lec.4

Heats of Solution and Mixing

1. **Heats of Solution, Dissolution, and Mixing**
2. Introducing the Effects of Mixing into the Energy Balance

-In this chapter we explain how mixing and solution of one component in another to form a binary solution affect the energy balance.

1. Heats of Solution, Dissolution, and Mixing

We have assumed that when a stream consists of several components, the total properties of the stream are the appropriately weighted sum of the properties of the individual components. For such **ideal solutions**, we could write down for the heat capacity of an ideal mixture, for example

$$Cp_{mixture} = x_A Cp_A + x_B Cp_B + x_C Cp_C +. .$$

or, for the enthalpy, $\Delta \hat{H}_{mixture} = x_A \Delta \hat{H}_A + x_B \Delta \hat{H}_B + x_C \Delta \hat{H}_C +. . .$

- In particular, mixtures of gases have been treated as ideal solutions.

- However, you must take into consideration other types of mixtures. You can prepare various kinds of binary solutions or mixtures:

a. gas-gas. **b.** gas-liquid. **c.** gas-solid. **d.** liquid-liquid. **e.** liquid-solid. **f.** solid-solid.

- You can ignore the energy changes that occur on mixing for cases a, c, and f. They are negligible. The other mixtures constitute **real solutions.**

- When a gaseous or solid **solute** (the compound to be dissolved) is mixed with a liquid **solvent** (the compound in which the solute is dissolved), the energy effect that occurs is referred to as the heat (**really enthalpy**) of solution.

- When a liquid is mixed with a liquid, the energy effect is called the **heat (enthalpy) of mixing.**

- The negative of the heat of solution or mixing is the **heat (enthalpy) of dissolution.**
- The heat of solution can be positive **(endothermic)** or negative **(exothermic).**
Heat (enthalpy) of solution The enthalpy change that occurs when a solute is mixed with a solvent.

-You can treat heats of solution/mixing in the same way you treat chemical reactions

Example.1. Application of Heat of Solution Data

You are asked to prepare an ammonium hydroxide solution at 77°F by dissolving gaseous NH_3 in water. Calculate the amount of cooling needed in British thermal units to prepare a 3.0% (mass fraction) solution containing 1 lb mol of NH_3

Composition	State	$-\Delta\hat{H}_f^o$ (Btu/lb mol)	$-\Delta\hat{H}_{soln}^o$ (Btu/lb mol)
	g	19,900	0
$1H_2O$	aq	32,600	12,700
$2H_2O$	aq	33,600	13,700
$3H_2O$	aq	34,000	14,100
$4H_2O$	aq	34,200	14,300
$5H_2O$	aq	34,350	14,450
$10H_2O$	aq	34,600	14,700
$20H_2O$	aq	34,700	14,800
$30H_2O$	aq	34,700	14,800
$40H_2O$	aq	34,700	14,800
$50H_2O$	aq	34,750	14,850
$100H_2O$	aq	34,750	14,850
$200H_2O$	aq	34,800	14,900
∞H_2O	aq	34,800	14,900

Solution:

The solution will be presented in abbreviated form.

Reference temperature: $77^{\circ}F$

Basis: 1 lb mol NH3 ≡ 17 lb NH3

$$\text{wt \% NH}_3 = \frac{\text{lb NH}_3}{\text{lb H}_2\text{O} + \text{lb NH}_3}(100)$$

$$3 = \frac{17(100)}{17 + m_{H_2O}} \qquad m_{H_2O} = 550 \text{ lb or about 30 lb mol H}_2\text{O}$$

From the table above, the $\Delta\hat{H}_{soln}^o = -14{,}800$ Btu/lb mol NH3, which is equal to 14,800 Btu removed from the system

Example.2. If the heat of formation of LiCl(s) is -408.78 kJ/kg, calculate heat of formation of LiCl in 10 moles of water. The heat of solution -32.84 kJ/kg LiCl.

Solution:

$\Delta\hat{H}^{\circ}_{f,LiCl(s)} = -408.78 \frac{kJ}{kg}$, $10 mole\ of\ H2O$, $\Delta\hat{H}^{\circ}_{solution} = -32.84\ kJ/kg\ LiCl$

Li + ½ Cl_2 → LiCl(s) $\Delta\hat{H}^{\circ}_{f,LiCl(s)} = -408.78 \frac{kJ}{kg}$

LiCl(s) +10H_2O → LiCl.10H_2O $\Delta\hat{H}^{\circ}_{solution} = -32.84 \frac{kJ}{kg} LiCl$

Li + ½ Cl_2 + 10H_2O → LiCl.10H_2O $\Delta\hat{H}^{\circ}_{f,solution} = -441.62 \frac{kJ}{kg\ LiCl.10H2O}$

Enthalpy-concentration diagram:

- Enthalpy-concentration diagrams (H-x) are plots of specific enthalpy versus concentration (usually mass or mole fraction) with temperature as a parameter.

- Figure below illustrates one such plot. If available, such charts are useful in making combined material and energy balance calculations in distillation, crystallization, and all sorts of mixing and separation problems.

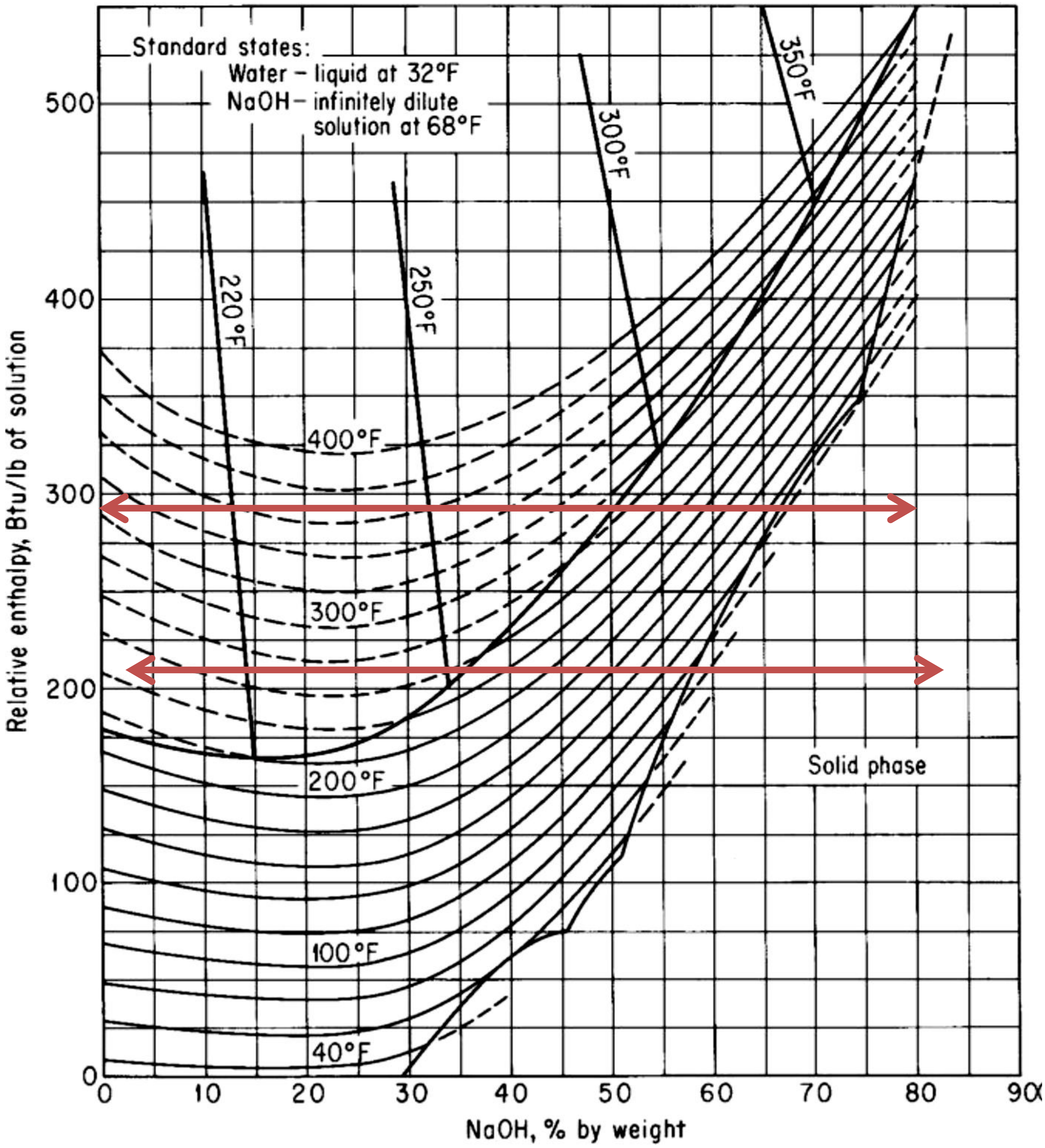


Figure. Enthalpy-concentration chart for sodium hydroxide-water

Example 3 . Application of an Enthalpy-Concentration Chart

Six hundred pounds of 10% NaOH per hour at 200°F are added to 400 lb/hr of 50% NaOH at 290°F in an insulated vessel. Calculate the following:

a. The final concentration of the exit solution
b. The final temperature of the exit solution
c. The pounds of water evaporated per hour during the process

Solution:

(a)

$$wt\%(final) = \frac{wt_1 \times wt\%(1) + wt_2 \times wt\%(2)}{wt(total)}$$

$$wt\%(final) = \frac{600 \times 10 + 400 \times 50}{1000} = 26\%(final\ concentration)$$

(b)

$$\Delta H(final) = \frac{\Delta H_1 \times wt_1 + \Delta H_2 \times wt_2}{wt(total)}$$

$$\Delta H(final) = \frac{152 \times 600 + 290 \times 400}{1000} = 207.2\ Btu$$

From chart for NaOH-H_2O (0.26 and 207.2 Btu) :
final temperature (T_{final}=232ºF)(a)

(c)

$Wt_{(total)} \times \Delta H(final) = (X_{(water\ evaporated\ )} \times \Delta_{H(steam\ table)}) + (Wt_{(total)} - x)\Delta H_{(from\ chart\ H-X)}$

$\Delta H_{(from\ chart)}$:-

(من مخطط الانثالبي التركيز عن طريق اسقاط النقطة النهائية على خط boiling point ثم يسارا الى خط الانثالبيي) .

$\Delta_{H(steam\ table)}$:-

(من steam table بالاعتماد على درجة الحرارة النهائية ($T_{(final)}$)

The enthalpy of the **saturated water vapor** (no NaOH is in the vapor phase) ∴ from the steam tables at 232°F is 1158 Btu/lb.

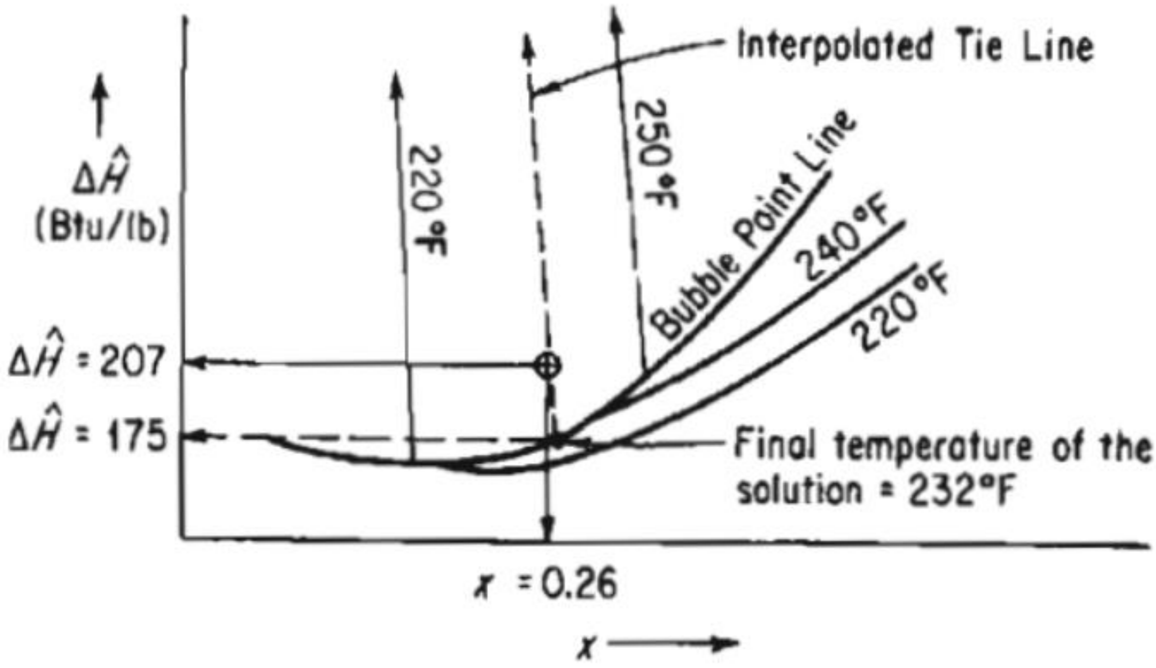
$$1000 \times 207.2 = (X \times 1158) + (1000 - X)175$$

X=32.8 of H_2O of evaporated/hr

Basis: 1000 lb of final solution

$$x(1158) + (1000 - x)\,175 = 1000\,(207.2)$$

$$x = 32.8 \text{ of } H_2O \text{ evaporated/hr}$$



Example 4. An insulated closed tank contains 250 kg of a 20% solution of sulfuric acid at its boiling point. One hundred pounds of a 98% solution of sulfuric acid at 98ºF are carefully added to the original solution with stirring. What are the final temperature, composition, and weight of solution in the tank?

Example 5. One thousand pounds of 10% NaOH at 100 ºF is to be forified to 30% NaOH by adding 73% NaOH at 200 ºF. How much 73% solution must be used? How much cooling must be provided so that the final temperature will be 70 ºF?