solve(eqnMoles,MC);

$$81.84052506$$

molar mass is 81.8 g/mol

[-] Problem 5

> restart:

Formulations

> eqnSolubility := ln(xB) = (DfusH/Rg)*(1/To - 1/T);

$$\text{eqnSolubility} := \ln(x_B) = \frac{D_{fusH} \left(\frac{1}{T_o} - \frac{1}{T} \right)}{R_g}$$

Given Values

> readmylib(pchemconstants):

> DfusH := 28.8e3: To := 217+ 273.15: T := 25 + 273.15:

Solution

```
> xBs := solve(eqnsolubility,xB);
```

```
xBs := .01055814697
```

```
> readmylib(atomicmasses):
```

```
MBz := 6*(AM[C] + AM[H]);
```

```
MBz := 78.1134
```

```
> eqnMoleFrac := xBs = nA/(nA + 1e3/MBz):
```

```
nAs := solve(eqnMoleFrac,nA);
```

```
nAs := .1366066637
```

anthracene is soluble to a mole fraction of 0.011 or a molality of 0.14 (mol/kg)

Problem 6a (NOT REQUIRED)

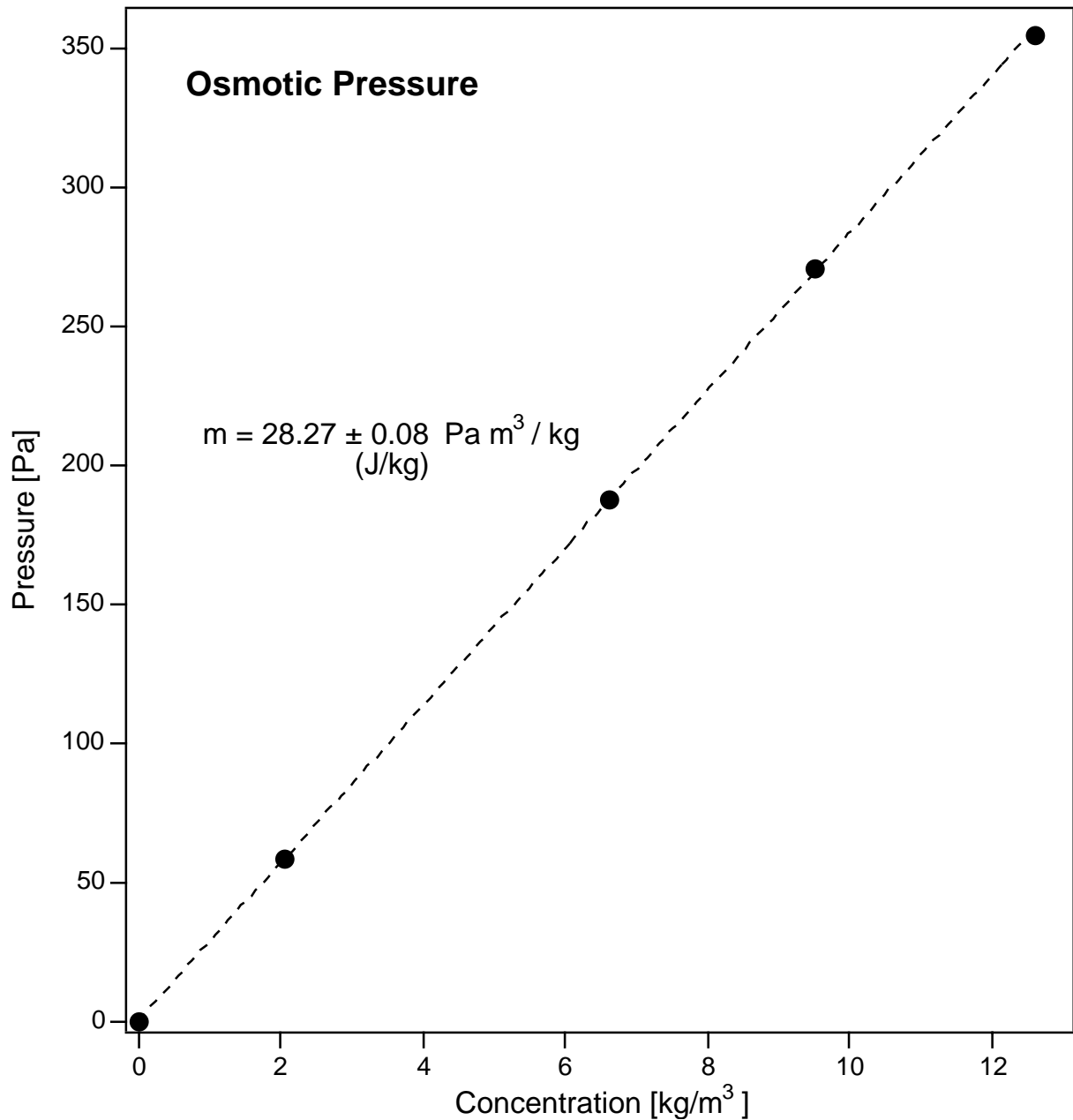
This is for E 7.16a, which was not required.

The plot below shows osmotic pressure (Pa) increases linearly with solute concentration (kg/m³).

The point at (0,0) MUST be intercepted!

The slope is the value RT/M_p , where M_p is the molar mass of the polymer in units of kg/mol.

Note: Concentrations in g/L are equal to concentrations in kg/m³!



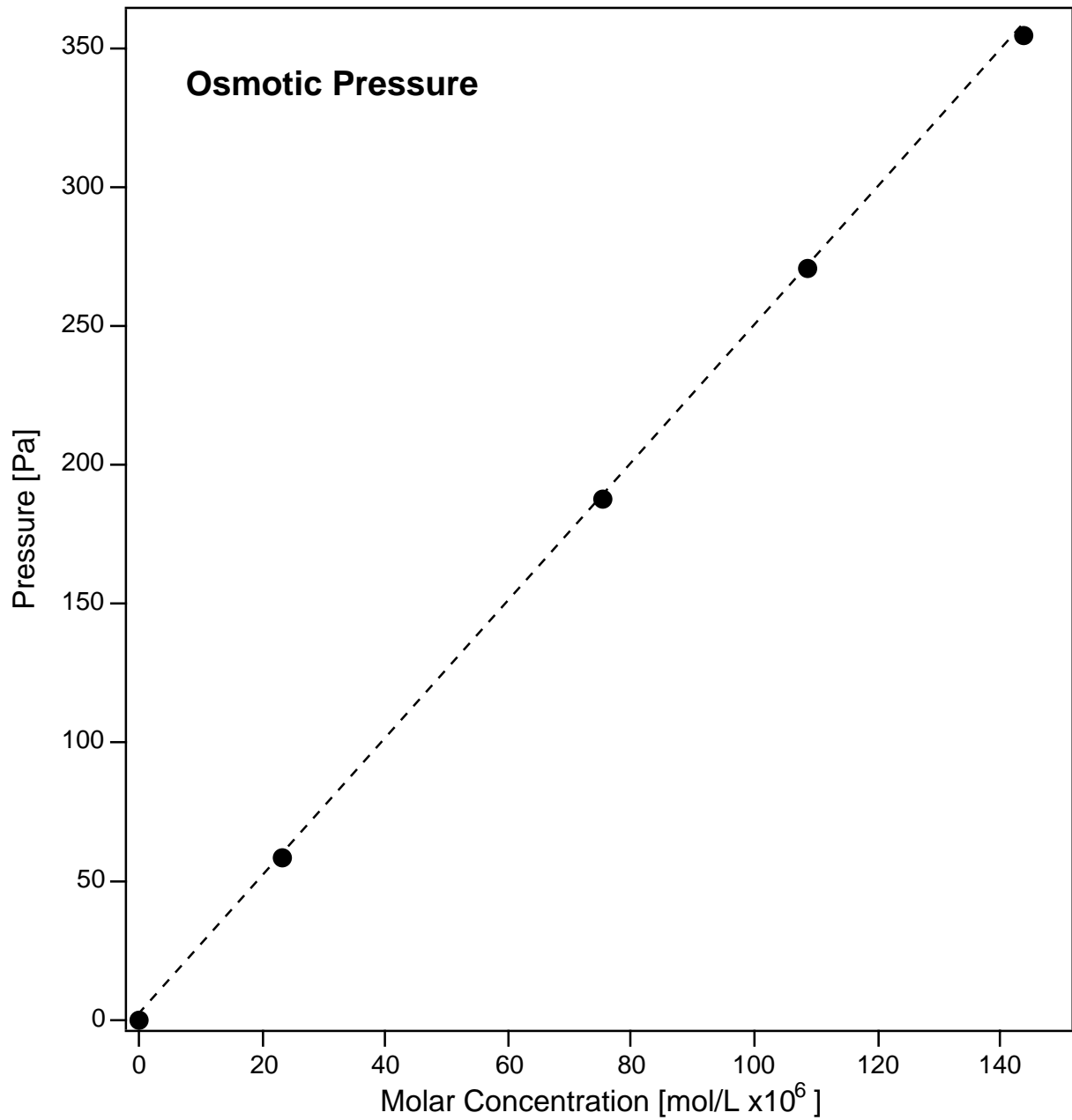
> Mpolymer := Rg*(25+273.15)/28.27; DMpolymer := 0.08/28.27*Mpolymer;

Mpolymer := 87.68911059

DMpolymer := .2481474654

molar mass is $87.7 \pm 0.2 \text{ kg/mol}$

Note: The solution key gives 87 kg/mol, which does not overlap the value shown here. The difference is because a higher value of slope was obtained in the answer key, possibly due to incorrect linear regression fitting. Statistical analysis shows that, for a fit with five points, the 95% confidence level standard error of the mean is 2.78 times greater than the reported standard deviation of the molar mass. Therefore, to 95% confidence, the molar mass is 87.7 ± 0.7 . To the 95% confidence level, our value is in agreement with the value reported in the solution key.



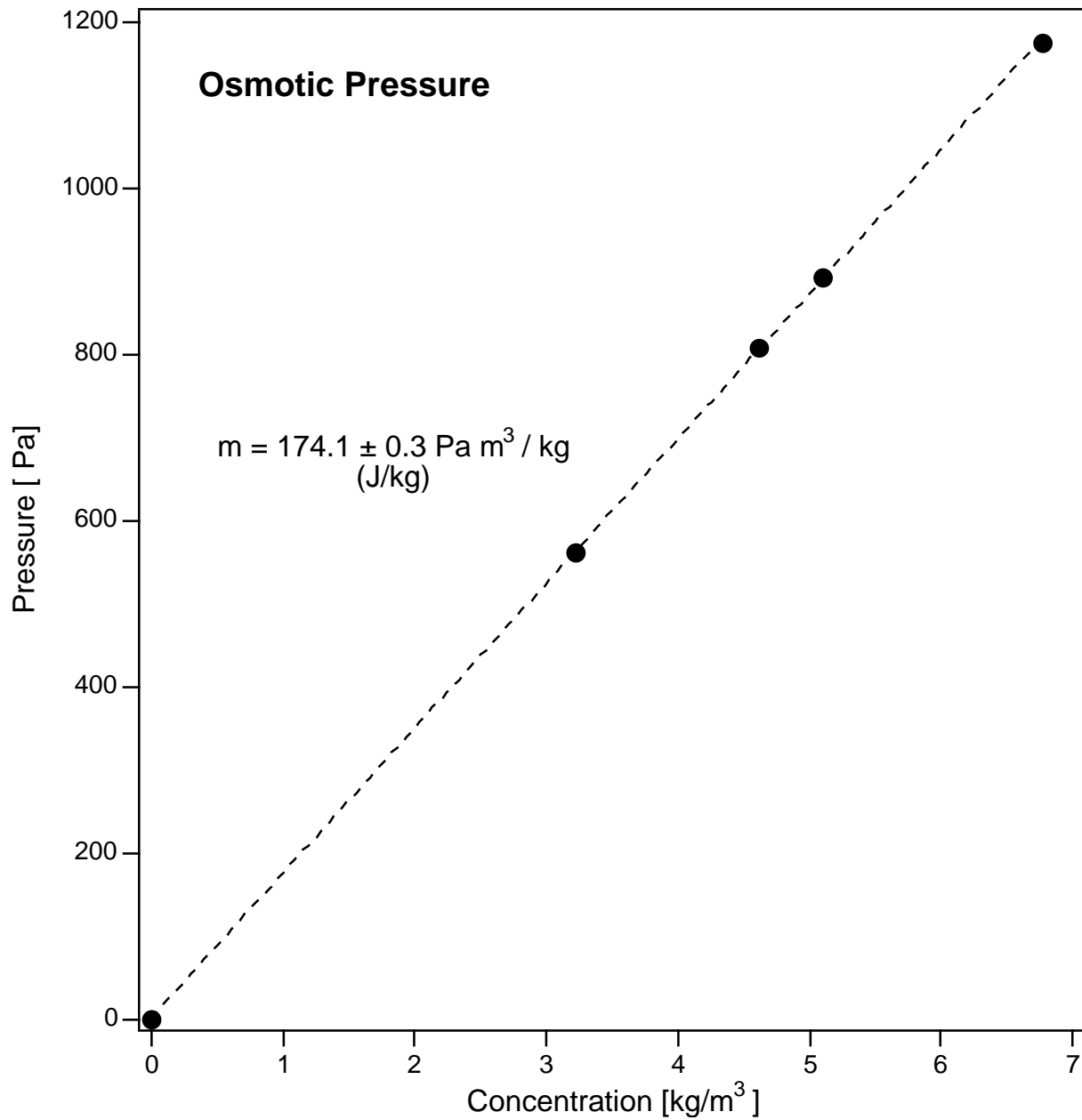
[-] Problem 6b (REQUIRED)

The plot below shows osmotic pressure (Pa) increases linearly with solute concentration (kg/m³). The point at (0,0) MUST be intercepted!

The slope is the value RT/M_p , where M_p is the molar mass of the polymer in units of kg/mol.

Note: Concentrations in g/L are equal to concentrations in kg/m³!

The density of water at 20°C is 0.99821 (CRC Handbook, 73rd Edition)

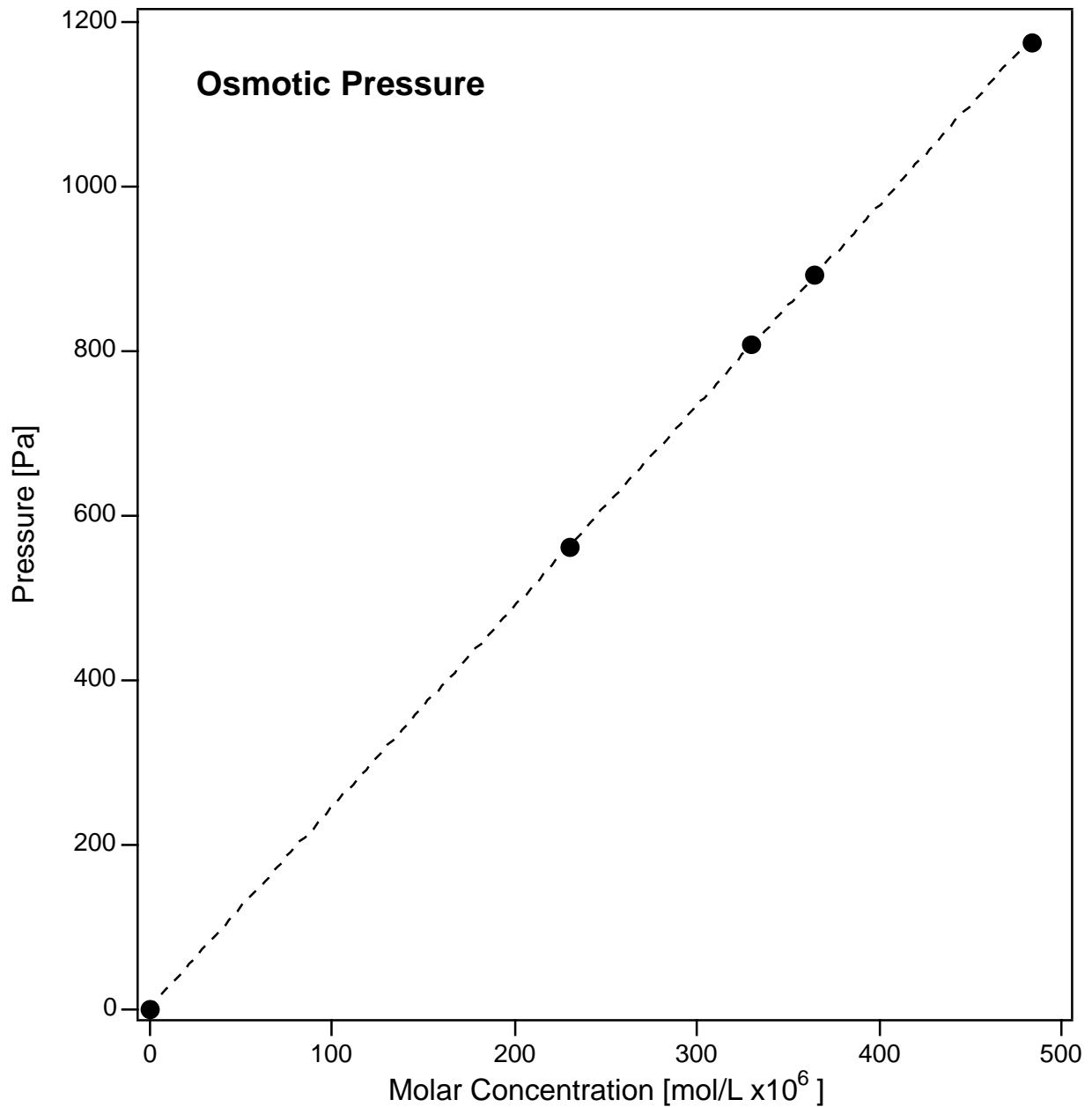


> Mpolymer := Rg*(20+273.15)/174.1; DMpolymer := 0.3/174.1*Mpolymer;

Mpolymer := 13.99999199

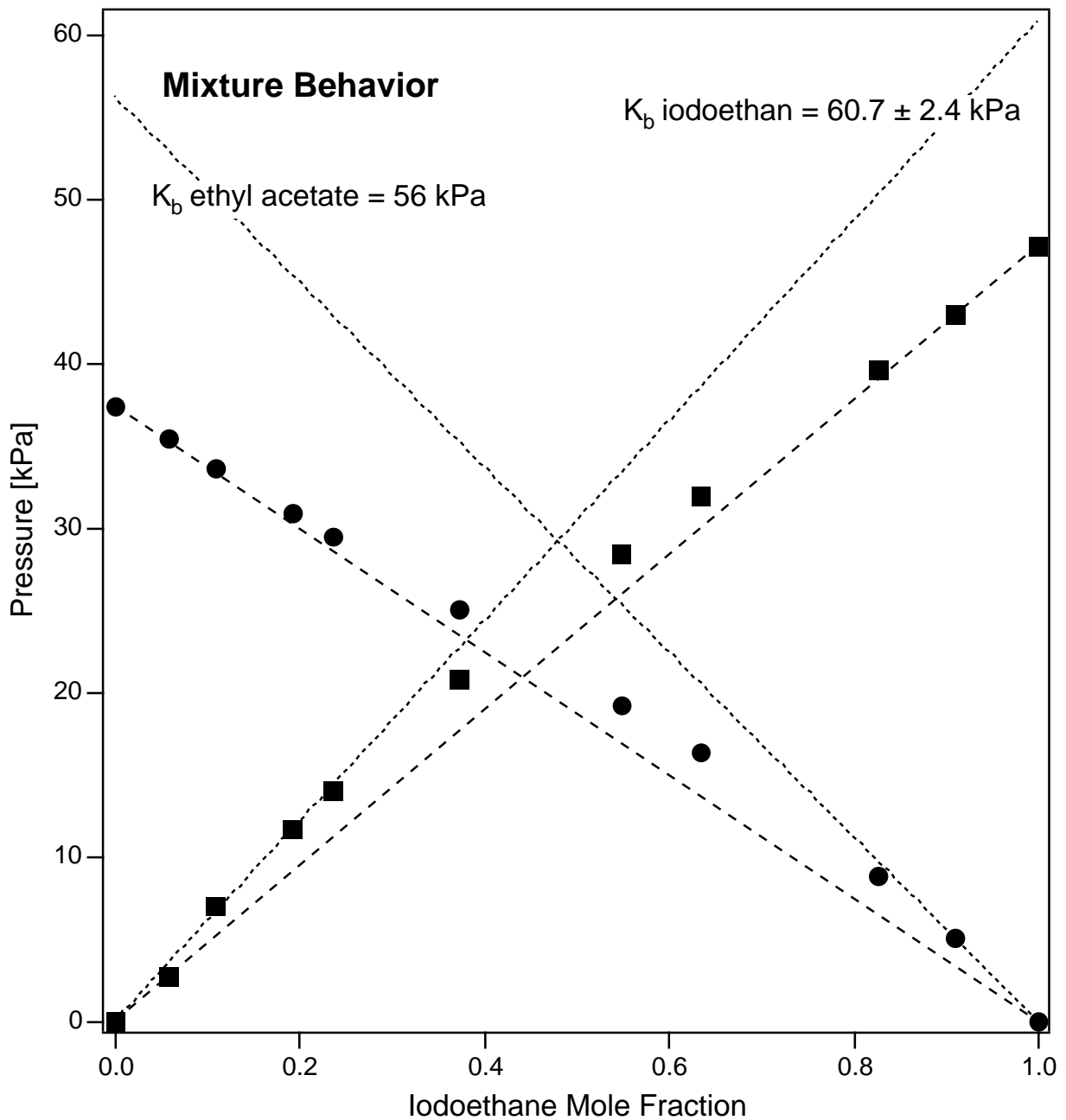
DMpolymer := .02412405282

polymer molar mass is $14.00 \pm 0.02 \text{ kg/mol}$
(agrees with solution key)



Problem 7

The data plot is given below. Iodoethane is shown as squares and ethylacetate as circles. The Raoult's and Henry's law lines are shown on the graph. Both components behave according to Raoult's law as they become pure (ie, for dilute solutions of the other component). Both components follow Henry's law if viewed as the solute in a solution.



For iodoethane, the Henry's law line was fit over the first three points. This gave a Henry's law constant of

$$K_b \text{ for iodoethane} = 60.7 \pm 2.4 \text{ kPa.}$$

For ethyl acetate, the Henry's law line was fit over the last two points. This gave a Henry's law constant of

$$K_b \text{ for ethyl acetate} = 56 \text{ kPa}$$

with no uncertainty (because two points define a straight line).

Activity and Activity Coefficients

Raoult's Law Basis

> $a[R] := p/p_o$; $g[R] := a[R]/x$;

$$a_R := \frac{p}{p_o}$$

$$g_R := \frac{p}{p_o x}$$

Henry's Law Basis

> $a[H] := p/K_b$; $g[H] := a[H]/x$;

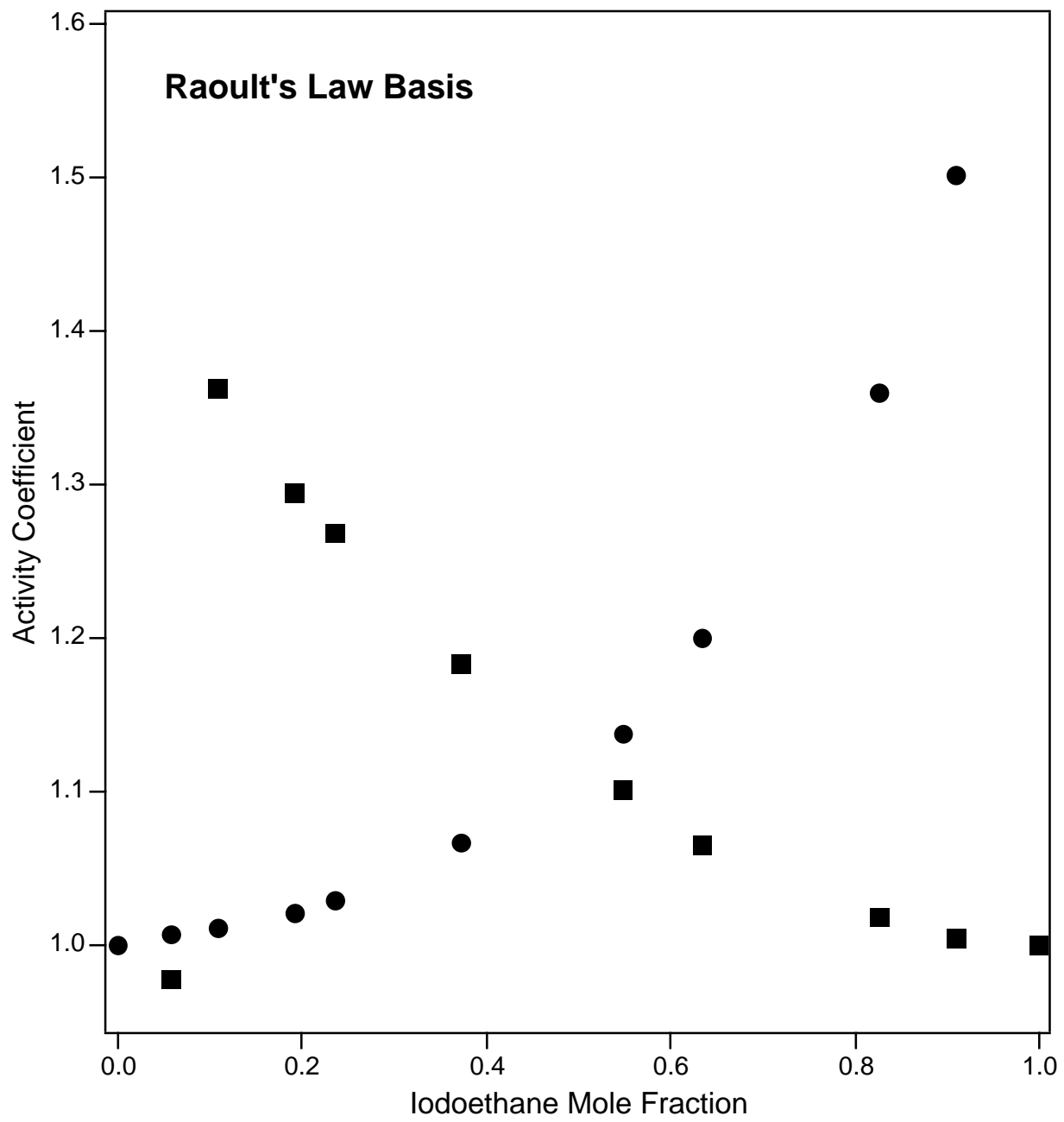
$$a_H := \frac{p}{K_b}$$

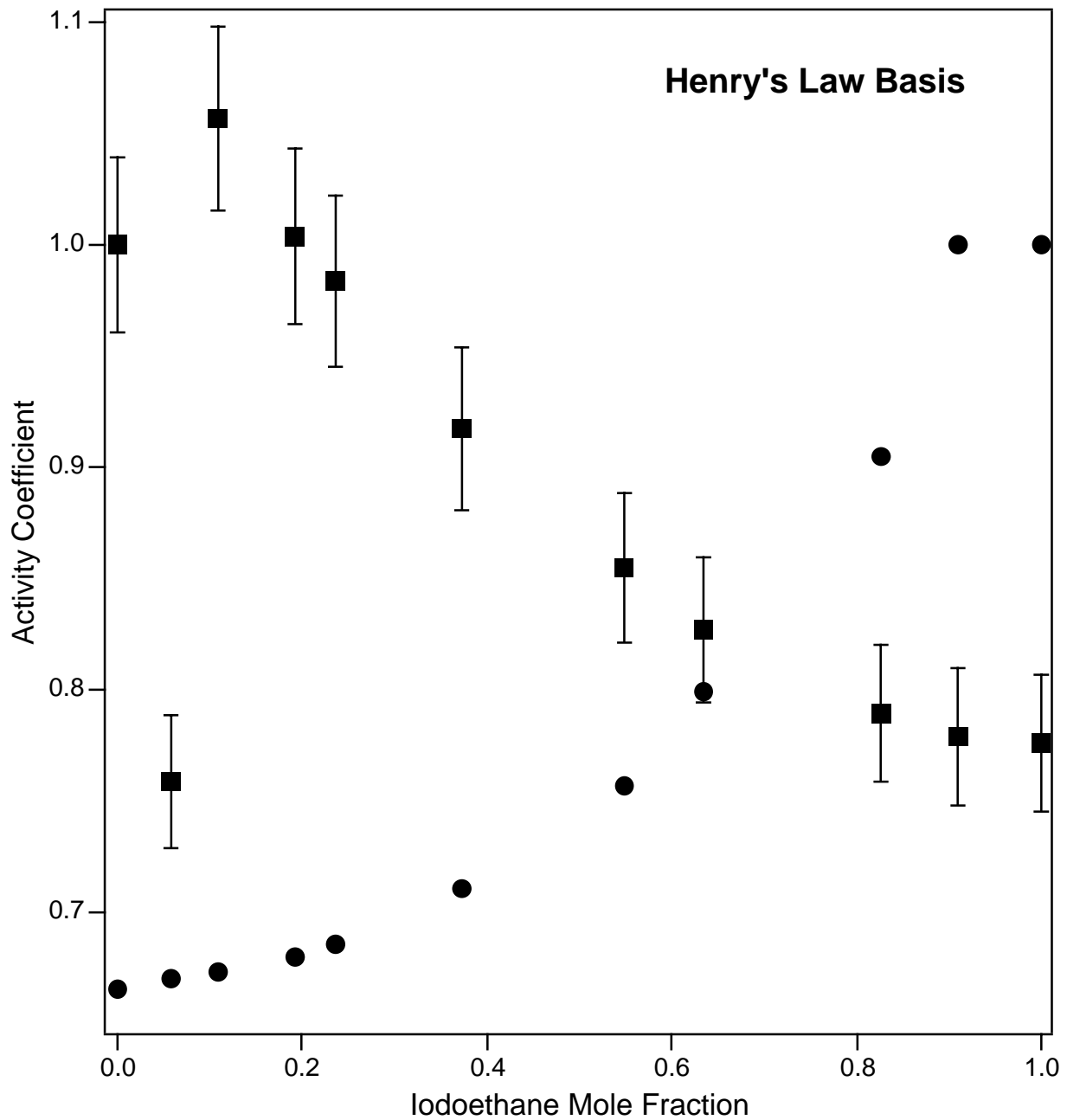
$$g_H := \frac{p}{K_b x}$$

The values of activity and activity coefficient on Raoult's and Henry's law bases are tabulated below as a function of increasing iodoethane mole fraction.

xi	aiR	giR	aaR	gaR	aiH	giH	aaH	gaH
0	0		1	1	0	1	0.6658	0.6658
0.0579	0.05659	0.9774	0.949	1.007	0.0439	0.7582	0.6318	0.6706
0.1095	0.1491	1.362	0.8998	1.01	0.1157	1.056	0.599	0.6727
0.1918	0.2482	1.294	0.8252	1.021	0.1925	1.004	0.5494	0.6798
0.2353	0.2982	1.268	0.7874	1.03	0.2314	0.9832	0.5243	0.6856
0.3718	0.4397	1.183	0.6701	1.067	0.3411	0.9174	0.4461	0.7102
0.5478	0.6036	1.102	0.5143	1.137	0.4682	0.8547	0.3424	0.7571
0.6349	0.6766	1.066	0.4383	1.2	0.5248	0.8266	0.2918	0.7993
0.8253	0.8401	1.018	0.2375	1.36	0.6517	0.7896	0.1581	0.9052
0.9093	0.9126	1.004	0.1362	1.502	0.7079	0.7785	0.0907	1
1	1	1	0		0.7757	0.7757	0	1

The following two plots show the activity coefficients as a function of iodoethane mole fraction on the Raoult's and Henry's law basis, respectively. For the Henry's law values, because the Henry's law constant for iodoethane has an uncertainty, each activity coefficient can be plotted with an associated uncertainty.





The data point at $x_i = 0.0579$ shows a significantly lower value of activity coefficient. In the plot of pressure versus mole fraction, the pressure data point at $x_i = 0.0579$ is significantly below the Henry's law line compared with data points near it. Based on the trend in the above data for iodoethane (the squares), the point at $x_i = 0.0579$ might therefore be rejected.

Accurate determination of the Henry's law constant depends on having accurate measurements of gas and liquid composition in dilute solutions. The values calculated for activity coefficient are also sensitive to the values of gas and liquid phase mole fractions at low iodoethane mole fraction.

The above experiment should be carefully repeated before the data is published as valid!

Problem 8

> restart:

Formulations

> eqnGasComp := $y_A = p_A/p_T$:

eqnActivityA := $a_A = p_A/P_{Ao}$: eqnActivityB := $a_B = p_B/P_{Bo}$:

eqnCoeffA := $g_A = a_A/x_A$: eqnCoeffB := $g_B = a_B/x_B$:

Given Values

> $p_T := 101.325$: $y_A := 0.314$: $x_A := 0.220$: $x_B := 1-x_A$:

$P_{Ao} := 73$: $P_{Bo} := 92.1$: $p_B := p_T - p_A$:

Solutions

> eqnGasComp;

$$.314 = .009869232667 p_A$$

> Digits := 4:

> $p_A := \text{solve}(\text{eqnGasComp}, p_A)$;

$$p_A := 31.81$$

> eqnActivityA; eqnActivityB;

$$a_A = .4358$$

$$a_B = .7545$$

> assign(eqnActivityA, eqnActivityB);

> eqnCoeffA; eqnCoeffB;

$$g_A = 1.981$$

$$g_B = .9673$$

Activities: A = 0.436, B = 0.755

Activity Coefficients: A = 1.98, B = 0.967

>