6.2 (a) General: $\theta = \sum N_i \bar{\theta}_i$ where $\bar{\theta}_i = (\partial \theta / \partial N_i)_{T,P,N_{j\neq i}}$ and

$$d\theta = \sum \bar{\theta}_i dN_i + \sum N_i d\bar{\theta}_i \tag{1}$$

However, we also have that

$$d\theta = \left(\frac{\partial \theta}{\partial T}\right)_{V,\underline{N}} dT + \left(\frac{\partial \theta}{\partial V}\right)_{T,\underline{N}} dV + \sum \left(\frac{\partial \theta}{\partial N_i}\right)_{T,V,N_{j\neq i}} dN_i \tag{2}$$

Subtracting (2) from (1) yields

$$0 = -\left(\frac{\partial \theta}{\partial T}\right)_{V,\underline{N}} dT - \left(\frac{\partial \theta}{\partial V}\right)_{T,\underline{N}} dV + \sum \left[\bar{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right] dN_i + \sum N_i d\bar{\theta}_i$$

At constant T and V

$$0 = \sum \left[\bar{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{T,V,\underline{N}}\right] dN_i + \sum N_i d\bar{\theta}_i$$

(general equation)

For $\theta = A$, $\bar{\theta}_i = \bar{A}_i$ and $\left(\frac{\partial \theta}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \bar{G}_i$. Thus,

$\bar{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \bar{A}_i - \bar{G}_i = -P\bar{V}_i$ and

$$\sum N_i d\bar{A}_i\Big|_{T,V} = P \sum \bar{V}_i dN_i\Big|_{T,V} \text{ specific equation for } \theta = A$$

(b) Following the analysis above, we also get

$$0 = -\left(\frac{\partial \theta}{\partial U}\right)_{V,\underline{N}} dU - \left(\frac{\partial \theta}{\partial V}\right)_{U,\underline{N}} dV + \sum \left[\overline{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{U,V,N_{j\neq i}}\right] dN_i + \sum N_i d\overline{\theta}_i$$

and, at constant U and V

$$0 = \sum \left[\overline{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{U,V,N_{j\neq i}}\right] dN_i + \sum N_i d\overline{\theta}_i$$

Now, choosing $\theta = S$, and using that $\left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} = -\frac{\overline{G}_i}{T}$, which is easily derived, yields

$$-T \sum N_i d\overline{S}_i\Big|_{U,V} = \sum \overline{H}_i dN_i\Big|_{U,V}$$

(c) Following a similar analysis to those above, we obtain

$$0 = -\left(\frac{\partial \theta}{\partial S}\right)_{V,\underline{N}} dS - \left(\frac{\partial \theta}{\partial V}\right)_{S,\underline{N}} dV + \sum \left[\overline{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{S,V,N_{j\neq i}}\right] dN_i + \sum N_i d\overline{\theta}_i$$

which, at constant V and S, reduces to

$$0 = \sum \left[\overline{\theta}_i - \left(\frac{\partial \theta}{\partial N_i}\right)_{S,V,N_{j\neq i}}\right] dN_i + \sum N_i d\overline{\theta}_i$$

Finally, using $\theta = U$, and $(\partial U/\partial N_i)_{S,V,N_{j\neq i}} = \overline{G}_i$ yields

$$\sum N_i d\overline{U}_i\Big|_{S,V} = \sum \{-P\overline{V}_i + T\overline{S}_i\} dN_i\Big|_{S,V}$$

6.3 (a) At constant U and V, $S =$ maximum at equilibrium

$$S = S^{\mathrm{I}} + S^{\mathrm{II}} = \sum_{i=1}^{C} N_i^{\mathrm{I}} \overline{S}_i^{\mathrm{I}} + \sum_{i=1}^{C} N_i^{\mathrm{II}} \overline{S}_i^{\mathrm{II}}$$

but

$$dS = 0 = \left(\frac{\partial S^{\mathrm{I}}}{\partial U^{\mathrm{I}}}\right)_{V,\underline{N}} dU^{\mathrm{I}} + \left(\frac{\partial S^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{U,\underline{N}} dV^{\mathrm{I}} + \sum \left(\frac{\partial S^{\mathrm{I}}}{\partial N_i^{\mathrm{I}}}\right)_{U,V,N_{j\neq i}} dN_i^{\mathrm{I}}$$
$$+ \left(\frac{\partial S^{\mathrm{II}}}{\partial U^{\mathrm{II}}}\right)_{V,\underline{N}} dU^{\mathrm{II}} + \left(\frac{\partial S^{\mathrm{II}}}{\partial V^{\mathrm{II}}}\right)_{U,\underline{N}} dV^{\mathrm{II}} + \sum \left(\frac{\partial S^{\mathrm{II}}}{\partial N_i^{\mathrm{II}}}\right)_{U,V,N_{j\neq i}} dN_i^{\mathrm{II}}$$

Since $U = U^{\mathrm{I}} + U^{\mathrm{II}} =$ constant, $dU^{\mathrm{II}} = -dU^{\mathrm{I}}$

Since $V = V^{\mathrm{I}} + V^{\mathrm{II}} = \text{ constant},\ dV^{\mathrm{II}} = -dV^{\mathrm{I}}$
and since $N_i = N_i^{\mathrm{I}} + N_i^{\mathrm{II}} = \text{ constant},\ dN_i^{\mathrm{II}} = -dN_i^{\mathrm{I}}$
Also,

$$\left(\frac{\partial S}{\partial U}\right)_{V,\underline{N}} = \frac{1}{T};\ \left(\frac{\partial S}{\partial V}\right)_{U,\underline{N}} = \frac{P}{T} \text{ and } \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} = -\frac{\overline{G}_i}{T}$$

(see previous problem)

Thus

$$dS = 0 = \left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T^{\mathrm{II}}}\right)dU^{\mathrm{I}} + \left(\frac{P^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{P^{\mathrm{II}}}{T^{\mathrm{II}}}\right)dV^{\mathrm{I}} - \sum_i \left(\frac{\overline{G}_1^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{\overline{G}_1^{\mathrm{II}}}{T^{\mathrm{II}}}\right)dN_i^{\mathrm{I}}$$

$$\Rightarrow T^{\mathrm{I}} = T^{\mathrm{II}};\ P^{\mathrm{I}} = P^{\mathrm{II}};\ \text{and } \overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}}$$

for equilibrium in a closed system at constant U and V.

(b) For a closed system at constant S and V, U has an extremum. Thus

$$dU = 0 = \left(\frac{\partial U^{\mathrm{I}}}{\partial S^{\mathrm{I}}}\right)_{V,\underline{N}} dS^{\mathrm{I}} + \left(\frac{\partial U^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{S,\underline{N}} dV^{\mathrm{I}} + \sum_i \left(\frac{\partial U^{\mathrm{I}}}{\partial N_i^{\mathrm{I}}}\right)_{S,V,N_{j\neq i}} dN_i^{\mathrm{I}}$$
$$+ \left(\frac{\partial U^{\mathrm{II}}}{\partial S^{\mathrm{II}}}\right)_{V,\underline{N}} dS^{\mathrm{II}} + \left(\frac{\partial U^{\mathrm{II}}}{\partial V^{\mathrm{II}}}\right)_{S,\underline{N}} dV^{\mathrm{II}} + \sum_i \left(\frac{\partial U^{\mathrm{II}}}{\partial N_i^{\mathrm{II}}}\right)_{U,V,N_{j\neq i}} dN_i^{\mathrm{II}}$$

but S, V and N_j, $j = 1, \cdots, C$ are constant. Thus

$$dU = 0 = \left(T^{\mathrm{I}} - T^{\mathrm{II}}\right)dS^{\mathrm{I}} + \left(P^{\mathrm{I}} - P^{\mathrm{II}}\right)dV^{\mathrm{I}} + \sum_i \left(\overline{G}_i^{\mathrm{I}} - \overline{G}_i^{\mathrm{II}}\right)dN_i^{\mathrm{I}}$$

$$\Rightarrow T^{\mathrm{I}} = T^{\mathrm{II}},\ P^{\mathrm{I}} = P^{\mathrm{II}} \text{ and } \overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}}$$

for equilibrium in a closed system at constant S and V.

6.4 (a) For a closed system at constant T and V, A is a minimum at equilibrium; thus $dA\big|_{V,\,T} = 0$. From Eqn. (6.2-5)

$$dA = -PdV - SdT + \sum \overline{G}_i dN_i \text{ or } dA\big|_{V,T} = \sum \overline{G}_i dN_i$$

But, $N_i = N_{i,\,0} + \nu_i X$. Thus $dN_i = \nu_i dX$ and

$$dA\big|_{V,T} = \left(\sum \nu_i \overline{G}_i\right)dX = 0 \text{ or } \left(\frac{\partial A}{\partial X}\right)_{V,T} = \sum_i \nu_i \overline{G}_i = 0.$$

(b) For a closed system at constant U and V, $S =$ maximum, or $dS\big|_{U,V} = 0$. From Eqn. (6.2-4) $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum \overline{G}_i dN_i$; thus

$$dS\big|_{U,V} = -\frac{1}{T}\sum \overline{G}_i dN_i \quad \text{or} \quad dS\big|_{U,V} = -\frac{1}{T}\left(\sum \overline{G}_i \nu_i\right) dX$$

and

$$\left.\frac{\partial S}{\partial X}\right|_{U,V} = -\frac{1}{T}\sum_i \nu_i \overline{G}_i = 0$$

6.5 Let m_i = molecular weight of species i. Multiplying Eqn. (6.3-2a) by m_i and summing over all species i yields, for a *closed* system

$$\sum m_i N_i = \text{total mass in system} = \underbrace{\sum m_i N_{i,0}}_{\substack{\text{total mass in} \\ \text{system initially}}} + X\sum \nu_i m_i$$

However, since the total mass is a conserved quantity,

$$\sum m_i N_i = \sum m_i N_{i,0} \Rightarrow X\sum \nu_i m_i = 0 \text{ , where } X \text{ can take on any value.}$$

Consequently, if this equation is to be satisfied for all values of X, then $\sum \nu_i m_i = 0$!

Similarly, in the multi-reaction case, starting from $N_i = N_{i,0} + \sum_{j=1}^{M} \nu_{ij} X_j$, we get

$$\sum_{i=1}^{C} m_i N_i = \sum_{i=1}^{C} m_i N_{i,o} + \sum_{i=1}^{C} m_i \sum_{j=1}^{M} \nu_{ij} X_j \Rightarrow \sum_{i=1}^{C} m_i \sum_{j=1}^{M} \nu_{ij} X_j = 0 = \sum_{j=1}^{M} X_j \sum_{i=1}^{C} \nu_{ij} m_i$$

Since the X_j's are not, in general, equal to zero, we have

$$\sum_{i=1}^{C} \nu_{ij} m_i = 0$$

In particular, for the reaction $H_2O = H_2 + (1/2)O_2$, or $H_2 + (1/2)O_2 - H_2O = 0$, we have

$$\sum_i \nu_{ij} m_i = (+1)(2) + \left(\frac{1}{2}\right)(32) + (-1)(18) = 0 .$$

6.6 From Eqns. (6.6-4) we have

$$\overline{V}_1 = \underline{V}_1 + \Delta\underline{V}_{\text{mix}} + x_2 \left.\frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1}\right|_{T,P} \tag{1}$$

and

$$\overline{V}_2 = \underline{V}_2 + \Delta\underline{V}_{\text{mix}} + x_1 \left.\frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1}\right|_{T,P} \tag{2}$$

Now since T, P and X, are the independent variables, we have that

$$d\overline{V}_1\big|_{T,P} = d\underline{V}_1\big|_{T,P} + d(\Delta\underline{V}_{\text{mix}})\big|_{T,P} + d\left[x_2 \frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1}\right]_{T,P}$$

(0 since pure component volume is a function of T and P only)

$$= \left.\frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1}\right|_{T,P} + \left.\frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1}\right|_{T,P} \frac{\partial x_2}{\partial x_1} dx_1 + x_2 \left.\frac{\partial^2(\Delta\underline{V}_{\text{mix}})}{\partial x_1^2}\right|_{T,P} dx_1$$

$$= x_2 \left.\frac{\partial^2(\Delta\underline{V}_{\text{mix}})}{\partial x_1^2}\right|_{T,P} dx_1 \quad \text{since} \quad \frac{\partial x_2}{\partial x_1} = -1$$

Similarly

$$d\overline{V}_2\big|_{T,P} = -x_1 \left.\frac{\partial^2(\Delta\underline{V}_{\text{mix}})}{\partial x_1^2}\right|_{T,P} dx_1$$

Thus

$$\sum x_i d\overline{V}_i\big|_{T,P} = x_1 x_2 \left.\frac{\partial^2(\Delta\underline{V}_{\text{mix}})}{\partial x_1^2}\right|_{T,P} dx_1 - x_2 x_1 \left.\frac{\partial^2(\Delta\underline{V}_{\text{mix}})}{\partial x_1^2}\right|_{T,P} dx_1 \equiv 0$$

Thus, $\overline{V}_1$ and $\overline{V}_2$ given by equations (1) and (2) identically satisfy the Gibbs-Duhem equation $\sum x_i d\overline{q}_i\big|_{T,P} = 0$.

A similar argument applies for the partial molar enthalpies of Eqn. (6.6-9).

6.7 (also available as a Mathcad worksheet)

The students can solve this problem by drawing tangent lines to the $\Delta\underline{V}_{\text{mix}}$ curves. Polak and Lu smoothed their data using the Redhich-Kister equation (see Eqn. (6.6-5a)). That is, they fitted their data to

$$\Delta\underline{V}_{\text{mix}} = x_1 x_2 \sum_{j=1}^{n} C_j (x_2 - x_1)^{j-1} = x_1(1-x_1)\sum C_j (1-2x)^{j-1}$$

Now

$$\frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1} = (1-x_1)\sum C_j (1-2x_1)^{j-1}$$

$$-x_1 \sum C_j (1-2x_1)^{j-1} - 2x_1(1-x_1)\sum C_j (j-1)(1-2x_1)^{j-2}$$

Thus $$\overline{V}_1 - \overline{V}_1 = (\Delta\underline{V}_{\text{mix}}) - x_2 \frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1} = (1-x_1)^2\{A - 2x_1 B\} \tag{1}$$

and

$$\overline{V}_2 - \underline{V}_2 = (\Delta \underline{V}_{\text{mix}}) - x_1 \frac{\P(\Delta \underline{V}_{\text{mix}})}{\P x_1} = x_1^2\{A + 2x_2 B\} \qquad (2)$$

where

$$A = \sum_{j=1}^{n} C_j (1-2x_1)^{j-1} \text{ and } B = \sum_{j=1}^{n} C_j (j-1)(1-2x_1)^{j-2}$$

Taking species 1 to be methyl formate, Polak and Lu found

	C_1	C_2	C_3	C_4
methyl formate - Methanol	−0.33259	−0.10154	−0.0516	0.0264
methyl formate - Ethanol	0.81374	−0.00786	0.0846	0.0448

[units are cc/mol; multiply by 10^{-3} to get m^3/kmol]

I have used the equations above and the constants given to find $\overline{V}_1 - \underline{V}_1$ and $\overline{V}_2 - \overline{V}_2$, since this leads to more accurate results than the graphical method.
The results are tabulated and plotted below.
Methyl formate - Methanol

	x_{MF}	0	0.1	0.2	0.3	0.4	0.5
$\Delta \underline{V}_{\text{mix}}$	(cc/mol)	0	–0.039	–0.065	–0.080	–0.085	–0.083
$\overline{V}_1 - \underline{V}_1$		–0.459	–0.329	–0.225	–0.148	–0.093	–0.058
$\overline{V}_2 - \underline{V}_2$		0	–0.007	–0.025	–0.051	–0.080	–0.109

	x_{MF}	0.6	0.7	0.8	0.9	1.0
$\Delta \underline{V}_{\text{mix}}$	(cc/mol)	–0.075	–0.063	–0.047	–0.027	0
$\overline{V}_1 - \underline{V}_1$		–0.035	–0.021	–0.011	–0.004	0
$\overline{V}_2 - \underline{V}_2$		–0.136	–0.162	–0.192	–0.236	–0.309

Thus $\overline{V}_{\text{MF}} = 62.78 + (\overline{V}_1 - \underline{V}_1)$ cc/mol or 10^{-3} m^3/kmol.
$\overline{V}_{\text{M}} = 40.73 + (\overline{V}_2 - \underline{V}_2)$.

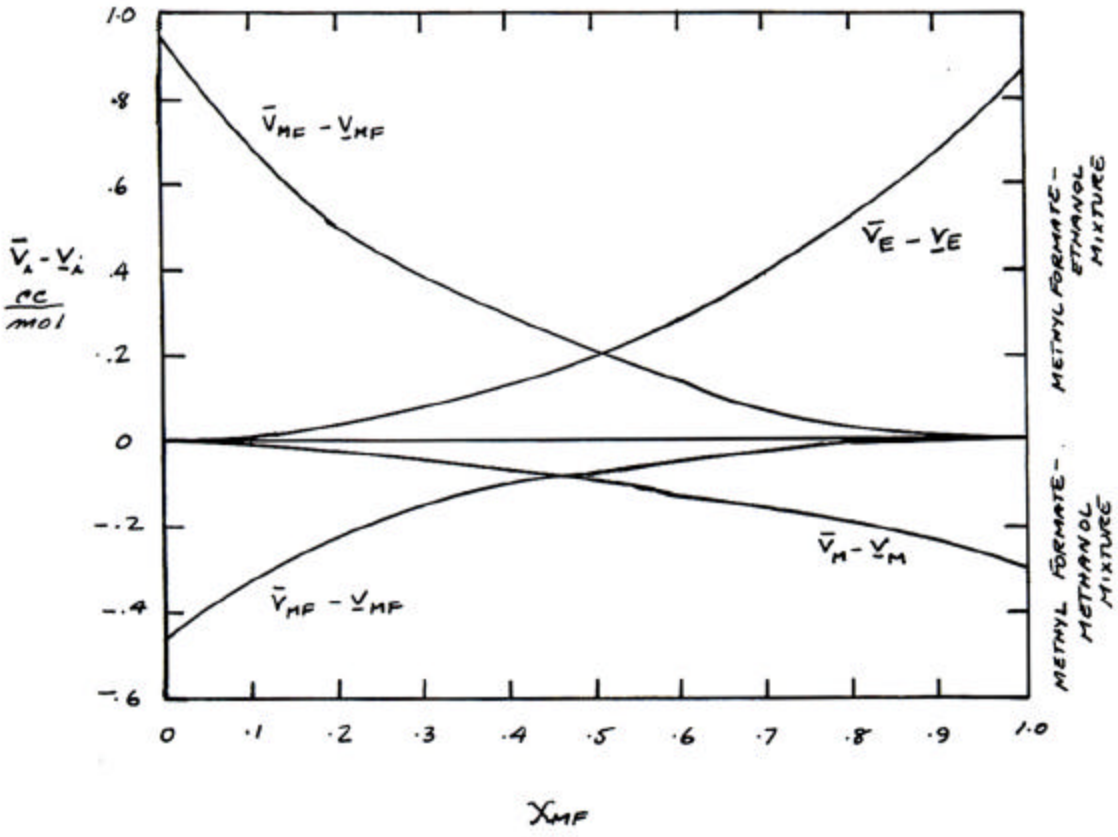
Methyl formate - Ethanol

	x_{MF}	0	0.1	0.2	0.3	0.4	0.5
$\Delta \underline{V}_{\text{mix}}$	(cc/mol)	0	0.080	0.136	0.174	0.196	0.203
$\overline{V}_1 - \underline{V}_1$		0.935	0.682	0.507	0.381	0.285	0.205
$\overline{V}_2 - \underline{V}_2$		0	0.013	0.043	0.085	0.137	0.201

	x_{MF}	0.6	0.7	0.8	0.9	1.0
$\Delta \underline{V}_{\text{mix}}$	(cc/mol)	0.196	0.174	0.134	0.077	0
$\overline{V}_1 - \underline{V}_1$		0.138	0.081	0.037	0.010	0
$\overline{V}_2 - \underline{V}_2$		0.284	0.390	0.522	0.680	0.861

Thus $\overline{V}_{\mathrm{MF}} = 62.78 + (\overline{V}_1 - \underline{V}_1)$ cc/mol. Multiply by 10^{-3} for $\mathrm{m}^3/\mathrm{kmol}$.

$\overline{V}_{\mathrm{E}} = 58.68 + (\overline{V}_2 - \underline{V}_2)$



6.8 This problem is similar to the last one, and will be treated in a similar fashion. Fenby and Ruenkrairergasa give their data in the form

$$\Delta \underline{H}_{\mathrm{mix}}(\mathrm{J/mol}) = x_2(1-x_2)\sum_{j=1}^{n} C_j(1-2x_2)^{j-1} \qquad (1)$$

where component 2 is the fluorobenzene. The constants given in the aforementioned reference and Fenby and Scott *J. Phys. Chem* **71**, 4103 (1967) are given below

System	C_1	C_2	C_3	C_4
$C_6H_6 - C_6F_5Cl$	–2683	929	970	0
$C_6H_6 - C_6F_5Br$	–3087	356	696	0
$C_6H_6 - C_6F_5I$	–4322	–161	324	0
$C_6H_6 - C_6F_6$	–1984	+1483	+1169	0
$C_6H_6 - C_6F_5H$	230	+578	+409	+168

If we replace x_2 with $1-x_1$ in Eqn. (1), we regain the equation of the previous illustration, except for a factor of $(-1)^{j-1}$ in the sum and the corresponding places in the other equations.

$x_{C_6H_6}$	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})_{C_6H_6}$	$(\overline{H}-\underline{H})_{C_6F_5Cl}$	$x_{C_6F_5Cl}$
0	0	–2642	0	1.0
0.1	–252	–2171	–39.2	0.9
0.2	–463	–1790	–130	0.8
0.3	–609	–1466	–242	0.7
0.4	–679	–1175	–349	0.6
0.5	–671	–903	–439	0.5
0.6	–590	–646	–506	0.4
0.7	–453	–409	–555	0.3
0.8	–284	–205	–601	0.2
0.9	–119	–57.8	–666	0.1
1.0	0	0	–784	0

[Note: J/mol]

	$C_6H_6-C_6F_5Br$			$C_6H_6-C_6F_5I$			
$x_{C_6H_6}$	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})$ C_6H_6	$(\overline{H}-\underline{H})$ C_6F_5Br	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})$ C_6H_6	$(\overline{H}-\underline{H})$ C_6F_5I	$x_{C_6F_5x}$
0	0	–2747	0	0	–3837	0	1.0
0.1	–263	–2248	–42.9	–359	–3119	–52.1	0.9
0.2	–488	–1829	–153	–657	–2489	–200	0.8
0.3	–654	–1469	–306	–883	–1937	–431	0.7
0.4	–751	–1149	–486	–1026	–1456	–740	0.6
0.5	–772	–861	–683	–1081	–1040	–1121	0.5
0.6	–717	–600	–893	–1042	–689	–1572	0.4
0.7	–595	–370	–1120	–910	–402	–2095	0.3
0.8	–420	–181	–1374	–688	–187	–2695	0.2
0.9	–212	–50.0	–1671	–382	–48.9	–3379	0.1
1.0	0	0	–2035	0	0	–4159	0

	$C_6H_6 - C_6F_6$			$C_6H_6 - C_6F_5H$			
$x_{C_6H_6}$	$\Delta \underline{H}_{mix}$	$(\overline{H} - \underline{H})$ C_6H_6	$(\overline{H} - \underline{H})$ C_6F_6	$\Delta \underline{H}_{mix}$	$(\overline{H} - \underline{H})$ C_6H_6	$(\overline{H} - \underline{H})$ C_6F_5H	$x_{C_6F_5}x$
0	0	–2298	0	0	61.0	0	1.0
0.1	–218	–1899	–31.2	–2.2	36.2	–1.1	0.9
0.2	–392	–1590	–93.0	–3.9	–2.8	+6.8	0.8
0.3	–502	–1332	–146	13.5	–42.3	+37.4	0.7
0.4	–536	–1097	–162	31.4	–72.3	+100	0.6
0.5	–496	–867	–125	57.5	–87.0	+202	0.5
0.6	–394	–637	–28.9	86.9	–84.5	344	0.4
0.7	–253	–413	+121	110	–66.7	524	0.3
0.8	–108	–212	+308	116	–39.4	+737	0.2
0.9	–4.5	–60.9	+503	85.9	–12.6	+973	0.1
1.0	0	0	+688	0	0	1217	0
			↑		↑	↑	

Note: Changes in sign in column

Relations among the unknowns $T^S = T^V$, $P^S = P^V$, no phase equilibrium relations, but 3 chemical equilibrium relations of the form $\sum \nu_{ij} \overline{G}_i = 0$.

$$8 \text{ unknowns} - 5 \text{ eqns.} = 3 \text{ unspecified unknowns or}$$
$$3 \text{ degrees of freedom}$$

6.10 (a) In general, for a binary, two-phase mixture $(C = 2,\ M = 0,\ P = 2)$
$F = C - M - P + 2 = 2 - 0 - 2 + 2 = 2$ degrees of freedom.
However, for an azeotrope there is the additional restriction $x_1 = y_1$, which eliminates one degree of freedom. Thus, there is only 1 degree of freedom for a binary, azeotropic system.

(b) In osmotic equilibrium $P^{\text{I}} \neq P^{\text{II}}$, since the membrane is capable of supporting a pressure difference, and $\overline{G}_2^{\text{I}} \neq \overline{G}_2^{\text{II}}$, where 2 is the species which does not pass through the membrane. Therefore, the independent unknowns are T^{I}, P^{I}, x_1^{I}, T^{II}, P^{II} and x_1^{II}. [Note, x_2^{I} and x_2^{II} are not independent unknowns since $x_2^{\text{I}} = 1 - x_1^{\text{I}}$ and $x_2^{\text{II}} = 1 - x_1^{\text{II}}$]. There are *two* equilibrium relations between these six unknowns: viz. $T^{\text{I}} = T^{\text{II}}$ and $\overline{G}_1^{\text{I}} = \overline{G}_1^{\text{II}}$. Consequently, there are four degrees of freedom … that is, as we shall see in Sec. 8.7, if T, P^{I}, P^{II} and x_1^{I} are specified, x_1^{II} will be fixed.

(c) Case I: $M = 0,\ C = 2,\ P = 2 \Rightarrow F = 2 - 0 - 2 + 2 = 2$
Case II: $M = 0,\ C = 2,\ P = 3 \Rightarrow F = 2 - 0 - 3 + 2 = 1$

6.11 (a) Gibbs Phase Rule: $F = C - M - P + 2$
$C = 2,\ M = 0 \Rightarrow F = 2 - 0 - P + 2 = 4 - P$ degrees of freedom.
Therefore, a maximum of 4 phases can exist at equilibrium (for example a solid, two liquids and a vapor, or two solids, a liquid and a vapor, etc.)

(b) Gibbs Phase Rule: $F = C - M - P + 2$
$C = 2,\ M = 1 \Rightarrow F = 2 - 1 - P + 2 = 3 - P$ degrees of freedom.
Therefore, a maximum of e phases can exist at equilibrium (for example a two liquids and a vapor, or a solid, a liquid and a vapor, etc.)

6.12 (a)
$$\frac{dN_i}{dt} = \dot{N}_i + \dot{N}_{i,\text{rxn}}$$
$$\frac{dU}{dt} = \sum \dot{N}_i \overline{H}_i + \dot{Q} - \cancel{\dot{W}_s}^{\,0} - P\frac{dV}{dt}$$
$$\frac{dS}{dt} = \sum \dot{N}_i \overline{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$$
$$T\frac{dS}{dt} - T\sum \dot{N}_i \overline{S}_i - T\dot{S}_{\text{gen}} = \dot{Q}$$

$$\frac{dU}{dt} = \sum \dot{N}_i \overline{H}_i + T\frac{dS}{dt} - T\sum \dot{N}_i \overline{S}_i - T\dot{S}_{\text{gen}} - P\frac{dV}{dt}$$

$$\frac{dU}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} = \sum \dot{N}_i\left(\overline{H}_i - T\overline{S}_i\right) - T\dot{S}_{\text{gen}}$$

$$\frac{dU}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} = \sum \dot{N}_i \overline{m}_i - T\dot{S}_{\text{gen}} = \sum\left(\frac{dN_i}{dt} - \boldsymbol{n}_i\frac{dX}{dt}\right)\overline{m}_i - T\dot{S}_{\text{gen}}$$

General expression

Now

System is only permeable to species 1

$$\frac{dU}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} - \left(\frac{dN_1}{dt} - \boldsymbol{n}_1\frac{dX}{dt}\right)\boldsymbol{m}_1 = -T\dot{S}_{\text{gen}} \le 0$$

When T and P constant

$$\frac{d}{dt}(U + PV - TS) - \frac{d}{dt}\left[(N_1 - \boldsymbol{n}_1 X)\boldsymbol{m}_1\right] \le 0$$

$$\frac{d}{dt}\left[G - (N_1 - \boldsymbol{n}_1 X)\boldsymbol{m}_1\right] \le 0$$

$\Rightarrow G - (N_1 - \boldsymbol{n}_1 X)\boldsymbol{m}_1 =$ minimum at equilibrium

(b) When T and V are constant

$$\frac{d}{dt}(U - TS) - \frac{d}{dt}\left[(N_1 - \boldsymbol{n}_1 X)\boldsymbol{m}_1\right] \le 0$$

$\Rightarrow A - (N_1 - \boldsymbol{n}_1 X)\boldsymbol{m}_1 =$ minimum at equilibrium

6.13 (a)

$2\text{N} \rightarrow \text{N}_2$

$2\text{O} \rightarrow \text{O}_2$

$2\text{N} + \text{O} \rightarrow \text{N}_2\text{O}$	$\text{N}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{N}_2\text{O}$
$2\text{N} + 2\text{O} \rightarrow 2\text{NO}$	$\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$
$2\text{N} + 4\text{O} \rightarrow \text{N}_2\text{O}_4$	$\text{N}_2 + 2\text{O}_2 \rightarrow \text{N}_2\text{O}_4$
$2\text{N} + 4\text{O} \rightarrow 2\text{NO}_2$	$\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$
$2\text{N} + 5\text{O} \rightarrow \text{N}_2\text{O}_5$	$\text{N}_2 + \frac{5}{2}\text{O}_2 \rightarrow \text{N}_2\text{O}_5$

$\Rightarrow 5$ independent reactions

(b) $F = C - M - P + 2 = 7 - 5 - 1 + 2 = 9 - 6 = 3$

$F = 3$ degrees of freedom

(c) 1 degree of freedom used in O_2:N_2 ratio $\Rightarrow$ 2 degres of freedom

6.14 Mass balance: $M_1 + M_2 = M_f$ Molecular weight $\text{H}_2\text{O} = 18.02$ g/mol

Energy balance: $M_1\hat{U}_1 + M_2\hat{U}_2 = M_f\hat{U}_f$

In each case the system is M_1 kg of solution 1 + M_2 kg of solution 2.

Since $Q = 0$, $W_s = 0$ (adiabatic mixing)

For liquids $\hat{U} \equiv \hat{H}$. Thus we have

$$\hat{H}_f = \frac{M_1\hat{H}_1 + M_2\hat{H}_2}{M_1 + M_2}$$

when $M_1 = M_2$; $\hat{H}_f = \frac{1}{2}\left(\hat{H}_1 + \hat{H}_2\right)$.

(a) Read from Figure 6.1-1

$$\hat{H}_1 = 6.9 \times 10^3 \text{ J/kg}$$
$$\hat{H}_2 = -6.1 \times 10^3 \text{ J/kg}$$

Thus $\hat{H}_f = \frac{1}{2}\left(5.410 \times 10^4\right) = 2.705 \times 10^4$ J/kg

To find the composition, so a sulfuric acid balance

$$\boldsymbol{r}_1 M_1 + \boldsymbol{r}_2 M_2 = \boldsymbol{r}_f M_f \Rightarrow \boldsymbol{r}_f = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2) \text{ since } M_1 = M_2$$

where $\boldsymbol{r}_i$ = weight percent of *i*th flow stream.

Thus $\boldsymbol{r}_f = \frac{1}{2}(10 + 90) = 50$ wt % sulfuric acid. From Figure 6.1-1

$$\begin{matrix} 50 \text{ wt \% } H_2SO_4 \\ \hat{H} = \hat{U} = 2.705 \times 10^4 \text{ J/kg} \end{matrix} \Rightarrow T_f \sim 110^\circ \text{C}$$

(b) Here $\hat{H}_1 = 6.9 \times 10^3$ J/kg,

$\hat{H}_2 = -3.186 \times 10^5$ J/kg $\Rightarrow \hat{H}_f = \frac{1}{2}(6.9 - 318.6) \times 10^3 = -1.56 \times 10^5$ J/kg and $\boldsymbol{r}_1 = 10$ wt %, $\boldsymbol{r}_2 = 60$ wt % $\Rightarrow \boldsymbol{r}_f = 35$ wt %. Using Figure 6.1-1, $T_f \sim 22^\circ \text{C}$.

Notice that there is a balance between the energy released in mixing, $\Delta\hat{H}_{\text{mix}}$, and the energy absorbed in heating the mixture, $C_{\text{P}}\Delta T$. In case (a), $\Delta\hat{H}_{\text{mix}}$ is very large, and $T_f > T_1$ or T_2, while in case (b) $\Delta\hat{H}_{\text{mix}}$ is smaller, so that $T_f \sim T_1$.

6.15 (a) MW $H_2O = 18.02$ g/mol; MW $H_2SO_4 = 98.08$ g/mol

$$100 \text{ g } H_2O = 5.55 \text{ mol}$$
$$100 \text{ g } H_2SO_4 = 1.02 \text{ mol}$$

Note: When these are mixed, a solution containing 5.44 mol H_2O /mol acid is formed. $\Delta\underline{H}_s$ for such a solution is –58,390 J/mol acid. Thus,

$$\text{total heat released} = 1.02 \text{ mol acid} \times (-58{,}390 \text{ J/mol acid}) = -59{,}558 \text{ J}$$

(Negative sign means that heat is released!)

(b) Adding another 100 grams of water produces a solution which contains 10.88 mol H_2O /mol acid. From the graph $\Delta\underline{H}_s = -64{,}850$ J/mol acid. However, –58,390 J/mol of acid were released in preparing the first solution, so that only –6,460 J/mol acid, or 6,590 J, are released on this further dilution.

(c) 60 wt % $H_2SO_4 \Rightarrow \dfrac{40/18.02}{60/98.08} = 3.629$ moles H_2O/moles acid for which $\Delta\underline{H}_s = -52{,}300$ J/mol acid, and

$$\Delta H_s = -52{,}300 \text{ J/mol acid} \times \frac{60 \text{ mol acid}}{98.08} = -31{,}990 \text{ J}$$

Note: Enthalpy of 60 WT% solution is –31,990 J relative to pure components at the same temperature. Similarly 25 wt % $H_2SO_4 \Rightarrow 16.27$ mol H_2O/mol acid, $\Delta\underline{H}_s \sim -68{,}830$ J/mol acid and

$$\Delta H_s = -68{,}830 \text{ J/mol acid} \times \frac{0.25 \times 75}{98.08} = -13{,}160 \text{ J}$$

Final solution $= 175$ grams; 78.75 grams acid $= 0.803$ mol,
96.25 grams water $= 5.347$ mol $\Rightarrow 6.66$ mol H_2O/mol acid. So that

$$\Delta\underline{H}_s = -60{,}670 \text{ J/mol acid}$$
$$\Delta H_s = -48{,}720 \text{ J}$$

Thus, enthalpy change on mixing, ΔH_{mix} is

$$\Delta H_{mix} = -48{,}720 - (-31{,}990 - 13{,}160) = -3570 \text{ J}$$

Thus, $3570 \text{ J} = 357$ kJ must be *removed* to keep solution isothermal!

(d) For 1 mole of solute: $(1+N_2)\underline{H}_{mix} = \underline{H}_1 + N_2\underline{H}_2 + 1\cdot\Delta\underline{H}_s\left(\dfrac{N_2}{N_1}\right)$ (argument of $\Delta\underline{H}_s$) and for N_1 moles of solute and N_2 moles of solvent.

$$(N_1+N_2)\underline{H}_{mix} = N_1\underline{H}_1 + N_2\underline{H}_2 + N_1\Delta\underline{H}_s\left(\frac{N_2}{N_1}\right) = H_{mix}$$

Now

$$\overline{H}_1 = \left(\frac{\partial H_{mix}}{\partial N_1}\right)_{T,P} = \underline{H}_1 + \Delta\underline{H}_s\left(\frac{N_2}{N_1}\right) + N_1\left.\frac{\partial(\Delta\underline{H}_s)}{\partial(N_2/N_1)}\right|_{T,P}\cdot\left.\frac{\partial(N_2/N_1)}{\partial N_1}\right|_{T,P}$$

or

$$\overline{H}_1 - \underline{H}_1 = \Delta\underline{H}_s\left(\frac{N_2}{N_1}\right) - \frac{N_2}{N_1}\left[\frac{\partial\Delta\underline{H}_s(N_2/N_1)}{\partial(N_2/N_1)}\right]_{T,P} \quad \text{since} \quad \frac{\partial(N_2/N_1)}{\partial N_1} = -\frac{N_2}{N_1^2}$$

Similarly, starting from $\overline{H}_2 = \left(\dfrac{\partial H_{mix}}{\partial N_2}\right)_{T,P}$ we obtain

$$\overline{H}_2 - \underline{H}_2 = \left.\frac{\partial\Delta\underline{H}_s(N_2/N_1)}{\partial(N_2/N_1)}\right|_{T,P}$$

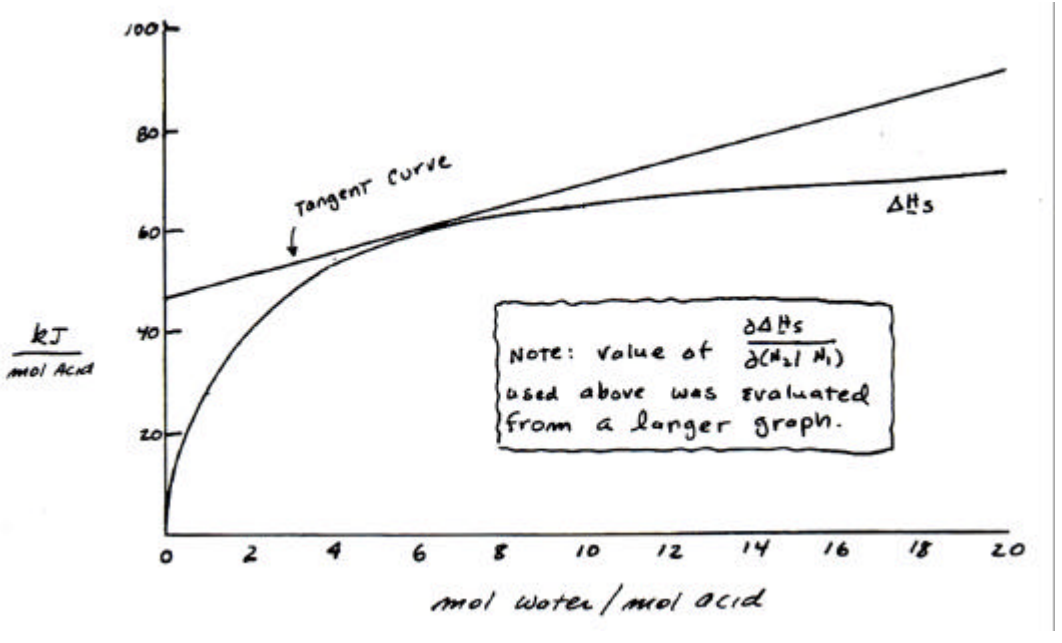
(e) 50 wt % acid $\Rightarrow \dfrac{50/18.02}{50/98.08} = 5.443$ mol H_2O/mol acid

$\Delta\underline{H}_s(5.443) = -58{,}370$ J/mol and, from the accompanying graph

$$\left.\frac{\partial\Delta\underline{H}_s(N_2/N_1)}{\partial(N_2/N_1)}\right|_{\text{at } N_2/N_1=5.443} = \frac{(-91{,}630)-(-46{,}030)}{20} = -2{,}280 \text{ J/mol}$$

so that $\overline{H}_2 - \underline{H}_2 = -2{,}280$ J/mol and

$$\overline{H}_1 - \underline{H}_1 = (-58{,}370) - 5.44(-2{,}280) = -45{,}967 \text{ J/mol}.$$



6.20 Note: Sorry about 1 set of data being given in alcohol wt% and other in water mole %, but this is the way the data appeared in the International Critical Tables.

(a) First will convert the data to mole fractions.

$$\text{wt\% A} = \frac{\text{kg A} \times 100}{\text{kg A} + \text{kg W}}; \; x_{\text{A}} = \frac{\text{kg A}/\text{MW}_{\text{A}}}{\text{kg A}/\text{MW}_{\text{A}} + \text{kg W}/\text{MW}_{\text{W}}}$$

$$\Rightarrow x_{\text{A}} = \frac{\text{wt\% A}}{\text{wt\% A} + (100 - \text{wt\% A})\,\text{MW}_{\text{A}}/\text{MW}_{\text{W}}}$$

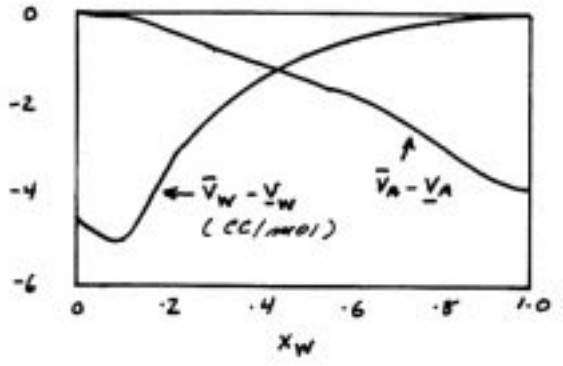
Also, $\underline{V}_{\text{mix}} = \overline{\text{MW}}/\rho_{\text{mix}}$ where $\rho_{\text{mix}} =$ mixture density and $\overline{\text{MW}}$ is the mole fraction averaged molecular weight of mixture (i.e., $\overline{\text{MW}} = \sum x_i \overline{\text{MW}_i}$)

Also, $\underline{V}_{\text{A}} = \text{MW}_{\text{A}}/\rho(100 \text{ wt\% alcohol})$ and

$\underline{V}_{\text{W}} = \text{MW}_{\text{W}}/\rho(0\% \text{ alcohol})$.

wt% alcohol	x_A	$\overline{MW}$	$\underline{V}_{mix} - \sum x_i \underline{V}_i$	$\Delta\underline{V}_{mix}$ (cc/mol) [multiply by 10^{-3} for $m^3/kmol$]
0	0	18	18.083–18.033	0
5	0.0202	18.566	18.765–18.846	–0.081
10	0.0417	19.168	19.521–19.711	–0.190
15	0.0464	19.809	20.315–20.633	–0.318
20	0.0891	20.495	21.159–21.690	–0.531
25	0.1151	21.231	22.077–22.678	–0.601
30	0.1436	22.021	23.088–23.813	–0.725
35	0.1740	22.872	24.091–25.036	–0.945
40	0.2069	22.793	25.442–26.360	–0.918
45	0.2425	24.790	26.809–27.793	–0.984
50	0.2813	25.876	28.317–29.355	–1.038
55	0.3235	27.058	29.978–31.053	–1.075
60	0.3699	28.357	31.823–32.920	–1.097
65	0.4209	29.785	33.865–34.973	–1.108
70	0.4773	31.364	36.147–37.243	–1.096
75	0.5440	33.120	38.710–39.766	–1.056
80	0.6102	35.038	41.600–42.592	–0.992
85	0.6892	37.298	44.883–45.771	–0.888
90	0.7788	39.806	48.663–49.377	–0.714
95	0.8814	42.679	53.070–53.507	–0.437
100	1.0	46.	58.280–52.280	0

The $\Delta\underline{V}_{mix}$ data are plotted, and the graphical procedure of Sec. 6.6 used to find $(\overline{V}_A - \underline{V}_A)$ and $(\overline{V}_W - \underline{V}_W)$. Results are given in the following table.



Next note that

$$\Delta \underline{H}_{\text{mix}}\begin{pmatrix}\text{per mole}\\ \text{mixture}\end{pmatrix} = \begin{matrix}\text{Heat evolved}\\ \text{per mole ethanol}\end{matrix} \times \begin{matrix}\text{Mole fraction}\\ \text{of ethanol}\end{matrix} \times \underset{\substack{\text{Since heat is}\\ \text{evolved, } \Delta \underline{H}_{\text{mix}}\\ \text{is negative.}}}{(-1)}$$

Once $\Delta \underline{H}_{\text{mix}}$ is computed, graphical procedure is used to get $\left(\overline{H}_{\text{A}} - \underline{H}_{\text{A}}\right)$ and $\left(\overline{H}_{\text{W}} - \underline{H}_{\text{W}}\right)$. Table below gives $\left(\overline{V}_{\text{A}} - \underline{V}_{\text{A}}\right)$, $\left(\overline{V}_{\text{W}} - \underline{V}_{\text{W}}\right)$, $\left(\overline{H}_{\text{A}} - \underline{H}_{\text{A}}\right)$ and $\left(\overline{H}_{\text{W}} - \underline{H}_{\text{W}}\right)$ as a function of the water mole fraction.

x_{W}	$\overline{V}_{\text{W}} - \underline{V}_{\text{W}}$	$\overline{V}_{\text{A}} - \underline{V}_{\text{A}}$	$\Delta \underline{H}_{\text{mix}}$	$\overline{H}_{\text{W}} - \underline{H}_{\text{W}}$	$\overline{H}_{\text{A}} - \underline{H}_{\text{A}}$
	cc/mol			kJ/mol	
0	–4.5	0	0.	–0.85	0
0.05			–0.0400	–0.099	+0.015
0.1	–5.0	–0.05	–0.0828	–1.15	+0.039
0.15			–0.142		
0.2	–3.43	–0.42	–0.201	–1.13	+0.038
0.25			–0.251		
0.3	–2.5	–0.78	–0.296	–0.85	–0.055
0.35			–0.337		
0.4	–1.22	–1.04	–0.382	–0.88	–0.03
0.45			–0.416		
0.5	–0.82	–1.37	–0.473	–1.02	+0.087
0.55			–0.541		
0.6	–0.58	–1.67	–0.603	–1.13	+0.183
0.65			–0.674		
0.7	–0.42	–2.0	–0.743	–1.175	+0.388
0.75			–0.805		
0.8	–0.17	–2.86	–0.854	–1.02	–0.26
0.85			–0.873	–0.79	–1.36
0.9	–0.025	–3.50	–0.780	–0.30	–5.0
0.95			–0.491		
1.0	0	–3.88	0. ↑	0.	? ↑