**INDIVIDUAL TASKS FOR CALCULATION**

**Example**

For reaction **A** (table 1), flowing in the gas phase, for temperature ***T*** and pressure ***P***, approximately, assuming ∆***Cp* = const** (does not depend on temperature), calculate

A) **Δ*H***, to draw a conclusion about the thermal effect of the reaction;

B) **Δ*S***, to draw a conclusion about the direction of spontaneous flow of the process in an isolated system;

C) **Δ*G***, to draw a conclusion about the direction of the spontaneous flow of the process at P and T = const;

D) the equilibrium constant ***K*0**;

E) indicate how pressure and temperature affect the equilibrium yield of reaction products.

Table 1

|  |  |  |  |
| --- | --- | --- | --- |
| № | Reaction **А** | ***Т*,** К | ***Р*⋅10-5,** Па  |
| 1 | CH3OH + 1,5O2 = CO2 + 2H2O | 600 | 2,026 |

 **First calculate ∆H0298, ∆S0298 (under standard conditions: T=298 K, P = 1∙105 Pa ) and ∆Cp.**

 **Take data for calculations from Table 2.**

1. **You calculate the heat effect of the reaction ∆H0298 (enthalpy):**



∆H0298 = [(∆H0(CO2) + 2·∆H0(H2O] – [∆H0(CH3OH) +1,5·∆H0(O2)]

∆H0298 = ( -393,51 + 2·(-241,84) – (-201,2 +1,5·0) = - 675,99 kJ/mol,

 **Note! For further calculations, take the calculated value ∆H0298 in joules (J)**

∆H0298  = - 675,99 kJ/mol = 675990 J/mol

 **Then** **calculate** **change of the heat capacity ∆Cp:**



∆Cp = [Cp(CO2) + 2·Cp(H2O] – [Cp(CH3OH) +1,5·Cp(O2)]

∆Cp = (37,13 +2·33,56) – (43,9 +1,5·29,36) = 16,31 J/mol ·K

**B)** **Сalculate the enthalpy of reaction ∆S0298 :**



∆S0298 = [(S0(CO2) + 2·S0(H2O] – [S0(CH3OH) +1,5·S0(O2)]

∆S0298 = (213,6 +2·188,74) – (239,7 + 1,5·205,03) = 43,84 J/mol ·K,

**С) Then you сalculate ∆HT , ∆ST and the free Gibb's energy ∆GT at T = 600 K ,**

 **(∆*Cp* = const).**



∆H600 = -675990 + 16,31( 600 – 298) = - 671064 J/mol, ∆H <0, heat is released, exothermic reaction.



∆S600 = 43,84 + 16,31 ln 600/298 = 55,22 J/mol ·K, ∆S>0, the direct reaction can proceed spontaneously (→)



G600 = -675990 - 600·55,22 = - 709122 J/mol = 709,122 kJ/mol, ∆G <0, the direct reaction can proceed spontaneously

**D)** **If you calculate value Kp then you can calculate the equilibrium constant *K*0:**

**To calculate Kp at** ***Cp* = const you use the second approximation of Ulich;**



R = 8,314 J/mol ·K - gas constant

lnKp = - (-675990)/8,314∙ 600 + 43,84/8,314 – 16,31∙(600-298)/ 8,314∙ 600 + 16,31/8,314∙ (ln 600/298) = 343

Kp = e343 = 2,72343

**K0 = Kр∙(Pgen) –Δn,** where Δn is the change in the number of moles of gaseous substances in the reaction.

∆n = 3-2,5 = 0,5

**K0 =** 2,72343 (2,026)-0,5

**E)** If the equilibrium shifts to the left, then the product yield decreases.

This reaction is exothermic, so when the temperature rises, the equilibrium shifts to the left and the yield of products decreases.

Since the reaction proceeds with an increase in volume (∆n = 0,5),

a increase in pressure will lead to a shift in the equilibrium to the left and a decrease in the yield of reaction products.

Thus, an increase in temperature and pressure will lead to a decrease in the yield of reaction products

**Table 2**

**Thermodynamic quantities for simple substances and compounds**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Substance | Δ*Η*0,кJ/mol | Δ*S*0,J/mol·K | *Ср*,J/mol·K | Equation coefficients*Ср = а + вТ + сТ2 + С´‒Т*‒2, J/(mol·K) |
| *а* | *b* · 103 | *с*´ ·10-5 | *с* · 106 |
| Cl2 (g) | 0 | 223,0 | 33,84 | 36,69 | 1,05 | −2,52 | – |
| H2 (g) | 0 | 130,6 | 28,83 | 27,28 | 3,26 | 0,502 | – |
| I2 (g) | 62,24 | 260,58 | 36,9 | 37,40 | 0,59 | −0,71 | – |
| 02 (g) | 0 | 205,03 | 29,36 | 31,46 | 3,39 | −3,77 | – |
| S2 (g) | 129,1 | 227,7 | 32,47 | 36,11 | 1,09 | −3,52 | – |
| CO(g) | −110,5 | 197,4 | 29,15 | 28,41 | 4,10 | −0,46 | – |
| CO2 (g) | −393,51 | 213,6 | 37,13 | 44,14 | 9,04 | −8,53 | – |
| COCl2 (g) | −223,0 | 289,2 | 60,67 | 67,16 | 12,11 | −9,03 | – |
| CaCO3 (sol) | −1206 | 92,9 | 81,85 | 104,5 | 21,92 | −25,94 | – |
| CaO (sol) | −635,1 | 39,7 | 42,80 | 49,63 | 4,52 | −6,95 | – |
| Ca(OH)2(sol) | −986,2 | (83,4) | 87,5 | 105,2 | 12,0 | −19,0 | – |
| HCl (g) | 92,30 | 186,70 | 29,16 | 26,53 | 4,60 | 1,09 | – |
| HI (g) | 25,94 | 206,30 | 29,16 | 26,32 | 5,94 | 0,92 | – |
| H2O(g) | −241,84 | 188,74 | 33,56 | 30,00 | 10,71 | 0,33 | – |
| H2S (g) | −20,15 | 205,64 | 33,93 | 29,37 | 15,40 | – | – |
| MgCO3 (sol) | −1096,2 | 65,69 | 75,52 | 77,91 | 57,74 | −17,41 | – |
| Mg(OH)2 (sol) | −924,66 | 63,14 | 76,99 | 54,56 | 66,11 | – | – |
| MgO (sol) | 601,24 | 26,94 | 37,41 | 42,59 | 7,28 | −6,19 | – |
| NO (g) | 90,37 | 210,62 | 29,83 | 29,58 | 3,85 | −0,59 | – |
| NO2 (g) | 33,89 | 240,45 | 37,11 | 42,93 | 8,54 | −6,74 | – |
| N2O4 (g) | 9,37 | 304,3 | 78,99 | 83,89 | 39,75 | −14,9 | – |
| PCl3 (g) | −277,0 | 311,7 | 72,05 | 80,12 | 3,1 | −7,99 | – |
| PCl5 (g) | −369,45 | 362,9 | 111,9 | 129,5 | 2,92 | −16,4 | – |
| SO2 (g) | −296,9 | 248,1 | 39,87 | 42,55 | 12,55 | −5,65 | – |
| SO2Cl2 (g) | −358,7 | 311,3 | 77,4 | 53,72 | 79,50 | – | – |
| SO3 (g) | −395,2 | 256,23 | 50,63 | 57,32 | 26,86 | −13,05 | – |
| CH4 (g) | −74,85 | 186,19 | 35,79 | 17,45 | 60,46 | – | −1,117 |
| C2H4(g) | 52,28 | 219,4 | 43,63 | 4,196 | 154,59 | – | −81,09 |
| C2H6 (g) | −84,67 | 229,5 | 52,70 | 4,494 | 182,26 | – | −74,86 |
| C6H6 (g) | 82,93 | 269,2 | 81,67 | 33,90 | 471,87 | – | −98,34 |
| C6H12 (g) | −123,1 | 298,2 | 106,3 | 51,72 | 598,8 | – | −230,0 |
| HCOOH (g) | −376,7 | 251,6 | 48,7 | 19,4 | 112,8 | – | −47,5 |
| CH3OН (g) | −201,2 | 239,7 | 43,9 | 15,28 | 105,2 | – | −31,04 |
| CH3I (g) | 20,5 | 253,0 | 44,1 | 19,16 | 92,67 | – | −32,28 |
| C2H5Cl (g) | −105,0 | 274,8 | 62,3 | 13,07 | 188,5 | – | −71,94 |