Introductory Chemical Engineering Thermodynamics

SOLUTIONS FOR HOMEWORK PROBLEMS: Chapter 17

(17.01) For their homework assignment…

Julie: ½ N2 + 3/2 H2 → NH3 Let ν_i be the stoichiometric coefficient of species *i*.

John: N2 + 3 H2 → 2 NH3 Note: $\nu_i^{John} = 2\nu_i^{Julie}$

Jacob: 1/3 N2 + H2 → 2/3 NH3 $\nu_i^{Jacob} = 2/3\ \nu_i^{Julie}$

a)

$\Delta G^{o,Julie} = \Sigma\ \nu_i^{Julie} \Delta G^o_{f,I}$

$\Delta G^{o,John} = \Sigma\ \nu_i^{John} \Delta G^o_{f,I} = \Sigma\ 2\nu_i^{Julie} \Delta G^o_{f,I} = 2\ \Delta G^{o,Julie}$

$\Delta G^{o,Jacob} = \Sigma\ \nu_i^{Jacob} \Delta G^o_{f,I} = \Sigma\ 2/3\ \nu_i^{Julie} \Delta G^o_{f,I} = 2/3\ \Delta G^{o,Julie}$

b)

$K_a^{Julie} = \exp[- \Delta G^{o,Julie}/RT]$

$K_a^{John} = \exp[- \Delta G^{o,John}/RT] = \exp[-2\ \Delta G^{o,Julie}/RT] = (K_a^{Julie})^2$

$K_a^{Jacob} = \exp[- \Delta G^{o,Jacob}/RT] = \exp[-2/3\ \Delta G^{o,Julie}/RT] = (K_a^{Julie})^{2/3}$

c) $K_a^{Julie} = y_{NH3}/(y_{N2}^{1/2} y_{H2}^{3/2})$

$K_a^{John} = y_{NH3}^2/(y_{N2} y_{H2}^3) = \{ y_{NH3}/(y_{N2}^{1/2} y_{H2}^{3/2})\}^2$

$K_a^{Jacob} = y_{NH3}^{2/3}/(y_{N2}^{1/3} y_{H2}) = \{ y_{NH3}/(y_{N2}^{1/2} y_{H2}^{3/2})\}^{2/3}$

Therefore the quantity $y_{NH3}/(y_{N2}^{1/2} y_{H2}^{3/2})$ will be the same for each student.

Since this can be solved in terms of the reaction coordinate when coupled with the stoichiometry, the mole fractions must be the same for each student.

d) The conversion, X_i of each species is a property of the reaction, not a property of the stoichiometric coefficients we use when we write the reaction.

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$X_i = (n_i^i - n_i^f)/n_i^i = -\nu_i\xi_i/n_i^i$ (see footnote at beginning of chapter)

Therefore,
$X_i = (\nu_i\xi_i/n_i^i)^{Julie} = (\nu_i\xi_i/n_i^i)^{John} = (\nu_i\xi_i/n_i^i)^{Jacob}$

$\xi_i^{John} = (\nu_i\xi_i/n_i^i)^{Julie}\,(n_i^i/\nu_i)^{John}$ $\xi_i^{Jacob} = (\nu_i\xi_i/n_i^i)^{Julie}\,(n_i^i/\nu_i)^{Jacob}$

(17.02) Does adding more N2 to the equilibrated mix result in more NH3? Why?

Solution:
Write the rxn as given in example 17.9, and consider e.g. 100bars and 708.8K where K_a=(0.00859). Then, where A is the feed moles of N2 based on 3 moles of H2

$$\frac{\xi(1.5+A-\xi)}{\left[(1.5-1.5\xi)^3(A-0.5\xi)\right]^{1/2}} = 100(0.00859) = 0.859;\ \textit{and}\ \ y_{N2} = \frac{(A-0.5\xi)}{(1.5+A-\xi)}$$

To obtain $y_{N2} = 0.55$, solving simultaneously, $A = 1.794$ with ξ=0.3542 = n_{NH3} compared to 0.3125 when A=0.5 as in example 17.9. When increasing A to 1.794, ξ increases slightly, but yNH3 decreases a lot. So more moles of NH3 are formed per mol of H2, but the composition of the product has a smaller mol fraction of NH3. Whether to increase the amount of N2 depends on the objective, which may depend on the economics of separating so much N2.

(17.03) The production of NO by direct oxidation…

$0.5N_2 + 0.5O_2 = NO$
Basis: 1 mol air feed

	n^i	n^f
O_2	0.21	$0.21 - 0.05\xi$
N_2	0.79	$0.79 - 0.5\xi$
NO	0	$0 + \xi$
total	1	1

ΔH°_{298} = 90.25 kJ/mol, ΔG°_{298} = 86.58 kJ/mol

Intermediate Calculations, J and I defined in text

Δa	Δb	Δc	Δd
-0.28	5.849E-03	-1.238E-05	6.978E-09

R (kJ/mol-K)	0.008314
ΔH°_{298} (kJ/mol)	90.25
ΔG°_{298} (kJ/mol)	86.58
ln $K_{a,298}$	-34.92792
J (kJ/mol)	90.169124
I	-1.555137

$K = y_{NO} / \text{sqrt}(y_{N2}y_{O2}) = \xi / \text{sqrt}(0.21 - 0.5\xi)/\text{sqrt}(0.79 - 0.5\xi)$
squaring both sides and rearranging:
$(1 - 0.25K^2)\xi^2 + 0.5K^2\xi - 0.1659K^2 = 0$
setting up the quadratic formula, the coefficients a,b,c are listed below.
The conversion of O2 is $0.5\xi/0.21$.

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Reaction T(C)	1300	1325	1350	1375	1400
Reaction T(K)	1573.15	1598.15	1623.15	1648.15	1673.15
ΔH^o_T (kJ/mol)	91.58071243	91.72274	91.8771	92.04446	92.22551
ΔG^o_T (kJ/mol)	70.30743595	69.96826	69.62677	69.2828	68.93619
ln K_a	-5.375527712	-5.26591	-5.1595	-5.05614	-4.95567
K_a	0.004628476	0.005165	0.005745	0.00637	0.007043
a	0.999994644	0.999993	0.999992	0.99999	0.999988
b	1.07114E-05	1.33E-05	1.65E-05	2.03E-05	2.48E-05
c	-3.55404E-06	-4.4E-06	-5.5E-06	-6.7E-06	-8.2E-06
ξ	0.001879873	0.002097	0.002332	0.002584	0.002856
% O2 conv	0.469968291	0.524242	0.582897	0.646124	0.714115

Reaction T(C)	1425	1450	1475	1500
Reaction T(K)	1698.15	1723.15	1748.15	1773.15
ΔH^o_T (kJ/mol)	92.42095	92.63148	92.85785	93.10081
ΔG^o_T (kJ/mol)	68.58677	68.23436	67.87879	67.51986
ln K_a	-4.85796	-4.76288	-4.67031	-4.58011
K_a	0.007766	0.008541	0.009369	0.010254
a	0.999985	0.999982	0.999978	0.999974
b	3.02E-05	3.65E-05	4.39E-05	5.26E-05
c	-1E-05	-1.2E-05	-1.5E-05	-1.7E-05
ξ	0.003148	0.003461	0.003794	0.00415
% O2 conv	0.787063	0.865159	0.948598	1.037573

(17.04) The following reaction reaches equilibrium …

Solution:

Using short-cut van't Hoff: C6H5CH=CH2 + H2 ⇔ C6H5CH2CH3

Compound	Gf(kJ/mole at 298K and 1 bar)	Hf(kJ/mole at 298K and 1 bar)
Styrene (C6H5CH=CH2)	213.18	147.36
Ethylbenzene	130.73	29.92
H2	0	0
Δrxn	-82.45	-117.44

T	298	873
Ka	2.789E14	7.863

→ Ka(298)= exp(82450/8.314/298)= 2.789E14

Ka = 2.789E14exp[117,440/8.314*(1/T-1/298.15)] = 7.863

b) $Ka = y_{etb}/(y_{H2}*y_{styrene})P = \xi*(4-\xi)/[P(1-\xi)(3-\xi)] = 7.863 \Rightarrow \xi = 0.843$

$y_{etb} = \xi /(4-\xi) = 0.267$; $y_{H2} = (3-\xi)/(4-\xi) = 0.683$; $y_{styrene} = (1-\xi)/(4-\xi) = 0.05$

c) repeat at 2 bar, $K_aP = 15.73 \Rightarrow \xi = 00914$, $y_{etb} = \xi /(4-\xi) = 0.296$; $y_{H2} = (3-\xi)/(4-\xi) = 0.676$; $y_{styrene} = (1-\xi)/(4-\xi) = 0.028$

(17.05) For the cracking reaction…

$C_3H_{8\,(g)} \rightarrow C_2H_{4\,(g)} + CH_{4\,(g)}$

a) Feed = 1 mol of C_3H_8

Fractional conversion = $-\nu_{C3}\xi/n_{C3}^{\,i} = +\xi$

$\Delta G^o_{rxn} = 1(-50450) + 1(68430) +(-1)(-24290) = +42270$ J/mol

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$K_{a298} = \exp(-\Delta G^\circ_{rxn}/R*(298.15)) = 3.9283x10^{-8}$

$\Delta H^\circ_{rxn} = +82296.4$ J/mol

$K_{aT} = K_{a298}*\exp[(-\Delta H^\circ_{rxn}/R)*(1/T - 1/298)]$

When conversion = 75%, $\xi = 0.75$

At equilbrium $K_{aT} = [(\xi/(1+\xi)]^2/[(1-\xi)/(1+\xi)] = 1.2857 =$
$K_{a298}*\exp[(-\Delta H^\circ_{rxn}/R)*(1/T - 1/298.15)]$. Solving for T, gives T = 622.7 K
For more precision, use KaCalc.xls: T=623⇒ Ka=1.333; … T=621.6⇒ Ka=1.286

b) K_a at 600 K = 0.7045561, feed basis 0.5 mol C3H8, 0.5 mol N2
Assume ideal gas law is valid, so at P = 1 bar
$K_a = [(\xi/(1+\xi)]^2 /[(0.5-\xi)/(1+\xi)] = 0.7045561 \Rightarrow \xi = 0.36287$
So fractional conversion of $C_3H_8 = \xi/n_{C3}^i = 0.36287/0.5 = 72.57\%$ (=0.7309 by KCalc.xls)

(17.06) Ethanol can be manufactured by the vapor…

(a)

Stoichiometric		$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	Constants for C_P in J/mol-K			
Number	Name	(kJ/mol)	(kJ/mol)	a	b	c	d
-1	ETHYLENE	52.51	68.43	3.806	1.566E-01	-8.348E-05	1.755E-08
-1	WATER	-241.835	-228.614	32.24	1.924E-03	1.055E-05	-3.596E-09
1	ETHANOL	-234.95	-167.73	9.014	2.141E-01	-8.390E-05	1.373E-09
enter all species above line 14				Intermediate Calculations, J and I defined in text			
				Δa	Δb	Δc	Δd
Reaction T(K)	398.15			-27.032	5.558E-02	-1.097E-05	-1.258E-08
ΔH°_T (kJ/mol)	-46.581			R (kJ/mol-K)		0.008314	
ΔG°_T (kJ/mol)	5.383			ΔH°_{298} (kJ/mol)		-45.625	
ln K_a	-1.626101633			ΔG°_{298} (kJ/mol)		-7.546	
K_a	0.19669487			ln $K_{a,298}$		3.0441915	
				J (kJ/mol)		-39.913811	
				I		-4.4936957	

the equilibrium constant doesn't depend on P
(Note: shortcut method gives $K_a = 0.2062$
(b)
basis: 100 moles feed,

	in	out
C2H4	25	25 - ξ
H2O	75	75 - ξ
C2H5OH	0	ξ

$K_aP = \xi(100-\xi)/(25-\xi)/(75-\xi) \Rightarrow K_aP(25-\xi)(75-\xi) - \xi(100-\xi) = 0$

P is 1 bar, solving for x iteratively using solver (note: can also use quadratic formula)

$\xi = 3.18$
(Note: shortcut method gives $\xi = 3.32$

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(17.07) Ethylene is a valuable feedstock…

$C_2H_5OH \rightarrow C_2H_4 + H_2O$

$\Delta G^o_{298} = 68.43 - 228.614 + 167.73 = 7.546$

$\Delta H^o_{298} = 52.51 - 241.835 + 234.95 = 45.625$

$\ln K_a = \frac{-\Delta G^o}{RT} = \frac{-7.546}{(8.314\times10^{-3})(295.15)} = -3.044$

$K_a = 0.048$ at 298 K

at 150 °C (423.15 K)

$\Delta H_r(298) = 45.625$ kJ/mol

van't Hoff: $\ln K = \frac{-45.625}{8.314\times10^{-3}}\left(\frac{1}{423.15} - \frac{1}{298.15}\right) - 3.044$

$= 5.437 - 3.044 = 2.393$

$K_a = 10.95$

1 = EtOH, 2 = Ethylene, 3 = water

(a) $K_a = (y_2y_3P)/y_1$

$n_1 = 1 - \xi$ $\quad y_1 = (1-\xi)/(1+\xi)$

$n_2 = 0 + \xi$ $\quad y_2 = \xi/(1+\xi)$

$n_3 = 0 + \xi$ $\quad y_3 = \xi/(1+\xi)$

$n_T = 1 + \xi$

$K_a = 10.95 = \xi^2 P/(1-\xi)(1+\xi)$, $\quad P = 1$ bar $\quad \Rightarrow \xi = 0.957$

% reacted = $[1 - (1-\xi)]/1 * 100\% = \xi * 100\% = 95.7$ % reacted

(b) adding the inert should increase conversion because the effect of Le Chatelier's principle is mitigated by the inert.

$n_1 = 0.5 - \xi$ $\quad y_1 = (0.5-\xi)/(1+\xi)$

$n_2 = 0 + \xi$ $\quad y_2 = \xi/(1+\xi)$

$n_3 = 0 + \xi$ $\quad y_3 = \xi/(1+\xi)$

$n_{inert} = 0.5$

$n_T = 1 + \xi$

$K_a = 10.95 = \xi^2 P/(0.5-\xi)(1+\xi)$, $\quad P = 1$ bar $\quad \Rightarrow \xi = 0.486$

% reacted = $[0.5 - (0.5-\xi)]/0.5\ 100\% = 2*\xi * 100\% = 97$ % reacted

Yes, inert helps conversion.

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(17.08) The catalyzed methanol synthesis reaction…

Species	n^i	n^f
1-CO	5	$5-\xi$
2-H2	5	$5-2\xi$
3-MeOH	0	ξ
	10	$10-2\xi$

$0 < \xi < 2.5$

$K_a = \xi (10-2\xi)^2 / (5-2\xi)^2 (5-\xi) P^2$

$= 4\xi (5-\xi) / (5-2\xi)^2 P^2$

Simplify expression and get,

$K_a P^2 (25 - 20\xi + 4\xi^2) = 20\xi - 4\xi^2$

$(K_a P^2 + 1)\xi^2 - 5 (K_a P^2 + 1)\xi + (25/4) K_a P^2 = 0$

Let $M = K_a P^2$, then get $\xi^2 - 5\xi + (25/4)(M / (M+1)) = 0$

$\xi = 2.5 - 2.5(1 - M / (M+1))^{1/2} = 0$

(**Note** that only the negative sign makes sense, $\xi < 2.5$)

Use short-cut van't Hoff

$\Delta G^0_{298} = -162.24 + 137.16 = -25.08$ kJ/ mole ⟶ $\ln K_{a\,298} = 10.118$

$\Delta H^0_{298} = -200.94 + 110.53 = -90.41$ kJ/ mole

Use the RXNADIA page in the Rxn.xls to solve for the adiabatic temperature, but change the formula for M and then use solver or Goal seek to adjust T until energy balance closes.

Adiabatic Synthesis of Ammonia — Protected without a password

Feed Temperature (K)	473.15					
Outlet Temperature(K)	541.7422		Heat Capacity Constants			
P(bar)	10			*a*	*b*	*c*	*d*
Standard State Heat of Reaction	-90410	J/mol	CO	3.09E+01	-1.29E-02	2.79E-05	-1.27E-08
at 298K			H2	2.71E+01	9.27E-03	-1.38E-05	7.65E-09
K_a (298.15)	24785.15		CH3OH	2.12E+01	7.09E-02	2.59E-05	-2.85E-08

K_a at reaction T	0.00187	M	0.186976 η	0.2053365

	Inlet			Outlet		
	moles	H(J/mol)	totals	moles	H(J/mol)	totals
CO	5	5143.499	25717.5	4.794663	7192.505	34485.64
H2	5	5094.807	25474.04	4.589327	7103.741	32601.39
CH3OH	0	8877.999	0	0.205337	12998.07	2668.978
Total			51191.53			69756.01

Balance($\eta H^{in} n^{in} - \eta H^{out} n^{out} - \eta\eta H$)=	-1.06E-07 J

NOTE: The inlet moles cannot be changed without recalulating a formula for η

Use solver to set value of Balance to zero by adjusting Feed Temperature, Outlet Temperature, or P.

Limiting reactant is H2, conversion = $(2\xi)/5 * 100\% = 10.3\%$

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(17.09) A gas stream composed of 15 mol% SO_2, 20 mol% O_2...

Assume that the only reaction is oxidation of SO2 to SO3
SO2 + 1/2 O2 = SO3

For SO3, thermochemical data will be taken from "The Properties of Gases and Liquids, 4th, ed., Reid, Prausnitz, and Poling.
The enthalpy of formation is -396.0 kJ/mol at 1 atm, and requires no pressure correction
The Gibbs energy of formation is -371.3 kJ/mol at 1 atm. The pressure correction is -0.5RTln 1/1.013, which is insignificant.

Stoichiometric		$\Delta H^o_{f,298}$	$\Delta G^o_{f,298}$	Constants for C_p in J/mol-K			
Number	Name	(kJ/mol)	(kJ/mol)	a	b	c	d
-1	SULFUR DIOXI	-296.81	-300.14	23.85	6.699E-02	-4.961E-05	1.328E-08
-0.5	OXYGEN	0	0	28.11	-3.680E-06	1.746E-05	-1.065E-08
1	SULFUR TRIO	-396	-371.3	19.21	1.374E-01	-1.176E-04	3.700E-08
enter all species above line 14				Intermediate Calculations, J and I defined in text			
				Δa	Δb	Δc	Δd
Reaction T(K)	753.15			-18.695	7.041E-02	-7.672E-05	2.905E-08
ΔH^o_T (kJ/mol)	-98.824			R (kJ/mol-K)		0.008314	
ΔG^o_T (kJ/mol)	-28.202			ΔH^o_{298} (kJ/mol)		-99.19	
ln K_a	4.503874631			ΔG^o_{298} (kJ/mol)		-71.16	
K_a	90.36659102			ln $K_{a,298}$		28.707218	
				J (kJ/mol)		-96.125254	
				I		-1.606754	

	in	out
SO2	15	15 - ξ
O2	20	20 - 0.5ξ
SO3	0	ξ
N2	65	65
Total		100 - 0.5ξ

$$K_a = y_{SO3}P / [(y_{SO2}P)(y_{O2}P)^{1/2})] = \xi(100-0.5\xi)^{1/2} / [(15 - \xi)(20 - 0.5\xi)^{1/2}P^{1/2}]$$

Using P = 2 bar, ξ = 14.69 (shortcut method also gives 14.7)
conversion = 14.69/15 = 0.98, 98% conversion

(b)The solution will use the heat of reaction method,
$0 = \Sigma\, nH^{in} - \Sigma\, nH^{out} + Q - \xi\Delta H_R^o \Rightarrow Q = \Sigma\, nH^{out} - \Sigma\, nH^{in} + \xi\Delta H_R$
$n_i(out) = n_i(in) + \nu_i\xi$

	n(out)	H(out)(J/mol)	n*H (kJ)
SO2	0.31	21289.39	6.622
O2	12.66	14285.66	180.793
SO3	14.69	28797.95	423.012
N2	65.00	13590.92	883.410
Sum			1493.836

For the inlet

	n(in)	H(in)(J/mol)	n*H (kJ)
SO2	15.00	-125.06	-1.876
O2	20.00	-92.51	-1.850

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SO3	0.00	-159.33	0.000
N2	65.00	-91.91	-5.974
Sum			-9.700

Q = 1494 + 9.7 + 14.7*(-99.19) = 45.6 kJ for every 100 mol feed

This neglects any heat loss from the reactor.

(17.10) The feed gas to a methanol synthesis reactor is composed of

a) For the calculation of Ka's, use the Kcalc.xls

Stoichiometric		$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	Constants for C_P in J/mol-K			
Number	Name	(kJ/mol)	(kJ/mol)	a	b	c	d
-1	CARBON MON	-110.53	-137.16	30.87	-1.285E-02	2.789E-05	-1.272E-08
-2	H2	0	0	27.14	9.274E-03	-1.381E-05	7.645E-09
1	METHANOL	-200.94	-162.24	21.15	7.092E-02	2.587E-05	-2.852E-08
enter all species above line 14				Intermediate Calculations, J and I defined in text			
				Δa	Δb	Δc	Δd
Reaction T(K)	550			-64	6.522E-02	2.560E-05	-3.109E-08
ΔH°_T (kJ/mol)	-99.019			R (kJ/mol-K)		0.008314	
ΔG°_T (kJ/mol)	33.309			ΔH°_{298} (kJ/mol)		-90.41	
ln K_a	-7.284297141			ΔG°_{298} (kJ/mol)		-25.08	
K_a	0.00068623			ln $K_{a,298}$		10.117721	
				J (kJ/mol)		-74.392049	
				I		-22.759103	

Stoichiometric		$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	Constants for C_P in J/mol-K			
Number	Name	(kJ/mol)	(kJ/mol)	a	b	c	d
-1	CARBON DIOX	-393.51	-394.38	19.8	7.344E-02	-5.602E-05	1.715E-08
-1	H2	0	0	27.14	9.274E-03	-1.381E-05	7.645E-09
1	CARBON MON	-110.53	-137.16	30.87	-1.285E-02	2.789E-05	-1.272E-08
1	WATER	-241.835	-228.614	32.24	1.924E-03	1.055E-05	-3.596E-09
enter all species above line 14				Intermediate Calculations, J and I defined in text			
				Δa	Δb	Δc	Δd
Reaction T(K)	550			16.17	-9.364E-02	1.083E-04	-4.111E-08
ΔH°_T (kJ/mol)	39.405			R (kJ/mol-K)		0.008314	
ΔG°_T (kJ/mol)	18.494			ΔH°_{298} (kJ/mol)		41.145	
ln K_a	-4.044345576			ΔG°_{298} (kJ/mol)		28.606	
K_a	0.017521167			ln $K_{a,298}$		-11.540172	
				J (kJ/mol)		39.610606	
				I		5.1448653	

Calculation of ξ_1 and ξ_2.
Assume a basis of 100 moles feed and set up a table as follows:

Species	n^i	n^f
1-H2	75	$75 - 2\xi_1 - \xi_2$
2-CO	12	$12 - \xi_1 + \xi_2$
3-MeOH	0	ξ_1
4-CO2	8	$8 - \xi_2$
5-H2O	0	ξ_2
6-N2	5	5
	100	$100 - 2\xi_1$

$K_{a1} = y_3 P / [(y_1)^2 P^2 \; y_2 P] = y_3 / [(y_1)^2 P^2 \; y_2] = n_3 n^2 / (n_1)^2 n_2 P^2$

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$K_{a2} = (y_2 P\, y_5 P) / (y_1 P\, y_4 P) = n_2 n_5 / n_1 n_4$

$OBJ1 = K_{a1} P^2 (n_1)^2 n_2 - n_3 n^2 = 0$
$= K_{a1} P^2 (75 - 2\xi_1 - \xi_2)^2 (12 - \xi_1 + \xi_2) - \xi_1 (100 - 2\xi_1)^2 = 0$
$OBJ2 = K_{a2} n_1 n_4 - n_2 n_5 = 0$
$= K_{a2} (75 - 2\xi_1 - \xi_2)(8 - \xi_2) - (12 - \xi_1 + \xi_2)(\xi_2) = 0$

Table of Results (x values below for basis of 100 moles feed).

Ka1	6.86E-04	P(bar)	100
Ka2	1.75E-02		
ξ1	10.2967	OBJ1	-8.58E-07
ξ2	1.70412	OBJ2	-8.41E-10

	ni	nf	y
1 - H2	75	52.70247	0.663704
2 - CO	12	3.407417	0.042911
3 - MeOH	0	10.2967	0.1296706
4 - CO2	8	6.29588	0.0792866
5 - H2O	0	1.70412	0.0214607
6 - N2	5	5	0.0629671
		79.40659	

(17.11) The 10/25/93 issue of Chemical and Engineering News ...

Solution:
Using short-cut van't Hoff and Gibbs energy minimization.

	Hf (J/mole)	Gf (J/mole)	Gf350/ RT	Moles feed	ni	log(ni)	Yi	ni(Gi/RT+lnyi)
cis butene	-6990	65900	29.12	0.5	0.143	-0.84	0.143	3.897
trs butene	-11180	63010	29.00	0.5	0.162	-0.79	0.162	4.394
isobutene	-16910	58110	27.68	0	0.605	-0.22	0.605	16.450
1-butene	-126	71340	29.59	0	0.090	-1.05	0.090	2.436
					1.000			27.178
								27.1779
C-bal	4	4						
Hbal	8	8						

Hint: I found Cp values for all species in Reid et al.(1987) and typed into KaCalc

cis-2-BUTENE	-7.4	65.5	0.4396	2.95E-01	-1.02E-04	-6.16E-10
trans-2-BUTENE	-11	63.4	18.32	2.56E-01	-7.01E-06	-8.99E-09

Alternate values of Cp gave isoC4ene from 0.629-0.625.
e.g. Webbook gives Cp values at T=[150-1200] that can be regressed.

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(17.12) Acrylic acid is produced....

Basis: 1 mole C3H6
1 mole C3H6
8 mole H20
1.5(1.5 mole O2 req'd by rxn1) = 2.25 mol O2
2.25*79/21 = 8.464 mol N2
1 – propylene, 2 – O2, 3 – Acylic, 4 – Water, 5 – CO2, 6 - Acetic

$n_1 = 1 - \xi_1 - \xi_2$
$n_2 = 2.25 - 1.5\xi_1 - 2.5\xi_2$
$n_3 = \xi_1$
$n_4 = 8 + \xi_1 + \xi_2$
$n_5 = \xi_2$
$n_6 = \xi_2$
$n_{N2} = 8.464$
$n_{total} = 19.714 - 0.5\xi_1 - 0.5\xi_2$
$K_{a1} = y_3y_4/(y_1y_2^{3/2}P^{1/2}) =$
$\xi_1(8+\xi_1+\xi_2)(19.714 - 0.5\xi_1 - 0.5\xi_2)^{1/2}/[(1-\xi_1 - \xi_2)(2.25-1.5\xi_1-2.5\xi_2)^{3/2}P^{1/2}]$
$K_{a2} = y_6y_5y_4/(y_1y_2^{5/2}P^{1/2}) =$
$\xi_2^2(8+\xi_1+\xi_2)(19.714 - 0.5\xi_1 - 0.5\xi_2)^{1/2}/[(1-\xi_1 - \xi_2)(2.25-1.5\xi_1-2.5\xi_2)^{5/2}P^{1/2}]$

K values shown below:

Stoichiometric		$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	Constants for C_P in J/mol-K			
Number	Name	(kJ/mol)	(kJ/mol)	a	b	c	d
-1	PROPYLENE	19.71	62.14				
-1.5	O2	0	0				
1	ACRYLIC ACID	-336.5	-286.3				
1	WATER	-241.835	-228.614				
enter all species above line 14				Intermediate Calculations, J and I defined in text			
				Δa	Δb	Δc	Δd
Reaction T(K)	583.15			0	0.000E+00	0.000E+00	0.000E+00
ΔH°_T (kJ/mol)	-598.045			R (kJ/mol-K)		0.008314	
ΔG°_T (kJ/mol)	-556.989			ΔH°_{298} (kJ/mol)		-598.045	
ln K_a	114.8831073			ΔG°_{298} (kJ/mol)		-577.054	
K_a	7.81807E+49			ln $K_{a,298}$		232.79391	
				J (kJ/mol)		-598.045	
				I		8.4681452	

Stoichiometric		$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$	Constants for C_P in J/mol-K			
Number	Name	(kJ/mol)	(kJ/mol)	a	b	c	d
-1	PROPYLENE	19.71	62.14				
-2.5	O2	0	0				
1	ACETIC ACID	-434.425	-376.685				
1	CARBON DIOX	-393.51	-394.38				
1	WATER	-241.835	-228.614				
enter all species above line 14				Intermediate Calculations, J and I defined in text			
				Δa	Δb	Δc	Δd
Reaction T(K)	583.15			0	0.000E+00	0.000E+00	0.000E+00
ΔH°_T (kJ/mol)	-1089.480			R (kJ/mol-K)		0.008314	
ΔG°_T (kJ/mol)	-1035.378			ΔH°_{298} (kJ/mol)		-1089.48	
ln K_a	213.5544529			ΔG°_{298} (kJ/mol)		-1061.819	
K_a	5.56571E+92			ln $K_{a,298}$		428.35679	
				J (kJ/mol)		-1089.48	
				I		11.158943	

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The reactions and approximate *Ka* values are

C3H6 + 1.5 O2 = CH2=CH-COOH + H2O 10^{49}

C3H6 + 2.5 O2 = CH3-COOH + H2O + CO2 10^{92}

The feeds on basis of 1 mole of C3H6 are {1, 2.25, 9, 8} for {C3H6, O2, N2, H2O}. The problem is that these *Ka* values are like infinity over infinity, so the ratio of one reaction to the other is hard to figure out. Another way to write the second reaction is:

CH2=CH-COOH + O2 = CH3-COOH + CO2 10^{43}

The system of equations is linearly dependent and any 2 out of 3 ways of writing the reaction is acceptable. Looking at the latter version shows that acrylic will be converted to acetic iff O2 is sufficient ($10^{43}<10^{49}$). So this is more of a mass balance problem than thermo problem. Since we only have 2.25 moles of O2, we can't make pure acetic acid. The equation to solve is $n_{O2}=2.25-2.5\xi_2-1.5\xi_1=0$; $n_{C3}=1-\xi_1-\xi_2=0 \Rightarrow \xi_1 = 0.25, \xi_2 = 0.75$.

i.e. 2.25-1.5 = 0.75 "excess" O2 to allow 2nd rxn. 0.75/1.00$\Rightarrow$ 75% = ξ_2. Note: Gibbs minimization is a problem because all goes to CO2 and H2O, inevitably. It may be possible to reconsider whether n_{C3} is zero by plotting Gibbs energy vs. ξ_2 (ξ_1 inferred).

(17.13) As part of a methanol synthesis process one side reaction…

Solution:

ΔH_{rxn} ~ -102kJ/mole and K_{600K} ~ 20,000. Coke formation will be strongly favored if it is kinetically possible from poor catalyst design. High pressure will only favor coke formation even more strongly.

$CO_g + H_{2,g} \rightarrow C_s + H_2O_g$ at 600 K, 100 atm

ΔH_{rxn}^{298} = -131305 J/mol

ΔG_{rxn}^{298} = -91454 J/mol

Using Kcalc,

$K_a^{298} = 1.052 \times 10^{16}$

K_a^T = 15,993

	Feed	n^f	moles of solid	moles in gas phase
CO_g	1	$1-\xi$	0	$1-\xi$
$\xi H_{2,g}$	1	$1-\xi$	0	$1-\xi$
C_s	0	$0+\xi$		0
H_2O_g	0	$0+\xi$	0	$0+\xi$
				$2-\xi$

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$$K_a^T = a_c \cdot \frac{\xi}{(2-\xi)} \cdot \frac{(2-\xi)}{(1-\xi)} \cdot \frac{(2-\xi)}{(1-\xi)} \cdot \frac{1}{P \cdot P} \cdot P \qquad P = 100 \text{ atm}$$

Solving → $\xi = 0.9994$

(17.14) Hydrogen gas can be produced by the following reactions

Balance equations – Basis 1 mole propane, 5 mole water

C3H8	1-ξ1
H2O	5-3 ξ 1- ξ 2
CO	3 ξ1– ξ2
H2	7 ξ1+ ξ2
CO2	ξ2

Total $6 + 6\,\xi_1$

Reaction 1

$$K_{a1} = \frac{(y_{CO})^3 (y_{H2})^7 P^6}{(y_{C3H8})(y_{H2O})^3} = \frac{(3\xi_1 - \xi_2)^3 (7\xi_1 + \xi_2)^7 P^6}{(6+6\xi_1)^6 (1-\xi_1)(5-3\xi_1-\xi_2)^3}$$

$$\text{obj1} = \frac{K_{a1}}{P^6}(6+6\xi_1)^6(1-\xi_1)(5-3\xi_1-\xi_2)^3 - (3\xi_1-\xi_2)^3(7\xi_1+\xi_2)^7 = 0$$

Reaction 2

$$K_{a2} = \frac{(y_{CO2})(y_{H2})}{(y_{CO})(y_{H2O})} = \frac{\xi_2(7\xi_1+\xi_2)}{(3\xi_1-\xi_2)(5-3\xi_1-\xi_2)}$$

$$\text{obj2} = K_{a2}(3\xi_1-\xi_2)(5-3\xi_1-\xi_2) - \xi_2(7\xi_1+\xi_2) = 0$$

shortcut at 700 K:

	initial	Final	y final		
propane	1	0.410499	0.043043	Ka1	6.67E-03
water	5	1.943264	0.20376	Ka2	7.474
co		0.480272	0.050359	Squiggle1	0.589501369
co2		1.288232	0.135077	Squiggle2	1.288232273
h2		5.414742	0.567761	obj 1	2.31861E-07
	6	9.537008		obj 2	4.46754E-12

shortcut at 750 K:

	initial	Final	y final		
propane	1	0.181257	0.01661	Ka1	2.01E+00
water	5	1.365527	0.125135	Ka2	4.665
co		1.277987	0.117113	squiggle1	0.818743369
co2		1.178243	0.107972	squiggle2	1.178243226
h2		6.909447	0.63317	obj 1	-8.45874E-07
	6	10.91246		obj 2	1.40332E-13

rigorous at 700 K:

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	initial	Final	y final		
propane	1	0.290364	0.028307	Ka1	1.47E-01
water	5	1.433338	0.139731	Ka2	9.296
co		0.691152	0.067378	squiggle1	0.709635699
co2		1.437755	0.140162	squiggle2	1.437755321
h2		6.405205	0.624422	obj 1	-2.34286E-08
	6	10.25781		obj 2	4.08562E-14

rigorous at 750 K:

	initial	Final	y final		
propane	1	0.054717	0.004688	Ka1	6.38E+01
Water	5	0.95824	0.082099	Ka2	6.04
Co		1.629939	0.139649	Squiggle1	0.945283269
co2		1.205911	0.103319	squiggle2	1.205910536
h2		7.822893	0.670245	obj 1	-7.82311E-08
	6	11.6717		obj 2	0

(17.15) Write and balance the chemical reaction of carbon monoxide…

$2CO_{(g)} \rightarrow CO_{2(g)} + C_{(s)}$

The equilibrium constant for this reactions are

$\Delta G°298 = -120.06$ $\Delta H°298 = -172.45$

$\Delta G°700 = -48.411$ Ka = 4098 shortcut gives Ka = 4898

$\Delta G°750 = -39.519$ Ka = 565.5 shortcut gives Ka = 679

$Ka = \frac{y_{CO2}}{y_{CO}^2 P}$ take LHS from above, calculate RHS from previous problem

If LHS > RHS, carbon will form

At 700 K

4098 > 0.0674/0.1402/1 = 3.34

yes, carbon will form.

At 750 K

565.5 > 0.1396/(0.1333)^2 = 13.08

yes, carbon will form.
You can combine this reaction with the two reactions from the previous problem, and arrive at the same conclusion, but that is more tedious.

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(17.16) Catalytic converters on automobiles are designed to minimize …

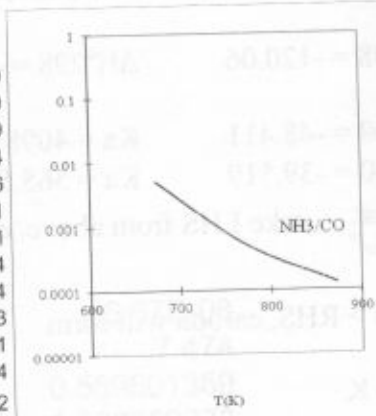
Gibbs energy minimization technique applied to the automobile exhaust problem. The feed composition is that reported by Taylor (Cat.Rev.Sci.Eng., 35:457,1993) (taking propane to be representative of the hydrocarbons).

Free energies of formation were determined from KaCalc.xls by treating the elements as reactants and the species as the products.

	Gf(773) J/MOL	Hf(773)	673 G/RT	moles feedppm	ni	log(ni)	yi	ni(Gi/RT+lnyi)	
N2O	139370	82140	23.5851		0.0000	-6	1.00113E-09	0.000	-3
NO	80740	90470	14.6549	1.05	0.0000	-6	1.00113E-09	0.000	-3
NO2	81030	32150	13.3516		0.0000	-6	1.00113E-09	0.000	-3
N2O4	239000	11730	37.4597		0.0000	-11	1.00113E-14	0.000	-3
NH3	39300	-60390	4.7189		0.0026	-2.58929	2.57751E-06	-0.021	-3
N2	0	0	0.0000	724	724.5237	2.8600526	0.725341587	-232.654	2
CO2	-395300	-394300	-70.6252	135	143.5549	2.1570179	0.143716903	-10417.071	2
CO	-180300	-110750	-30.6153	6.8	0.4951	-0.305264	0.000495708	-18.927	0
O2	0	0	0.0000	5.1	0.0000	-11	1.00113E-14	0.000	-3
H2	0	0	0.0000	2.3	4.8510	0.6858307	0.00485647	-25.843	1
H2O	-205020	-246170	-37.5927	125	125.4451	2.0984539	0.125586753	-4976.094	2
c3h8	118192	-125797	15.4822	0.75	0.0000	-11	1.00113E-14	0.000	-3
Total					998.8724			-15670.610	
O-bal	413.0500	413.050							
H-bal	260.6000	260.600							
C-bal	144.0500	144.050							
N-BAL	1449.0500	1449.050							

Results:

	Gf(773) J/MOL	Hf(773)	moles feed	873 yi	773 yi	673 yi
N2O	139370	82140		1.04E-13	4.0958E-20	1.001E-09
NO	80740	90470	1.05	8.35E-13	4.0964E-17	1.001E-09
NO2	81030	32150		8.24E-15	6.3641E-26	1.001E-09
N2O4	239000	11730		9.99E-18	1.2936E-48	1.001E-14
NH3	39300	-60390		2.23E-07	5.3440E-07	2.578E-06
N2	0	0	737	7.25E-01	7.2534E-01	7.253E-01
CO2	-395300	-394300	135	1.43E-01	1.4317E-01	1.437E-01
CO	-180300	-110750	0.75	1.70E-03	1.0373E-03	4.957E-04
O2	0	0	0.00051	5.17E-14	3.8310E-22	1.001E-14
H2	0	0		3.66E-03	4.3179E-03	4.856E-03
H2O	-205020	-246170	125	1.27E-01	1.2613E-01	1.256E-01
c3h8	118192	-125797	0.75	1.44E-16	2.2746E-32	1.001E-14
				8.73E+02	7.7300E+02	6.730E+02
NH3/CO				0.0001317	0.00051516	0.0051997
NH3/NO				267366.27	1.3045E+10	2574.5995



Hints:

a) Note that the convergence and precision have been changed to 1e-11 in options. Set quadratic and central options.

b) Start with log(ni)=-1 for all, then solve. Stop after each max iteration limit and look at solutions.

c) If any log(ni) goes less than -3, reset it to -3.

d) This eventually gives problem, but notice that c3h8, O2 and N2O4 are going to zero. Based on Gf values this seems obvious in retrospect.

e) Set log(ni) = -11 for c3h8, O2, and N2O4, then solve. Other species that go less than -11, reset to -6 and see where they go.

f) Watch the value of *G* that is the obj fun. Make sure it is getting as small as can be. Then you will see above result.

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(17.17). Styrene can be hydrogenated to ethyl benzene at moderate

conditions in both the liquid and gas phases. Calculate the equilibrium compositions in the vapor and liquid phases of hydrogen, styrene, and ethylbenzene at each of the following conditions?

Solution: (cf. Perry's Handbook for formation data)

Using short-cut van't Hoff: C6H5CH=CH2 + H2 = C6H5CH2CH3

Compound	Gf(kcal/mole at 298K and 1atm)	Hf(kcal/mole at 298K and 1atm)
Styrene (C6H5CH=CH2)	51.12	35.22
Ethylbenzene	31.28	5.72
H2	0	0
Δrxn	-19.84	-29.5

T	298	423	600
Ka	3.562e14	144e6	4583

→ Ka(298)= exp(19840/1.987/298)= 3.562e14

Ka = 3.562e14exp[29500/1.987*(1/T-1/298)] = 19.5E6

$Ka = y_{etb}/(Py_{H2}*y_{styrene}) = X*(4-X)/[P(1-X)(3-X)]$ = all large ⇒ complete conversion

$y_{etb} = 0.0$; $y_{H2} = 0.5$; $y_{styrene} = 0.5$

(17.18) Habenicht et al. (IEC Res., 34:3784, 1995) ...

Solution:

Sample solution of two simultaneous reactions with vle:
This system corresponds to the equilibrium analysis of the "ETBE
from t-Butyl Alcohol Process" (cf. Habenicht et al., IEC Res., 34:3784, 1995)
(for data cf. TRC page p-6090 in each book and Iborra et al., JChemE Data 34:1(1989)
and Prop Gas and Liq for all besides etbe)
TBA+etoh=etbe+water
TBA=ibutylene+water

Moles fed:	TBA	etoh	etbe	water	ibutylene	TOTAL
(excl. solv.)	0.027	0.832	0	0.141	0	1
Gf(298)	-177.6	-167.9	-121.7	-228.6	57	
Hf(298)	-312.46	-234.43	-316.5	-241.8	-17.1	
Cp	113	65.4	161.7	33.6	89.16	
Hvap	43569		35100			
Psat(bar)	13.307	14.867	14.57	7.917	57.4449	

(Details of input equations described in text by Elliott and Lira)

P(bar)	14.364
T(K)	443
DG1(298)	-4800
DH1(298)	-11410
DG2(298)	6000
DH2(298)	53560
Ka1(298)	6.9405
Ka2(298)	0.0888
Ka1	1.5373
Ka2	105.0171
KTBA	0.9264
KETOH	1.0350
KETBE	1.0141
KW	0.5511
KIB4	3.9991
X1	0.01070
X2	0.01547
L/F	0.99900

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yTBA	0.00075	
yEOH	0.83705	
yETBE	0.01069	
yW	0.09077	
yIC4	0.06074	
err1	0.00000	
err2	0.00000	
sum(yi)	1.00000	
	Z	γ
TBA	0.000814	
EtOH	0.808784	1.02
ETBE	0.010541	2.34
Water	0.164627	2.06
iC4	0.015233	6.05

Roughly, solubility limit ~> $1/\gamma^{\infty} \sim 1/6 = 0.17 >> 0.015$ so OK.

(17.19) Limestone ($CaCO_3$) decomposes upon heating

Solution:

$CaCO_{3,s} \rightarrow CaO_s + CO_{2,g}$

$\Delta G_{rxn}^{278} = +130380$ J/mol; $\Delta H_{rxn}^{278} = +178320$ J/mol

$K_a^{298} = 1.3984 \times 10^{-23}$

$$K_a^T = K_a^{298} \exp\left[\frac{-\Delta H_{rxn}^{298}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right] = \frac{a_{CaO}}{a_{CaCO_3}} \cdot \frac{y_{CO_2} P}{f_{CO_2}^0} = P = 1$$

The activities of the solids are 1, the vapor phase $y_{CO2} = 1$.

Solving for the T where $K_a = 1$,

$$\frac{R \ln K_{a,298}}{\Delta H_{298}} + 1/298.15 = 1/T$$

$T = 1110$ K

Note: more precise solution by KaCalc.xls gives 1150K.

(17.20) Two-tenths of a gram of CaCO3(s) is placed ...

MW = 100 g/mol, 0.2g/(100g/mol) = 0.002 mol, 50% conversion will be $\xi = 0.001$

$K = P = nRT/\underline{V} = \xi RT/\underline{V}$

$K\underline{V}/RT = 0.001$

Set up reaction on Kcalc.xls. $\Delta G^{o}_{298} = 130.38$ kJ/mol, $\Delta H^{o}_{298} = 178.32$ kJ/mol

Add cell for $\underline{V}/RT = 100/83.143/T$, where T is the reaction temperature.

Add cell for $K\underline{V}/RT$. Use Goal Seek to set this cell to 0.001 by changing T.

This occurs at 1104 K, where $\Delta G^{o}_{T} = 0.786$ kJ/mol, $K = P = 0.92 \rightarrow P = 0.92$ bar.

(17.21) ...synthesis of dimethyl carbonate (DMC) from methanol and CO2 at 350 K

(a) 2CH3OH + CO2 = CH3OCOOCH3 + H2O (H2O is the "highlighted byproduct.")

(b) ΔG_{298} = -452.4 -228.614- (-394.38 – 2*162.24) = 37.85; $Ka_{298} = \exp(-\Delta G/RT) = 2.32E\text{-}7$.

a,b,c,d not available for DMC, so use Shortcut vant Hoff:

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ΔH_{298} = -16.55kJ/mol => $\ln(K_a/Ka_{298}) = (16550/8.314)(1/T - 1/298.15)$ => Ka_{350} = 8.61E-8
=> P = 0.1/8.61E-8 = 1.162 E6 bars (FYI: 10GPa is considered quite high and this is 10x larger)
It makes you wonder about the feasibility of this concept, but polymerization should shift the equilibrium to the right.
(c) $y_i P = x_i \gamma_i P_i^{sat}$; Checking SSCED, γ^{∞} is very large for DMC, even in pure methanol. Therefore $y_i P = P_i^{sat}$ for DMC. For water and methanol, γ's range from 1 to 3.3 so you would need to know the extent of reaction to get the exact values. Note that the required high pressures would undermine the assumption about CO2 being absent from the liquid phase.

(17.22) Ethyl acetate is to be produced by a liquid phase reaction.

The balanced reaction is
EtOH + HOAc = EtOAc + H2O
First, determine the values at 298.15K for $\Delta G^{o}_{298.15}$ and $\Delta H^{o}_{298.15}$.
$\Delta G^{o}_{298.15}$ = -332.2 – 237.129 + 174.78 + 389.9 = -4.694 kJ/mol
$\ln K_{a,298.15}$ = 4694/8.31447/298.15 = 1.8935
$\Delta H^{o}_{298.15}$ = -480 – 285.83 + 484.5 + 277.69 = -3.64 kJ/mol
At 80C the value K_a will be:
$\ln K_a$ = (3640/8.314) (1/353.15 – 1/298.15) + 1.8935 = 1.6648 → K_a = 5.285
(a) The material balance will be:

	in	out
EtOH	1	1-ξ
HOAc	1	1-ξ
EtOAc	0	ξ
H2O	0	ξ

since the reaction has the same number of moles of products and reactants, n_T is constant, and we can calculate the equilibrium constant using moles in place of mole fractions.
$5.285 = \xi^2/(1-\xi)^2$ → sqrt(5.285) = ξ/(1-ξ) → ξ = sqrt(5.285)/(1+sqrt(5.285)) = 0.697
From the basis of 1 mole of HOAc fed, the conversion is 69.7%.
(b) The material balance will be:

	in	out
EtOH	3	3-ξ
HOAc	1	1-ξ
EtOAc	0	ξ
H2O	0	ξ

$5.285 = \xi^2/(3-\xi)(1-\xi)$→ $5.285(3-\xi)(1-\xi) - \xi^2 = 0$. This could be solved with the quadratic, but using trial and error, (solver tool), ξ = 0.922.
For the basis of 1 mol of HOAc, the conversion is 92.2%, better than (a). The disadvantage is that the conversion of ethanol is lower, ξ/3= 0.307, 30.7%.

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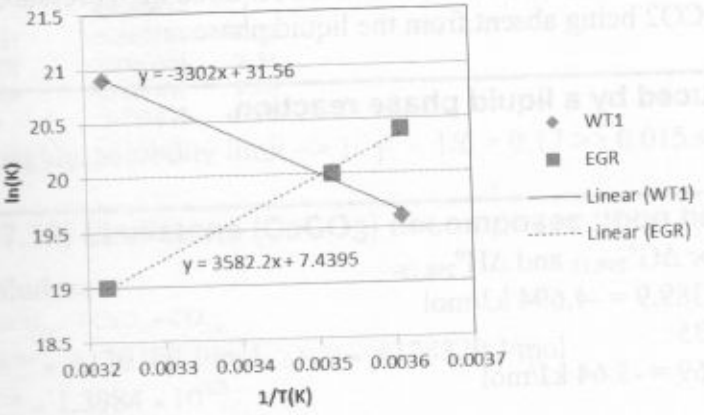
(17.23) Hamilton, et al., have studied the binding of DNA chromosomes …

			lnK		ΔG(J/mol)	
T(C)	T(K)	1/T	WT1	EGR1	WT1	EGR1
4	277.15	0.003608	19.6	20.4	-45162.8	-47006.2
11	284.15	0.003519	20	20	-47248.5	-47248.5
37	310.15	0.003224	20.9	19	-53892.5	-48993.2



$$\ln K = \frac{-\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \text{ and } \frac{\partial \ln K}{\partial (1/T)} = -\frac{\Delta H^o}{R}$$

The binding of the two chromosomes is similar, but the enthalpies are opposite. The slope is ΔH/R and the intercept is ΔS/R. The values are:

	ΔH(J/mol)	ΔS(J/mol-K)
WT1	27452.828	262.3898
EGR1	-29782.4108	61.852

(b) For both systems, the entropy increases with binding, but much more for the WT1. Both binding events have a positive entropy change. A lot of structural changes occur during binding, including changes in water of solvation (or sometimes called water of hydration), so the positive entropy change is common. The energy change for WT1 is unfavorable, but the large entropy increase makes the process favorable.

We can calculate ΔG = -RTlnK, but also we can use the enthalpy and entropy, ΔG = ΔH – TΔS as tabulated below. The values for lnK below are calculated from lnK = -ΔG/RT.

	WT1		EGR1	
T(K)	ΔG(J/mol)	lnK	ΔG(J/mol)	lnK
277.15	-45268.5162	19.64587	-46924.7	20.36463
284.15	-47105.245	19.93938	-47357.7	20.04622
310.15	-53927.3809	20.91354	-48965.8	18.9894

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(17.24) The enthalpy of reaction for many biological reactions and surfactants…

(a) $\Delta H_T^o = \Delta H_R^o + \Delta C_P(T - T_R)$

Inserting into Eqn. 17.26, $\frac{\Delta G_T^o}{RT} = -\int_{T_R}^{T}\left[\frac{\Delta H_R^o + \Delta C_P(T-T_R)}{RT^2}\right]dT + \frac{\Delta G_R^o}{RT_R}$

$$\frac{\Delta G_T^o}{RT} = \frac{\Delta H_R^o}{R}\left(\frac{1}{T}-\frac{1}{T_R}\right) - \frac{\Delta C_P}{R}\ln\left(\frac{T}{T_R}\right) - \frac{\Delta C_P T_R}{R}\left(\frac{1}{T}-\frac{1}{T_R}\right) + \frac{\Delta G_R^o}{RT_R}$$

$$\Delta G_T^o = \Delta H_R^o\left(1-\frac{T}{T_R}\right) - \Delta C_P T\ln\left(\frac{T}{T_R}\right) - \Delta C_P(T_R - T) + \Delta G_R^o\left(\frac{T}{T_R}\right)$$

$$\Delta G_T^o = \frac{-\Delta H_R^o}{T_R}(T-T_R) + \Delta C_P\left[(T-T_R) - T\ln\left(\frac{T}{T_R}\right)\right] + \Delta G_R^o\left(\frac{T}{T_R}\right)$$

(b) since $\Delta G = \Delta H - T\Delta S$, then $\Delta S = (\Delta H - \Delta G)/T$

combining ΔH and ΔG from above,

$$\frac{\Delta H_T^o - \Delta G_T^o}{T} = \frac{\Delta H_R^o}{T} + \frac{\Delta C_P}{T}(T-T_R) + \frac{\Delta H_R^o}{T_R T}(T-T_R) - \frac{\Delta C_P}{T}\left[(T-T_R) - T\ln\left(\frac{T}{T_R}\right)\right] - \Delta G_R^o\left(\frac{1}{T_R}\right)$$

$$\Delta S_T^o = \frac{\Delta H_R^o - \Delta G_R^o}{T_R} + \Delta C_P\ln\left(\frac{T}{T_R}\right) = \Delta S_R^o + \Delta C_P\ln\left(\frac{T}{T_R}\right)$$

(17.25) Lysozyme (MW = 14.313 kDa) undergoes a phase transition…

Errata part (d), US printing 1-3, Int printing 1. Part d, T_R should be T_m.

(c) Show that the relation for $[N]/[U]$ is $\ln\frac{[U]}{[N]} = \frac{-\Delta C_P}{R}\left[\left(1-\frac{T_m}{T}\right) - \ln\left(\frac{T}{T_m}\right)\right] - \left[1-\frac{T_m}{T}\right]\frac{\Delta S_{T_m}}{R}$

where from problem 17.24 $T_R = T_m$. For a solution of overall concentration 1 mg/mL, plot $[U]$ as a function of temperature for $20 \le T \le 110$ °C, and provide a tabular summary of $[U]$ at 60°C and 90°C.

Solution:

(a) At a 'melting temperature' the Gibbs energy change should be zero. Since $\Delta G = \Delta G^o + RT\ln \Pi(a)^{vi} = 0$. Taking the concentration as the activity, then $\Pi(a)^{vi} = c_U/c_N$. Since the concentrations are equal at the melting temperature, then $\Delta G^o = -RT\ln K = 0$.

(b) the concentration is 1mg/L, but 2mL of solution are used, thus 2 mg of protein unfolds, 0.0755J/2mg of protein that unfolds;
$\Delta H_{Tm} = (0.0755\ J/2mg)\ (10^3 mg/g)(14313\ g/mol) = 540.3\ kJ/mol$.
Since $\Delta G_{Tm} = \Delta H_{Tm} - T\Delta S_{Tm} = 0$, $\Delta S_{Tm} = 540.3/(78+273.15) = 1.538\ kJ/mol\text{-}K$.

(c) We can choose T_R. Selecting $T_R = T_m$ is convenient. Then at 23C, for the UNFOLDING, $\Delta H = 540.3\ kJ/mol + 6.3(23 - 78) = 193.8\ kJ/mol$, endothermic. Using the results from 17.24(b), $\Delta S = 1.54 kJ/mol\text{-}K + 6.3\ln(296.15/351.15) = 0.46\ kJ/mol\text{-}K$. Thus for FOLDING, $\Delta H_{folding} = -193.8\ kJ/mol$, $\Delta S = -0.46\ kJ/mol\text{-}K$. The energy contributes to a negative value of ΔG, but the entropy makes it less negative. The folding is driven by energy at 23C.

(d) Starting with the result of 17.24(a), recognizing $\Delta G^o = -RT\ln\Pi(a)^{vi}$ on the LHS. For the RHS, note that $\Delta G_R^o = 0$ when $T_R = T_m$ so the last term drops,

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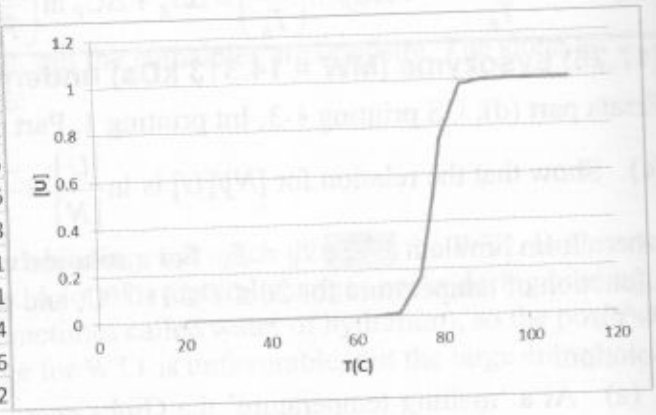
$$-RT\ln([U]/[N]) = \frac{-\Delta H^{o}_{T_m}}{T_{T_m}}(T - T_m) + \Delta C_P\left[(T - T_m) - T\ln\left(\frac{T}{T_m}\right)\right]$$

Noting that $\Delta H_{Tm}/T_m = \Delta S_{Tm}$, then

$$\ln([U]/[N]) = \frac{\Delta S^{o}_{T_m}}{R}\left(1 - \frac{T_m}{T}\right) - \frac{\Delta C_P}{R}\left[\left(1 - \frac{T_m}{T}\right) - \ln\left(\frac{T}{T_m}\right)\right]$$

The equation from (d) will be used to generate [U]/[N]. For a basis of 1 mg/mL, [N] + [U] = 1 mg/mL. [U] = 1-[N], then K = [U]/[N]=(1-[N])/[N], [N] = 1/(1+K).

ΔS	1.5834	kJ/mol-K	Tm(K)	351.15
ΔCp	6.3	kJ/mol-K	R	0.00831447
T(C)	T(K)	K	[N]	[U]
20	293.15	2.17E-11	1	2.17044E-11
25	298.15	8.97E-11	1	8.97242E-11
30	303.15	4.36E-10	1	4.3648E-10
35	308.15	2.47E-09	1	2.47054E-09
40	313.15	1.61E-08	1	1.61005E-08
45	318.15	1.2E-07	1	1.1964E-07
50	323.15	1E-06	0.999999	1.00457E-06
55	328.15	9.45E-06	0.999991	9.45158E-06
60	333.15	9.89E-05	0.999901	9.88613E-05
65	338.15	0.001142	0.99886	0.001140284
70	343.15	0.014451	0.985755	0.014244793
75	348.15	0.199281	0.833833	0.1661672
78	351.15	1	0.5	0.5
80	353.15	2.976398	0.251484	0.748516126
85	358.15	47.8824	0.020457	0.979542738
90	363.15	825.4538	0.00121	0.998790011
95	368.15	15176.05	6.59E-05	0.999934111
100	373.15	296228	3.38E-06	0.999996624
105	378.15	6113237	1.64E-07	0.999999836
110	383.15	1.33E+08	7.53E-09	0.999999992



(e) $\Delta S = \Delta H/T_m$, so $\Delta S = [48.6 + 6.3\,(T_m - 273.15)]/T_m$, where T_m in K.

(f)The same relation from part (d) applies.

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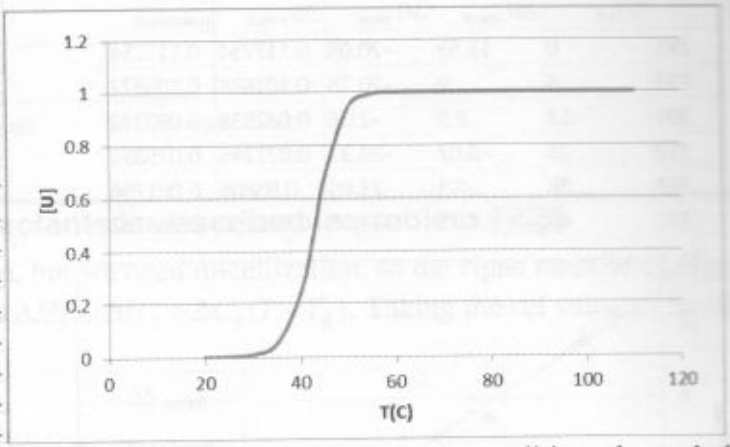
ΔS	1.010596	kJ/mol-K	Tm(K)	316.15
ΔCp	6.3	kJ/mol-K	R	0.008314

T(C)	T(K)	K	[N]	[U]
20	293.15	0.000663	0.999338	0.000662
25	298.15	0.002453	0.997553	0.002447
30	303.15	0.010728	0.989386	0.010614
35	308.15	0.054776	0.948069	0.051931
40	313.15	0.323073	0.755816	0.244184
43	316.15	1	0.5	0.5
45	318.15	2.179551	0.31451	0.68549
50	323.15	16.66478	0.05661	0.94339
55	328.15	143.184	0.006936	0.993064
60	333.15	1371.532	0.000729	0.999271
65	338.15	14538.74	6.88E-05	0.999931
70	343.15	169382.7	5.9E-06	0.999994
75	348.15	2154998	4.64E-07	1
80	353.15	29761946	3.36E-08	1
85	358.15	4.44E+08	2.25E-09	1
90	363.15	7.1E+09	1.41E-10	1
95	368.15	1.22E+11	8.23E-12	1
100	373.15	2.21E+12	4.52E-13	1
105	378.15	4.26E+13	2.35E-14	1
110	383.15	8.67E+14	1.15E-15	1



(g) when $T_m = 23$, $\Delta H_{unfold} = 193$ kJ/mol, and $\Delta S_{unfold} = 0.653$. At this condition, the enthalpy is positive, and discourages unfolding. The entropy is positive and favors unfolding. The energy will still favor folding, but the entropy now favors unfolding.

(h) There is a lot that happens when the protein unfolds. It is unlikely that there are voids before or after folding. There must be a change in the water of hydration. Forming hydrogen bonds tends to lead to a volume increase, so there must be breaking of hydrogen bonds. This is also consistent with the endothermic unfolding.

The effect of pressure on Gibbs energy is $\left(\partial G/\partial P\right)_T = V$. If the relation applies to both the folded state and unfolded state, then $\left(\partial(\Delta G_{unfold})/\partial P\right)_T = \Delta V_{unfold}$. Assuming that the volume change is independent of pressure, $\Delta G_{p2} = \Delta G_{p1} + \Delta V(P_2\text{-}P_1)$ at the same T. If the melting temperature is 73, when $\Delta G_{p2} = 0$, then $\Delta G_{p1} = -\Delta V(P\text{-}P_R)$, or $P = P_R - \Delta G_{P1}/\Delta V$. Using the equation from 17.24(a), where $T_R = T_m$, and $\Delta G_R^\circ = 0$, T =

$\Delta G_{P1} = -(540.3/351.15)(-5)+6.3[(-5) - 346.15\ln(346.15/351.15)] = 7.468$ kJ/mol

$P = 0.1 + (7468\text{ J/mol})/(40\text{ cm}^3\text{/mol}) = 186.8$ MPa.

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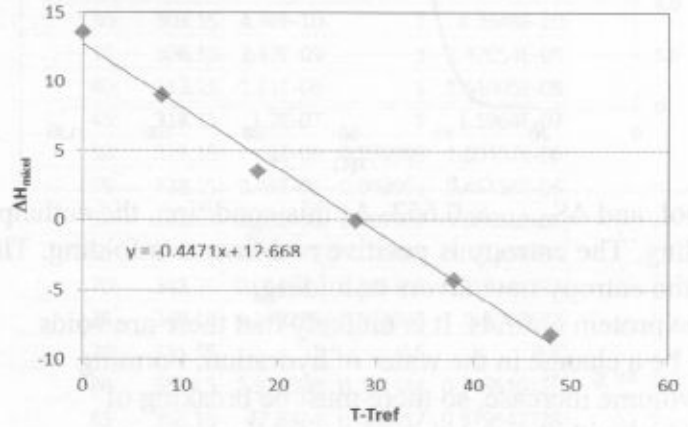
(17.26) Surfactants clump together to form organized structures…

(a) note the table is for demicellization, but we need micellization, so the signs must be changed. The heat of formation will be fitted to $\Delta H_T^o = \Delta H_R^o + \Delta C_P(T - T_R)$. Taking the ref value as the first in the table,

T	$T-T_{ref}$	ΔH_{micell}	ΔG_{micell}	ΔS_{micell}	ΔS_{micell} (calculated)
285	0	13.53	-20.03	0.117754	0.117754
293	8	9	-20.78	0.101638	0.105377
303	18	3.5	-21.6	0.082838	0.090372
313	28	-0.07	-22.37	0.071246	0.075855
323	38	-4.3	-23.05	0.05805	0.061794
333	48	-8.25	-23.62	0.046156	0.048162



From the slope, ΔCp = -447.1 J/mol-K. The heat capacity of the micelle is less than the heat capacity before formation. Thus hydrogen bonds were broken when the micelle forms.

(b) The entropy of formation is calculated from $\Delta S_T^o = \dfrac{\Delta H_T^o - \Delta G_T^o}{T}$ and tabulated above. The entropy of formation above is positive, thus the entropy is greater after forming the micelle than before. This is consistent with breaking hydrogen bonds. Since the heat capacity is $(\partial S/\partial T)_P = C_P$, then $(\partial \Delta S/\partial T)_P = \Delta C_P$, and $\Delta S = \Delta S_R + \Delta C_P \ln(T/T_R)$. we should be able to use a ref temperature of 285 as before and plot ΔS_{micell}. The calculations are tabulated in the last column of the table in (a) and a plot is shown below with the data. The value of ΔCp by fitting the heat capacity is consistent.

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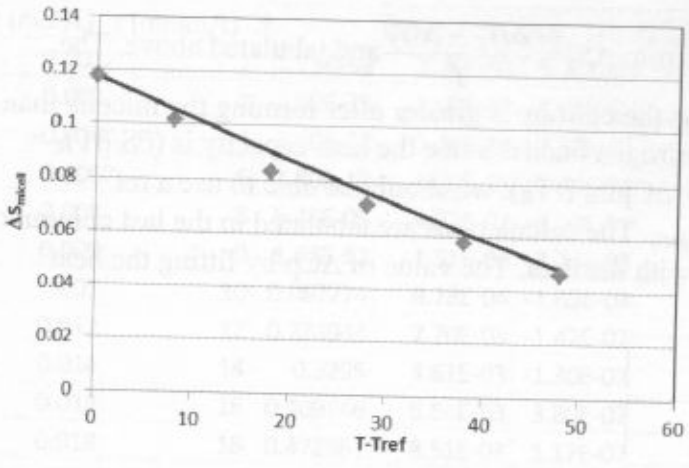
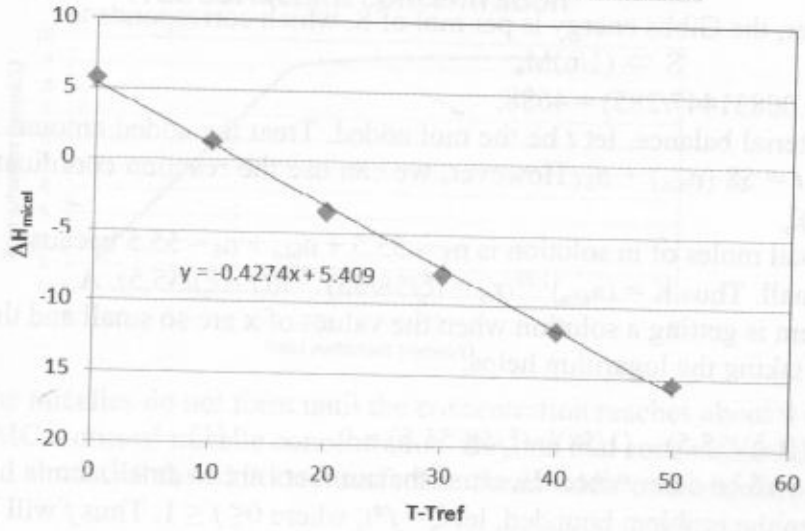


(17.27) Micelle formation in surfactants is described in problem 17.26

(a) note the table is for demicellization, but we need micellization, so the signs must be changed. The heat of formation will be fitted to $\Delta H_T^o = \Delta H_R^o + \Delta C_P(T - T_R)$. Taking the ref value as the first in the table,

T	$T-T_{ref}$	ΔH_{micell}	ΔG_{micell}	ΔS_{micell}	ΔS_{micell} (calculated)
283	0	5.74	-36.18	0.148127	0.148127
293	10	1.29	-37.64	0.132867	0.133285
303	20	-3.53	-38.64	0.115875	0.118942
313	30	-7.92	-39.8	0.101853	0.105064
323	40	-11.78	-40.76	0.089721	0.091623
333	50	-15.46	-41.63	0.078589	0.078591



From the slope, ΔCp = -427.4 J/mol-K. The heat capacity of the micelle is less than the heat capacity before formation. Thus hydrogen bonds were broken when the micelle forms.

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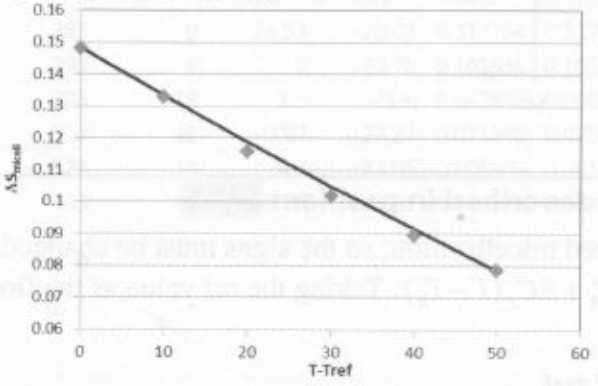
(b) The entropy of formation is calculated from $\Delta S_T^o = \frac{\Delta H_T^o - \Delta G_T^o}{T}$ and tabulated above. The entropy of formation above is positive, thus the entropy is greater after forming the micelle than before. This is consistent with breaking hydrogen bonds. Since the heat capacity is $(\partial S/\partial T)_P = C_P$, then $(\partial \Delta S/\partial T)_P = \Delta C_P$, and $\Delta S = \Delta S_R + \Delta C p \ln(T/T_R)$. we should be able to use a ref temperature of 285 as before and plot ΔS_{micell}. The calculations are tabulated in the last column of the table in (a) and a plot is shown below with the data. The value of ΔCp by fitting the heat capacity is consistent.



(17.28) For nonylglucoside, NG, thermodynamic data for demicellization...

Errata, US printing 1-3, International printing 1. An additional hint is necessary to match the data with the given reaction. Newer printings will append this hint:

Also, the thermodynamic data are per mol of surfactant, thus model the reaction written as $S \Leftrightarrow (1/n)M_n$.

Solution:

The reaction is $nS = M_n$. However, the Gibbs energy is per mol of S, which corresponds to

$$S \Leftrightarrow (1/n)M_n$$

$K = \exp(-\Delta G/RT) = \exp(20.03/0.00831447/285) = 4688.$

$K = (x_{Mn})^{1/58}/x_S$. Writing the material balance, let t be the mol added. Treat the added amount as $S_o = t$. The material balance is: $t = 58\ (n_{Mn}) + n_S$. However, we can use the reaction coordinate. Then $n_S = t - \xi$, and $n_{Mn} = (1/58)\xi$.

For a basis of 1L solution, the total moles of in solution is $n_T = 55.5 + n_{Mn} + n_S \sim 55.5$ because the amount of surfactant is so small. Thus $K = (x_{Mn})^{1/58}/x_S = (\xi/58/55)^{1/58}/((t - \xi)/55.5)$. A challenging aspect of this problem is getting a solution when the values of x are so small and the powers are so large. Solving by taking the logarithm helps.

$K((t - \xi)/55.5) = \xi/58/55.5$ or

$$\text{obj} = \ln K + \ln((t-\xi)/55.5) - (1/58)\ln(\xi/58/55.5) = 0. \qquad (1)$$

For each value of t, a value of ξ will be determined. Because the numbers are so small, the maximum value of $\xi = t$. To keep the problem bounded, let $\xi = f^*t$, where $0 \le f \le 1$. Thus f will be the iteration variable for each value of t to solve Eqn (1). Hint: it is easiest to start with the largest value of t. The smallest values require modification of the default convergence criteria, or manual guessing (manual guessing was used here). The concentrations will be $C(S) = (t - \xi)1000$ mmol/L. $C(M) = (\xi/58)1000$ mmol/L.

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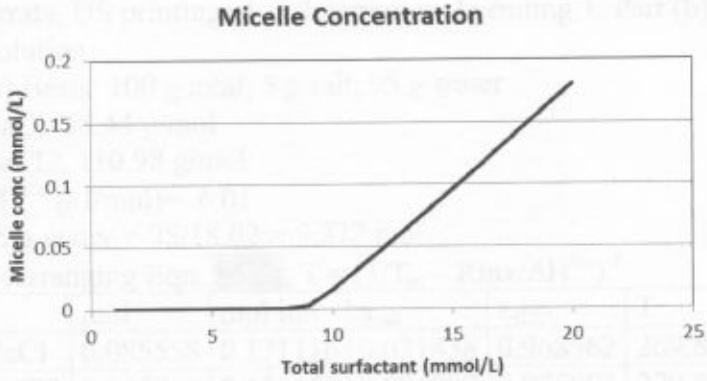
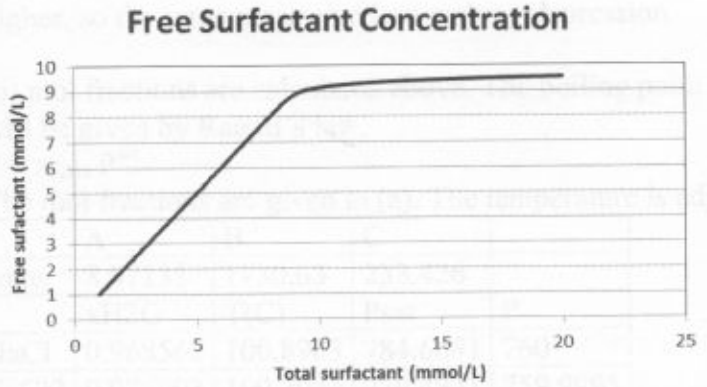
t (mol/L)	t (mmol/L)	f	ξ	obj	C(S) mmol/L	C(M) mmol/L
0.001	1	1.75E-56	1.75E-59	5.72E-04	1.00E+00	3.02E-58
0.002	2	1.00E-39	2.00E-42	1.65E-02	2.00E+00	3.45E-41
0.004	4	3.60E-22	1.44E-24	7.37E-04	4.00E+00	2.48E-23
0.006	6	1.00E-12	6.00E-15	2.43E-02	6.00E+00	1.03E-13
0.008	8	5.40E-05	4.32E-07	-9.20E-07	8.00E+00	7.45E-06
0.009	9	1.67E-02	1.51E-04	-3.74E-08	8.85E+00	2.60E-03
0.01	10	0.087774	8.78E-04	-1.65E-08	9.12E+00	1.51E-02
0.012	12	0.224944	2.70E-03	-1.42E-07	9.30E+00	4.65E-02
0.014	14	0.3295	4.61E-03	-1.30E-07	9.39E+00	7.95E-02
0.016	16	0.409746	6.56E-03	3.80E-07	9.44E+00	1.13E-01
0.018	18	0.472961	8.51E-03	1.17E-07	9.49E+00	1.47E-01
0.02	20	0.523963	1.05E-02	-6.18E-09	9.52E+00	1.81E-01





The micelles do not form until the concentration reaches about 9 mmol/L. This is known as the CMC – critical micelle concentration. Beyond that concentration, the free surfactant is constant and almost all the additional surfactant forms additional micelles.

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