Lecture №11. Material and heat balance of crystallization.

Aim: Characterize the crystallization process. Write the balance equation for the entire amount of substance and for anhydrous crystallizing substance.Give the heat balance equation for the crystallization process.

Lecture summary: Crystallization is the formation of a solid phases in the form of crystals from solutions and melts. The mass of the crystalline phase is determined from the material balance of the crystallization process by the sum of the mass of the solute and the solvent and by the mass of the solute.

Let's designate the amount of the initial solution G_1, the amount of the mother liquor G_2, the number of crystals G_{cr}. and the amount of evaporated solvent W.

The content of anhydrous crystallizing substance (in mass fractions) in the initial solution is denoted by x_1, in the mother solution by x_2 and in crystals x_{cr}.

If the substance crystallizes in anhydrous form, then $x_{cr} = 1$. If the substance crystallizes in the form of crystalline hydrate, then $x_{cr.} = M/M_{cr.}$ - the ratio of molar masses of anhydrous solute and crystalline hydrate.

The balance equation for the entire amount of substance:

$$G_1 = G_2 + G_{cr.} + W$$

and for anhydrous crystallizing substance:

$$G_1\, x_1 = G_2\, x_2 + G_{cr.}\, X_{cr.}$$

In crystallizers with water or brine cooling, W = 0. In this case, knowing G_1, x_1, x_2, and x_{cr}, the values of G_2 and G_{cr} are found by joint solution of the equations.

In crystallizers with the removal of a part of the solvent (crystallizers with air cooling, evaporators with crystallization of a part of the substance), the value of W or G_{cr} is set, after which it is also possible to jointly solve these equations.

In vacuum crystallizers, *W* cannot be taken arbitrarily, it is determined by the joint solution of the equations of material and heat balances.

The mass of the crystals formed is determined from the equation of the material balance of the crystallizer

$$G_{кр} = \frac{G_1(x_2 - x_1) - Wx_2}{x_2 - x_{кр}},$$

where G_1 is the mass of the initial solution, kg; x_1 is the concentration of the initial solution in terms of anhydrous salt, mass fractions or %; x_2 - concentration of anhydrous salt of the mother liquor after crystallization, mass fraction or%; *W* is the mass of the evaporated solvent, kg; $x_{cr.}$ - the ratio of molar masses of anhydrous solute and crystalline hydrate.

With isohydric crystallization (without removing part of the solvent at $W = 0$):

$$G_{кр} = \frac{G_1(x_2 - x_1)}{x_2 - x_{кр}}.$$

The heat capacities of solids are calculated from the values of atomic heat capacities (Table 3) using the additivity rule:

$$M \cdot c = n_1 c_{a,1} + n_{a,2} c_{a,2} + \ldots + n_{a,i} c_{a,i}\ ,$$

where M is the molar mass of the compound, kg / kmol; $c_{a,i}$ - atomic heat capacity of the i-th element, J/(kg-at·K); $n_{a,i}$ - the number of atoms of the elements included in the compound.

Table 3

Atomic heat capacity of elements

State of substances	$c_{a,i}$, kJ/(kg-at·K)								
	C	H	N	O	Si	F	P	S	Э
Solid	7,5	9,6	11,3	16,8	15,9	21,0	22,6	22,6	26,0
Liquid	11,7	18,0	18,4	25,1	24,3	29,3	31,0	31,0	33,5

The heat balance equation for the crystallization process with cooling the solution and removing part of the solvent has the form

$$G_1 c_1 t_1 + G_{кр} q_{кр} = G_2 c_2 t_2 + G_{кр} c_{кр} t_2 + W I_п + Q,$$

where G_1, G_2 and $G_{cr.}$ - consumption of initial and mother liquors and crystals, kg/s; W is the consumption of the evaporated solvent, kg / s; c_1, c_2 and $c_{cr.}$ - specific heat capacities of initial and mother solutions and crystals, J/(kg·K); t_1 is the temperature of the initial solution, °C; t_2 - temperature of mother liquor and crystals, °C; q_{cr} - specific heat of crystallization of the solute, J/kg; I_v - enthalpy of removed solvent vapors, J/kg.

Considering the original solution as a mixture of mother liquor, crystals and evaporated water, one can write:

$$G_1 c_1 t = G_2 c_2 t + G_{кр} c_{кр} t + W c_в t,$$

where

$$G_2 c_2 t_2 + G_{кр} c_{кр} t_2 = G_1 c_1 t_2 - W c_в t_2,$$

where c_w is the specific heat capacity of water, J/(kg·K).

The heat flux released during crystallization is determined from the heat balance of crystallization

$$Q = G_1 c_1 (t_1 - t_2) + G_{кр} c_{кр} - W(I_{п} - c_{в} t_2) = G_1 c_1 (t_1 - t_2) + G_{кр} c_{кр} - W r_{вт.п},$$

where $r_{sec.v}$ is the specific heat of vaporization of the solvent, J/kg.

Questions to control:

1. Characterize the crystallization process.
2. Write the balance equation for the entire amount of substance and for anhydrous crystallizing substance.
3. Give the heat balance equation for the crystallization process.

Literature:

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