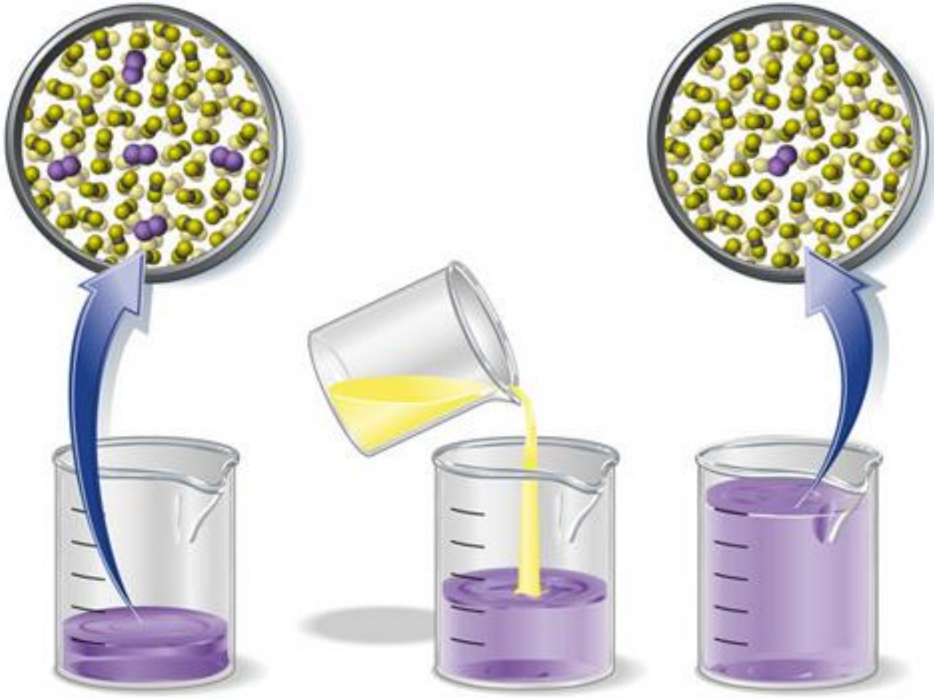
MME 2010
METALLURGICAL THERMODYNAMİCS II

Mixing of solutions and the associated heat effects



$$\frac{0.0050 \text{ mol } I_2}{0.10 \text{ L solution}} = 0.050 \text{ M } I_2$$

$$\frac{0.0050 \text{ mol } I_2}{0.50 \text{ L solution}} = 0.010 \text{ M } I_2$$

Molecular basis for mixture behavior

The relations between excess properties and property changes of mixing enables discussion of the molecular phenomena which give rise to observed excess property behavior

$$G^E = \Delta G - RT\sum x_i \ln x_i$$

$$S^E = \Delta S + R\sum x_i \ln x_i$$

$$H^E = \Delta H$$

$$V^E = \Delta V$$

Excess enthalpy which equals enthalpy of mixing, reflects differences in the strengths of intermolecular attraction between pairs of unlike species and pairs of like species.

Interactions between like species are disrupted in a standard mixing process and interactions between unlike species are promoted

More energy (ΔH) is required in the mixing process to break like attractions if the unlike attractions are weaker than the average of those between like species

In this case mixing is endothermic, $\Delta H = H^E > 0$

$\Delta H = H^E < 0$ if the unlike attractions are stronger and mixing process is exothermic

Observations made from Abbott’s analysis of NP/NP binary mixtures:

- Dispersion forces are the only significant attractive intermolecular forces for NP/NP mixtures
- Dispersion forces between unlike species are weaker than the average of dispersion forces between like species. Hence a positive excess enthalpy is usually observed for NP/NP mixtures

Property changes of mixing have common features:

- Each ΔM is zero for a pure species
- The Gibbs energy change of mixing ΔG is always negative
- The entropy change of mixing ΔS>0

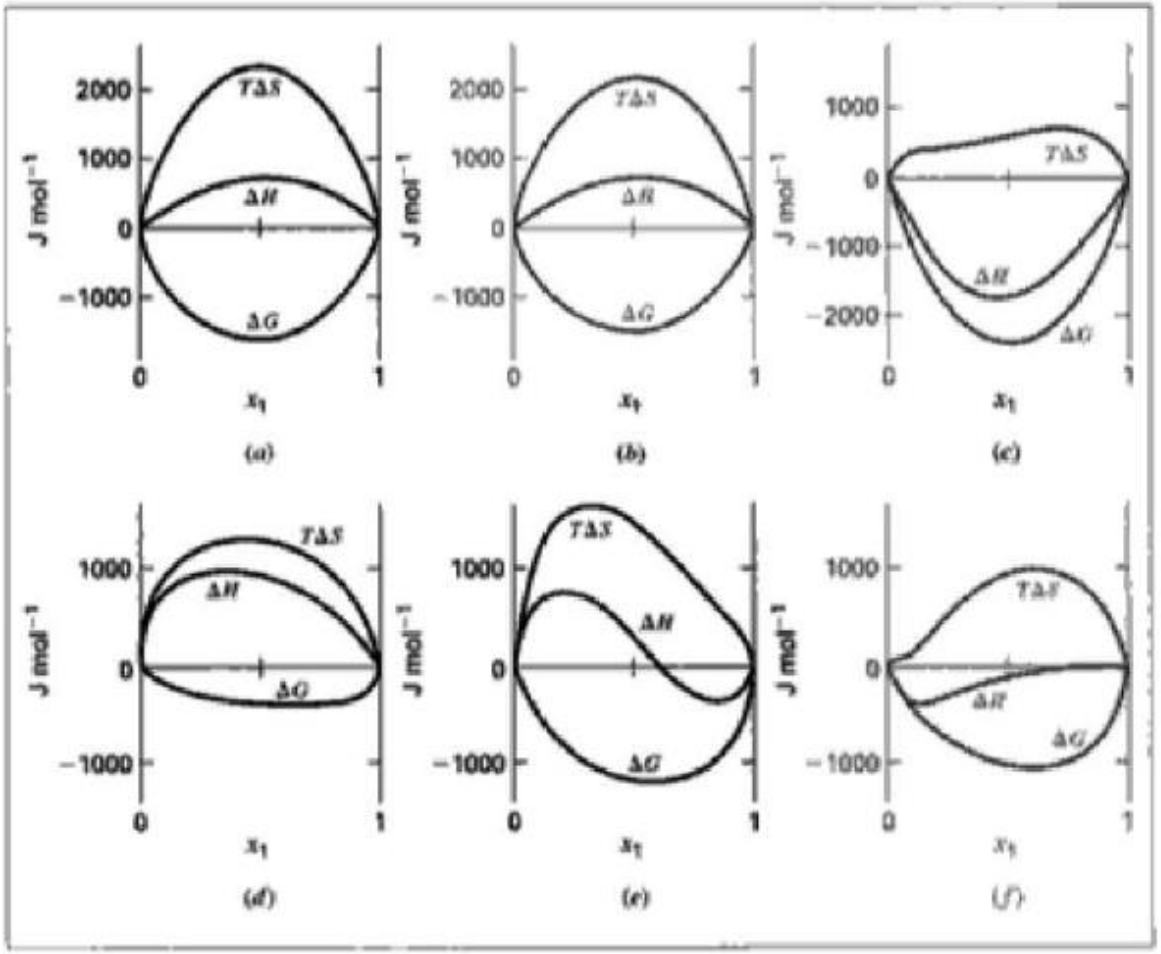


Figure 12.13: Property changes of mixing at 50°C for six binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

Effect of mixing in ideal solutions

Remember that the difference between the total molar property of ideal solution and pure molar properties of its components gives the effect of mixing

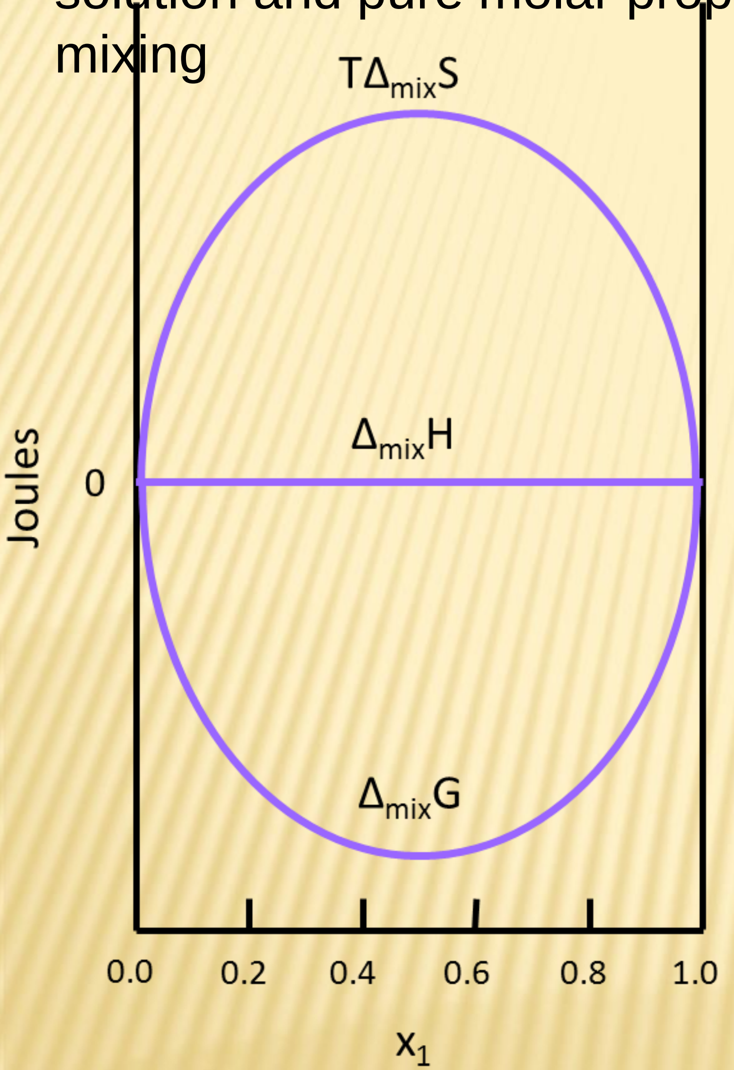


Figure 2. A graph of $T\Delta_{mix}S$, $\Delta_{mix}H$, and $\Delta_{mix}G$ as functions of x_1 for the mixing of two ideal gases.

$$M - \sum y_i M_i = change\ of\ M\ by\ mixing$$

$$H^{id} - \sum x_i H^{id}{}_i = 0$$

$$S^{id} - \sum x_i S^{id}{}_i = R \sum x_i \ln \frac{1}{x_i}$$

$$G^{id} - \sum x_i G^{id}{}_i = RT \sum x_i \ln x_i$$

In real solutions, activities of solution components relate the solution behavior to the equations derived for ideal gases and solutions:

$$a_i = \gamma_{\ i} x_i$$

The activity of pure and condensed phases is 1

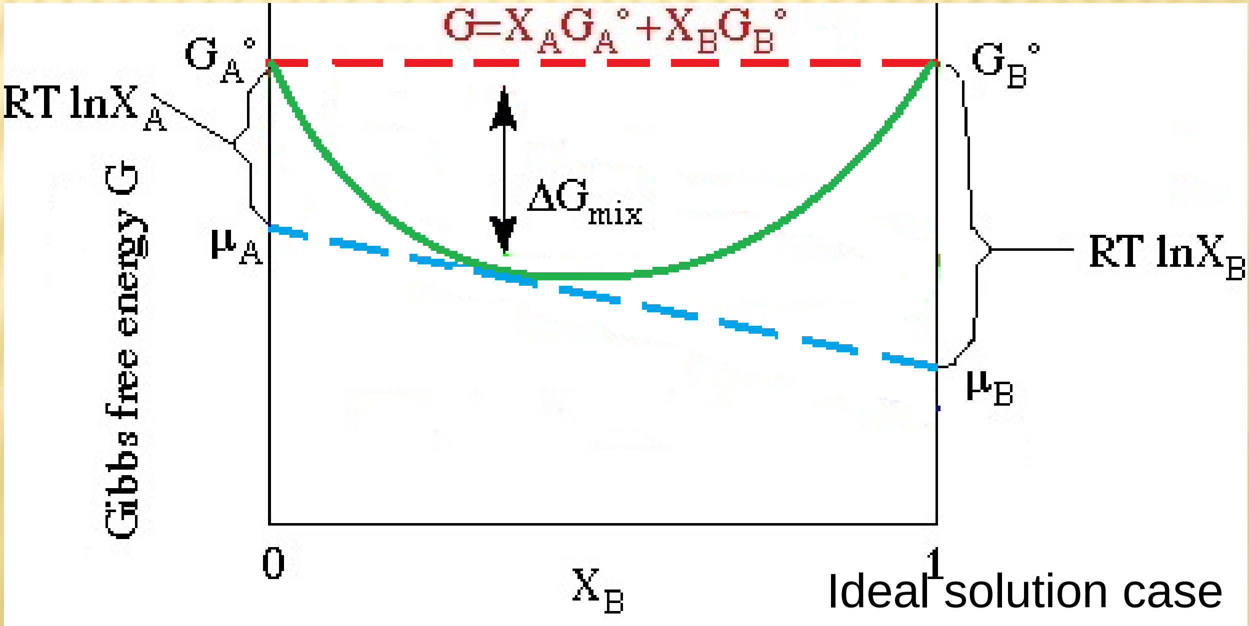
$$G_A{}^o = RT\ln a_A = 0$$

$$\overline{G}_A = RT\ln a_A$$

$$\overline{G}_A - G_A{}^o = \Delta\overline{G_A} = RT\ln a_A$$

$$\Delta G \quad = x_A\,(\overline{G}_A - G_A{}^o) + x_B(\overline{G}_B - G_B{}^o)$$

$$\Delta G \quad = x_A RT\ln a_A + x_B RT\ln a_B$$



Ideal solution case

Effect of mixing in real solutions

Similar to ideal solutions, entropy of mixing in real solutions is positive due to the irreversibility of the process

Gibbs free energy is again negative and proportional in quantity to the entropy change

Unlike ideal solutions, enthalpy of mixing is a finite value due to the difference between partial molar enthalpy and enthalpy of pure components

$$\Delta G \quad = \Delta H \quad - T\Delta S$$

$$\Delta G \quad = x_A\,(\overline{G}_A - G_A{}^o) + x_B(\overline{G}_B - G_B{}^o)$$

$$\Delta G \quad = x_A RT \ln a_A + x_B RT \ln a_B$$

$$\Delta S \quad = x_A\,(\overline{S}_A - S_A{}^o) + x_B(\overline{S}_B - S_B{}^o)$$

$$\Delta S \quad = x_A R \ln \frac{1}{a_A} + x_B R \ln \frac{1}{a_B}$$

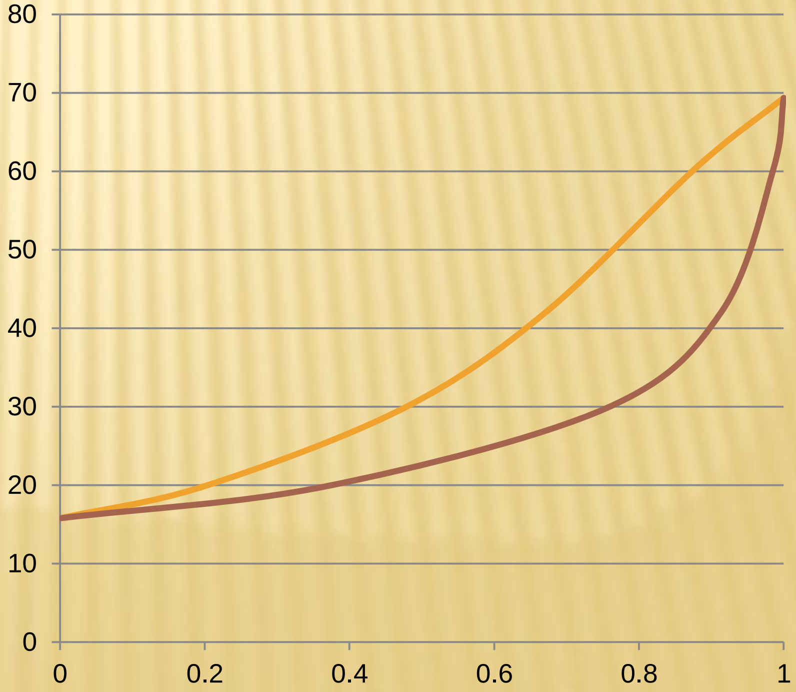
$$\Delta H \quad = x_A\,(\overline{H}_A - H_A{}^o) + x_B(\overline{H}_B - H_B{}^o)$$

Example - For the binary system of chloroform/dioxane at 50 C, the following vapor-liquid equilibrium data are given:

P kPa	x_1	y_1
15.79	0.000	0.000
19.89	0.200	0.369
29.82	0.475	0.755
42.10	0.672	0.914
60.38	0.878	0.986
69.36	1.000	1.000

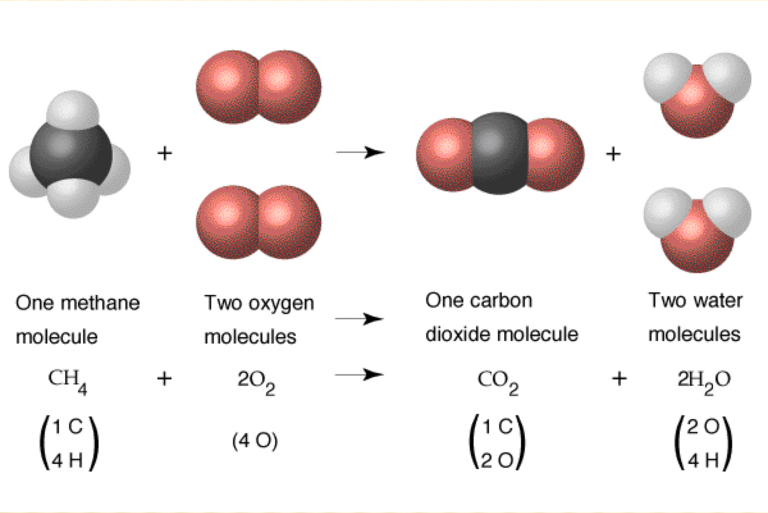
Determine the activity for both components for a mixture concentration of X_1= 0.48

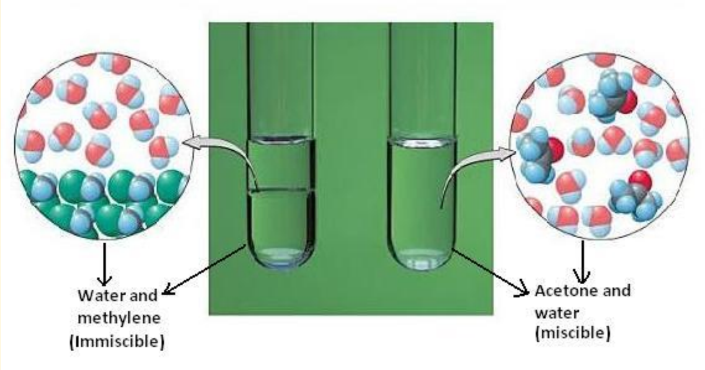
Find the Gibbs free energy of mixing, entropy of mixing and enthalpy of mixing if the total enthalpy of the mixture is represented as $H= x_1(20 + 50\, x_1) + x_2\, (30 + 40\, x_2)$



Heat effects of mixing processes

When a chemical reaction occurs, the energy of the products is different from the energy of the reactants at the same temperature and pressure because of the chemical rearrangement of the constituent atoms





A similar energy change occurs when a mixture is formed because interactions between the force fields of like and unlike molecules are different

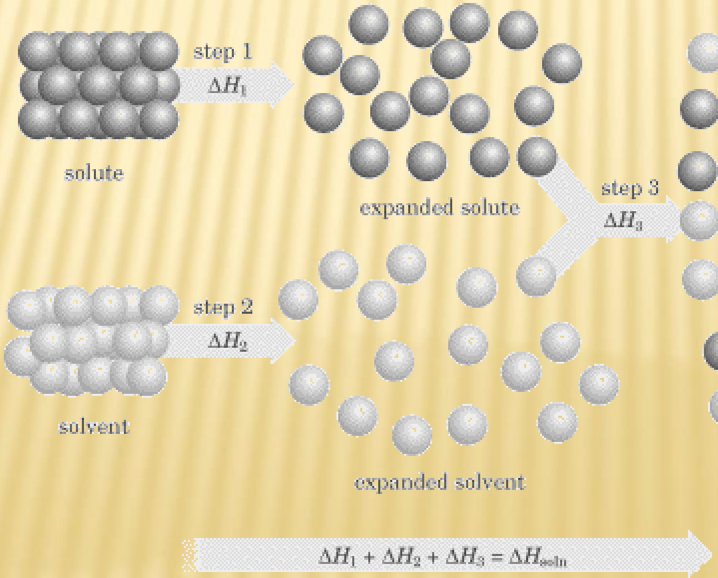
These energy changes are generally much smaller than those associated with chemical bonds, thus heats of mixing are generally much smaller than heats of reaction

The heat of mixing for a solution gives the enthalpy change when pure species are mixed at constant T and P to form one mole of solution:

$$\Delta H = H - \sum x_i H_i$$

For binary solutions, the following equation enables calculation of the enthalpies of binary mixtures from enthalpy data for pure species A and B from the heats of mixing

$$H = x_A H_A + x_B H_B + \Delta H$$



Heats of mixing are available in the literature for a limited number of temperatures

Heats of mixing are calculated for other temperatures by a method analogous to the calculation of standard heats of reaction at elevated temperatures from the value at 298 K, if heat capacities of the pure species and of the mixture are known

$$\begin{tikzcd}
A(800) \arrow[d, "1"'] & + & B(800) \arrow[d, "2"'] \arrow[r, "\Delta H_{800}"] & A+B(800) \\
A(298) & + & B(298) \arrow[r, "\Delta H_{298}", "3"'] & A+B(298) \arrow[u, "4"']
\end{tikzcd}$$

$$\Delta H_1 = \int_{800}^{298} C_{P(A)} dT$$

$$\Delta H_2 = \int_{800}^{298} C_{P(B)} dT$$

$$\Delta H_3 = \Delta H_{298}^{o}$$

$$\Delta H_4 = \int_{298}^{800} C_{P(A+B)} dT$$

$$\Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

When solids or gases are dissolved in liquids, the heat effect is called a heat of solution that is based on the dissolution of 1 mole of solute

$$\widetilde{\Delta H} = \frac{\Delta H}{x_A}$$

where x_A is the moles of solute per mole of solution and ΔH is the heat effect per mole of solution

Solution processes are represented analogous to chemical reaction equations by physical change equations:

$$LiCl(s) + 12H_2O(l) \rightarrow LiCl(12H_2O)$$

The designation $LiCl(12H_2O)$ means that the product is a solution of 1 mole of LiCl in 12 moles of H_2O. The enthalpy change for this process at 25 °C and 1 bar is

$$\widetilde{\Delta H} = -33614\, J$$

A solution of 1 mole of LiCl in 12 moles of H_2O has an enthalpy 33614 J less than that of 1 mole of pure LiCl(s) and 12 moles of pure $H_2O(l)$

Equations for solution physical changes are readily combined with equations for chemical reactions

Example – Calculating the heat of formation of LiCl in 12 moles of H_2O at 25 °C

The process is formation of 1 mole of LiCl from its constituent elements <u>in solution</u> in 12 moles of H_2O:

$$Li + \frac{1}{2}Cl_2 + 12H_2O(l) \rightarrow LiCl(12H_2O) \qquad \Delta H^o{}_{298}$$

The equation can be broken down to multiple equations for which heat changes are known

$$Li + \frac{1}{2}Cl_2 \rightarrow LiCl(s) \qquad \Delta H^o{}_{298} = -408610\,J$$

$$LiCl(s) + 12H_2O(l) \rightarrow LiCl(12H_2O) \qquad \widetilde{\Delta H}_{298} = -33614\,J$$

The enthalpy change of -442224 J for the overall process is known as the heat of formation of LiCl in 12 moles of H_2O

Note that the heat of formation of H_2O is not included in the calculation

Heats of solution are seldomly reported and must be calculated from the heats of formation by the reverse of the calculation just explained
Some heats of formation of 1 mole of LiCl given in the literature include:

$LiCl(s)$	$-408610\ J$
$LiCl.H_2O(s)$	$-712580\ J$
$LiCl.2H_2O(s)$	$-1012650\ J$
$LiCl.3H_2O(s)$	$-1311300\ J$
$LiCl\ in\ 3\ moles\ H_2O$	$-429366\ J$
$LiCl\ in\ 5\ moles\ H_2O$	$-436805\ J$
$LiCl\ in\ 8\ moles\ H_2O$	$-440529\ J$
$LiCl\ in\ 10\ moles\ H_2O$	$-441579\ J$
$LiCl\ in\ 12\ moles\ H_2O$	$-442224\ J$
$LiCl\ in\ 15\ moles\ H_2O$	$-442835\ J$

Example – Calculate the heat of solution of 1 mole of LiCl in 5 moles of H_2O

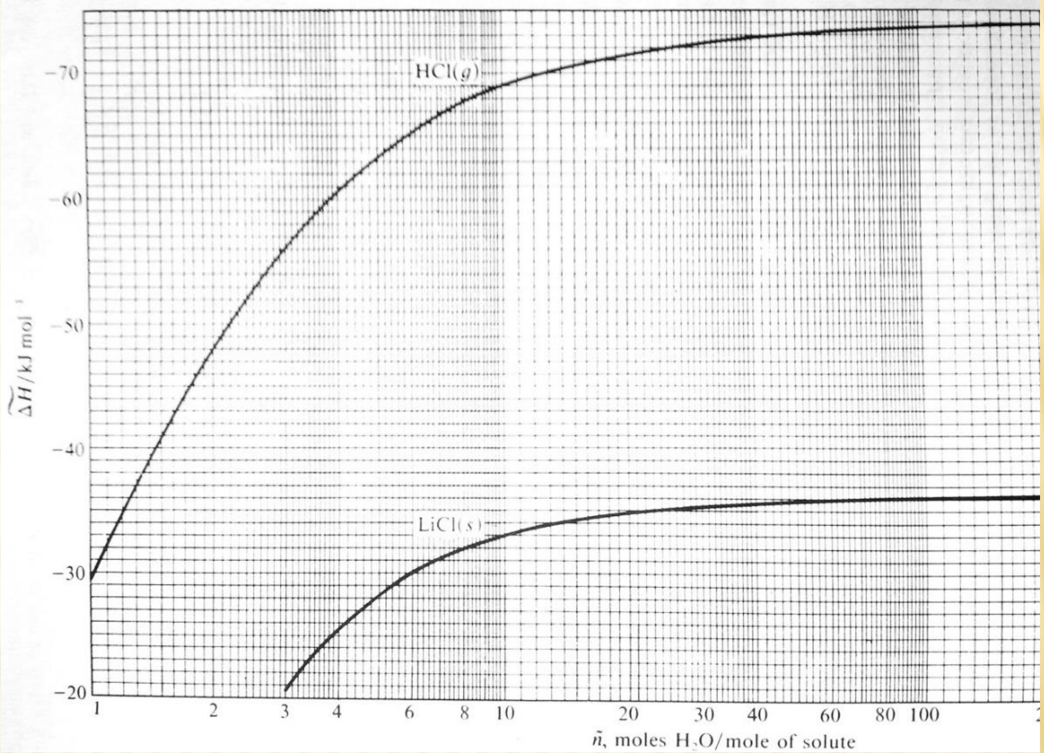
$$LiCl(s) + 5H_2O(l) \rightarrow LiCl(5H_2O)$$

The process is divided into two formation reactions of LiCl:

$$Li + \frac{1}{2}Cl_2 + 5H_2O(l) \rightarrow LiCl(5H_2O)$$

$$LiCl(s) \rightarrow Li + \frac{1}{2}Cl_2$$

The graph of heat of solution per mole of solute, $\widetilde{\Delta H}$, vs. the moles of solvent per mole of solute $\tilde{n}$, can be obtained from data given for each quantity of H_2O



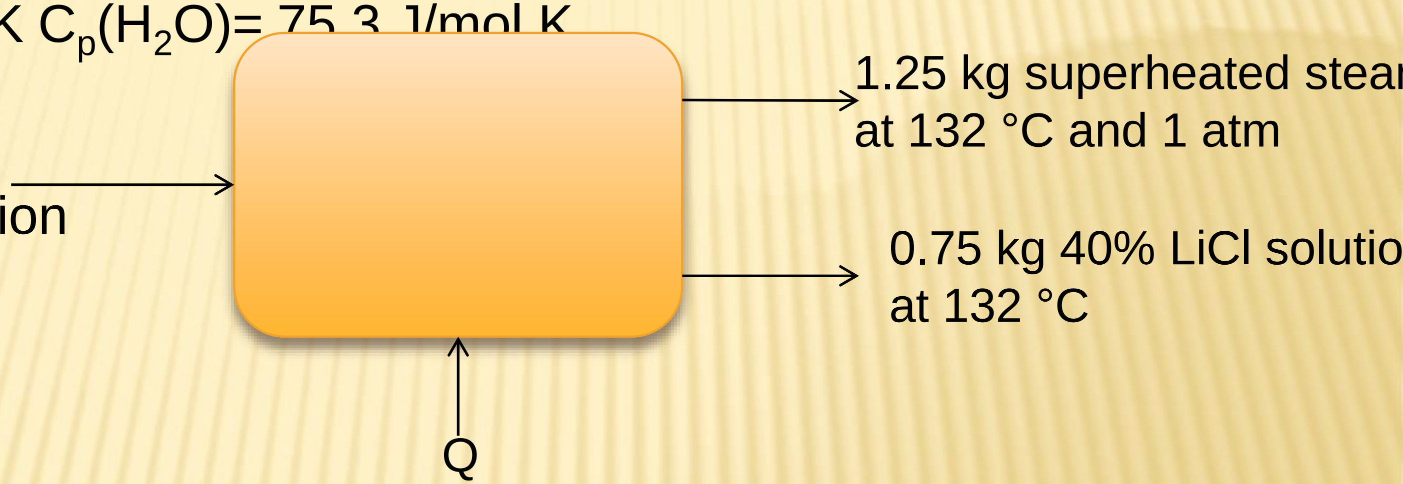
where $$\tilde{n} = \frac{x_2}{x_1} = \frac{1-x_1}{x_1}$$

and $$x_1 = \frac{1}{1+\tilde{n}}$$

Therefore $$\widetilde{\Delta H} = \frac{\Delta H}{x_1} = \Delta H(1+\tilde{n}), \quad \Delta \mathrm{H} = \frac{\widetilde{\Delta H}}{1+\tilde{n}}$$

Example – A rotary evaporator operating at atmospheric pressure concentrates a 15 wt% LiCl solution to 40 wt% solution by evaporation. The normal boiling point of a 40% LiCl solution is 132 °C and its specific heat is estimated as 2.72 kJ/kg.°C. The dilute solution enters the evaporator at the rate of 2 kg/s at 25 C. What is the heat transfer rate in the evaporator?

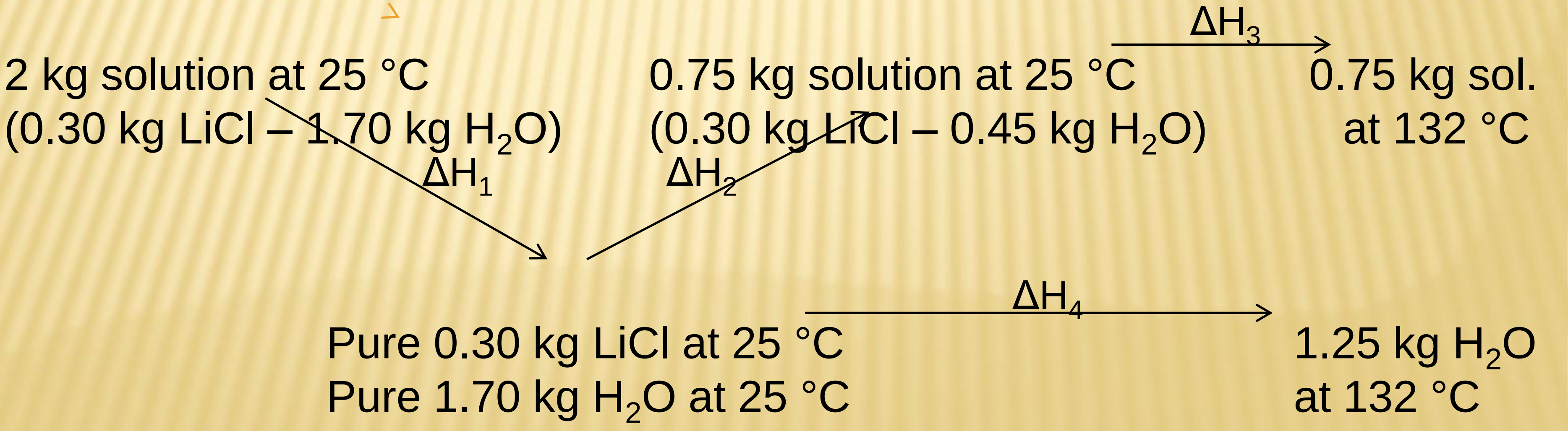
C_p(LiCl)= 48 J/mol.K C_p(H_2O)= 75.3 J/mol.K



1.25 kg superheated stea
at 132 °C and 1 atm

2 kg 15% LiCl solution
at 25 °C

0.75 kg 40% LiCl solutio
at 132 °C



2 kg solution at 25 °C
(0.30 kg LiCl – 1.70 kg H_2O)

0.75 kg solution at 25 °C
(0.30 kg LiCl – 0.45 kg H_2O)

0.75 kg sol.
at 132 °C

Pure 0.30 kg LiCl at 25 °C
Pure 1.70 kg H_2O at 25 °C

1.25 kg H_2O
at 132 °C

ΔH_T for 1 second = $\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

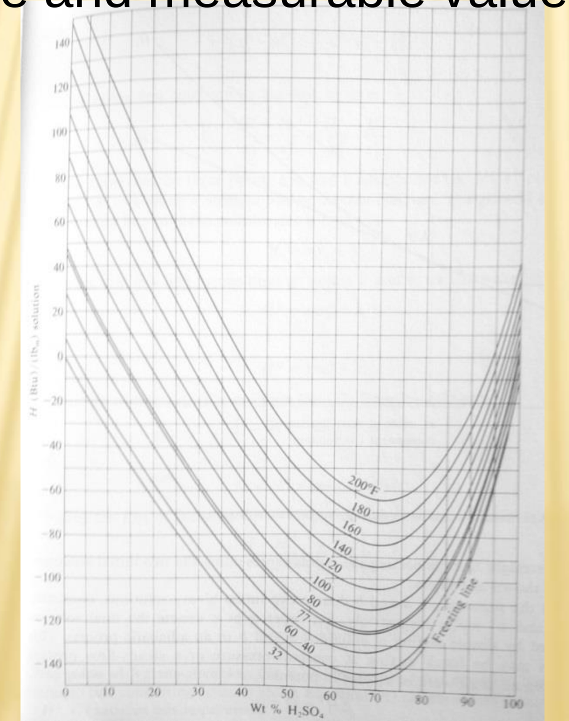
Enthalpy/concentration diagrams are the most convenient way to represent enthalpy data for binary solutions

These diagrams are graphs of the solution enthalpy plotted as a function of composition

Recall that $H = x_A H_A + x_B H_B + \Delta H$

Values of H depend not only on the heats of mixing of the solution, but also on the enthalpies H_A and H_B of the pure species

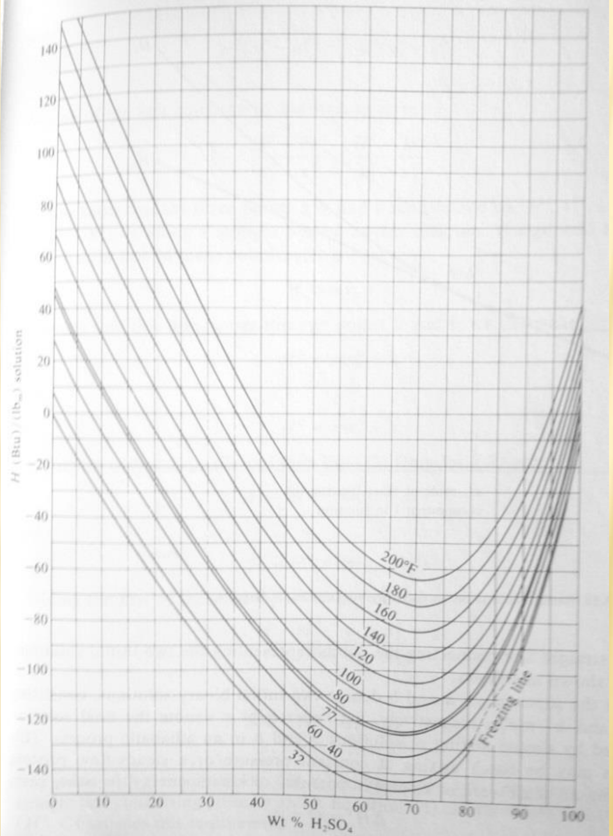
H is fixed for all solutions once H_A and H_B are known for a given T and P because ΔH has a unique and measurable value at each composition

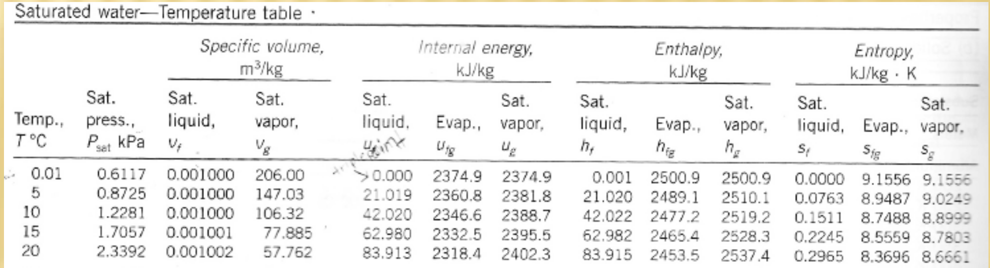


Arbitrary zero points are chosen for the enthalpies of pure species since absolute enthalpies are unknown

Thus the basis of an enthalpy/concentration diagram is H_1=0 for pure liquid H_2O at triple point of water, 0°C, and H_2=0 for some specified state of pure species 2

Triple point of water is the base of the steam tables, so it is simple to use the enthalpy values from the steam tables in conjunction with values taken from the enthalpy/concentration diagram





Saturated water—Temperature table

		Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg · K		
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.2281	0.001000	106.32	42.020	2346.6	2388.7	42.022	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.7057	0.001001	77.885	62.980	2332.5	2395.5	62.982	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.3392	0.001002	57.762	83.913	2318.4	2402.3	83.915	2453.5	2537.4	0.2965	8.3696	8.6661

For an ideal solution, isotherms on an enthalpy/concentration diagram are straight lines connecting the enthalpy of pure species 2 at $x_1 = 0$ with the enthalpy of pure species 1 at $x_1 = 1$ since

$$H^{id} = x_1 H_1 + (1 - x_1) H_2 = x_1 (H_1 - H_2) + H_2$$

The relation is illustrated as a dashed line in the figure at the right where variation of real solution enthalpy with concentration is given as the solid line, and the difference between the two gives the heat of mixing