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PHYSICAL CHEMISTRY Fundamentals of thermodynamics Chemical thermodynamics. Chemical equilibria

Laboratory works and examination questions

The manual is intended for students of Chemical Technology and Engineering and Organic Substances Technology faculties of the university

Minsk 2013

№ 1. DISSOLUTION PROCESS ENTHALPY DETERMINATION BY SOLUTION CALORIMETRY

To find the enthalpy change that accompanies a reaction, we could measure the temperature rise or fall when a known amount of reaction takes place in a thermally isolated system, such as a calorimeter. We need to know the heat capacity of the calorimeter and its contents, and also how much heat is transferred to or from the surroundings (or alternatively, be able to minimize that heat transfer).

In this experiment, solutions are formed in a calorimeter. The heat capacity of the calorimeter is determined by passing a known amount of electricity through the system before the reaction, and determining the resulting temperature change. The temperature rise on reaction could be measured using a precision thermometer. In the experiment you will measure the enthalpies of process of salt dissolution.

When either of the dissolution shown above occurs, heat is almost sure to be released or absorbed. Let the temperature change on the dissolution of n moles of salt in pure solvent be ΔT . Since the reactions occur at constant pressure (p = const), it is the enthalpy of dissolution of a mole of substance, ΔH , which is measured

$$\Delta H = -\left(\sum m_i \cdot c_i\right) \cdot \Delta T \tag{1}$$

where m_i is mass and c_i is the heat capacity of the calorimeter and its contents.

Let

$$-\left(\sum m_i \cdot c_i\right) = K \,, \tag{2}$$

where K is the calorimeter constant. Thus, the enthalpy of dissolution is

$$\Delta H = -Q = -K \cdot \Delta T. \tag{3}$$

In order to determine how much heat is released, we need to find the temperature rise when a defined amount of energy is put in. This is done, in this experiment, by heating the solution electrically.

Suppose that, instead of the reaction occurring, a current *I* at voltage *U* is switched through the heater for time *t*, and that the temperature then rises by an amount ΔT . The energy *Q* put into the system by the heater is

$$Q = I \cdot U \cdot t.$$

Eliminating *K* from equation (3):

$$K = \frac{Q}{\Delta T}.$$
(4)

The apparatus is sketched in Fig. 1. Through the lid of a calorimeter is mounted a thermometer. A stirrer, heater and a tube also pass through the lid. Current for the heater is supplied from an adjustable, stabilized power supply. A change-over switch connects this with the calorimeter, or with a dummy heater of the same resistance. The use of the dummy heater allows the current to be adjusted and to settle before the calorimeter itself is heated. The calorimeter heater should never be switched on in air, or it will burn out.

Work execution. Measure 300 ml distilled water into a measuring cylinder and add its in beaker. Weight about 5.00 g of salt using tube and technical scales. Rest the tube and the beaker in a calorimeter. Turn the stirrer controller.

Connect the power supply and heater. Check that the change-over switch is connected to the heater. Leave both running throughout the experiment.

Carry out the calibration of calorimeter. At the same moment as starting a timer, operate the changeover switch to turn on the heater. Continue recording the temperature at half-minute intervals. Half way during your measurements, note the voltage and current being passed through the heater. After exactly 3 minutes, turn off the heater. Continue to record the temperature until the readings stabilize (fig. 2).



Fig. 1. The calorimeter used in the experiment.

Observe any temperature change in the calorimeter due to heat transfer with the environment. Record the temperature with 30 s intervals during 3–5 min.

Press the rod attached to the tube to send over the salt into the distilled water to form the solution. Record and plot the temperature at half-minute intervals until the temperature settles, showing that thermal equilibrium has been reached.

At the end of the experiment switch off and disconnect all electrical circuits. Wash out the calorimeter and associated apparatus with distilled water.

Calculations. Draw graphs of decreasing *T* (increasing T), against time for each run. Calculate the calorimeter constant. Calculate the value of ΔH for dissolution process. Find the molar enthalpies of dissolution of the salt.



Fig. 2. The variation of temperature in the calorimeter with time

Examination questions

The first and the second laws of thermodynamics

Level A

- 1. Define or explain the following terms:
- *a*: internal energy;
- *b*: enthalpy;
- *c*: molar heat capacity;
- *d*: ideal gas.
- **2.** Explain the following terms :
- *a*: State of a System;
- **b**: Extensive Properties;
- c: Closed System;
- d: Isothermal Process.

3. State the first law of thermodynamics in as many ways as possible. Obtain the mathematical expression for the law with sign conventions.

4. Give a concise statement of the first law of thermodynamics. Deduce its mathematical form and explain the terms involved.

5. What do you understand by thermodynamic system and surroundings?

- 6. Which of the following are intensive properties:
- *a*: Density;
- **b**:Temperature;
- *c*: Volume;
- *d*: Mass.

7. State and explain First law of Thermodynamics.

8. Prove that $Q_V = \Delta U$ and $Q_P = \Delta H$.

9. Derive the expression for maximum work done when *n* moles of an ideal gas are expanded isothermally and reversibly from V_1 to V_2 volume.

10. (*a*) Explain the term enthalpy.

- (b) State the first law of thermodynamics.
- (c) Define C_P and C_V . State their relation.

11. (*a*) What are state functions?

(b) What are path functions?

12. (*a*) Describe open, closed and isolated systems.

(b) What do you understand by the terms: Extensive properties and Intensive properties. Give two examples of each category.

13. (*a*) Give two definitions of First law of thermodynamics.

(b) State "Kirchoff's Law".

14. (*a*) Under what conditions $\Delta U = \Delta H$ for a chemical reaction?

15. State the first law of thermodynamics. With the help of this law show that:

(a) Heat absorbed by a system at constant volume is equal to increase in internal energy of the system.

(b) Heat absorbed by a system at constant pressure is equal to the increase in the enthalpy.

16. (a) Distinguish between open, closed and isolated system. Give examples.

(b) Differentiate between reversible and irreversible processes.

17. Derive an expression for the work done by a gas in isothermal reversible expansion of an ideal gas.

18. Distinguish between

(a) State function and path function;

(b) Reversible and irreversible process.

19. Which of the following parameters are state functions : Q, H, U and W.

20. Define heat capacity at constant pressure and heat capacity at constant volume.

Level B (multiple choice questions)

1. The study of the flow of heat or any other form of energy into or out of a system undergoing physical or chemical change is called

(a) thermochemistry; (b) thermokinetics;

(c) thermodynamics; (d) thermochemical studies.

2. Thermodynamics is applicable to

(a) microscopic systems only; (b) macroscopic systems only;

(c) homogeneous systems only; (d) heterogeneous systems only.

3. Which is not true about thermodynamics?

(a) it ignores the internal structure of atoms and molecules;

(*b*) it involves the matter in bulk;

(c) it is concerned only with the initial and final states of the system;

(d) it is not applicable to macroscopic systems.

4. A system that can transfer neither matter nor energy to and from its surroundings is called *(a)* a closed system;

(b) an isolated system;

(c) an open system;

(d) a homogeneous system.

5. A thermos flask is an example of

(a) isolated system; (b) closed system;

(c) open system; (d) heterogeneous system.

6. A closed system is one which cannot transfer matter but transfer _____ to and from its surrounding

(a) heat; (b) work;

(c) radiations; (d) all of these.

7. A gas contained in a cylinder filled with a piston constitutes

(a) an open system; (b) a heterogeneous system;

(c) a closed system; (d) an isolated system.

8. A system that can transfer both energy and matter to and from its surroundings is called

(a) an isolated system; (b) a closed system;

(c) an open system; (d) a heterogeneous system.

9. A system in which no thermal energy passes into or out of the system is called

(a) adiabatic system; (b) an open system;

(c) a reversible system; (d) a closed system.

10. An intensive property does not depend upon

(a) nature of the substance; (b) quantity of matter;

(c) external temperature; (d) atmospheric pressure.

11. Which out of the following is not an intensive property?

(a) pressure; (b) concentration;

(c) density; (d) volume.

12. A property that depends upon the quantity of matter is called an extensive property. Which of the following is not an extensive property?

(*a*) mass; (*b*) volume;

(c) density; (d) internal energy.

13. Which of the following sets of properties constitute intensive properties?

(a) temperature, pressure and volume; (b) mass, density and volume;

(c) density, pressure and temperature; (d) internal energy, density and pressure.

15. In an adiabatic process _____ can flow into or out of the system.

(a) no heat; (b) heat;

(c) matter; (d) no matter.

16. An isobaric process takes place at constant _____.

(a) temperature; (b) pressure;

(c) volume; (d) concentration.

17. An isochoric process takes place at constant_____.

(*a*) volume; (*b*) temperature;

(c) pressure; (d) concentration.

18. An isobaric process takes place at constant_____.

(*a*) volume; (*b*) temperature;

(c) pressure; (d) concentration.

19. For a cyclic process, the change in internal energy of the system is

(a) always positive; (b) always negative;

(c) equal to zero; (d) equal to infinity.

20. Which of the following properties is not a function of state?

(*a*) concentration; (*b*) internal energy;

(c) enthalpy; (d) entropy.

21. The amount of heat required to raise the temperature of one mole of the substance by 1 K is called

(a) heat capacity; (b) molar heat capacity;

(c) molar heat; (d) molar capacity.

22. Heat capacity at constant pressure is the change in

(a) internal energy with temperature at constant volume;

(b) internal energy with temperature at constant pressure;

(c) enthalpy with temperature at constant volume;

(d) enthalpy with temperature at constant pressure.

23. Heat capacity at constant volume is the change in

(a) internal energy with temperature at constant volume;

(b) internal energy with temperature at constant pressure;

(c) enthalpy with temperature at constant volume;

(d) enthalpy with temperature at constant pressure.

24. Which of the following is not correct?

(a) H = U + P V; (b) H - U = PV;

(c) H - U - P V = 0; (d) H = U - P V.

25. A system absorbs 100 kJ heat and performs 50 kJ work on the surroundings. The increase in internal energy of the system is

(*a*) 50 kJ; (*b*) 100 kJ; (*c*) 150 kJ; (*d*) 5000 kJ.

№ 2. DETERMINATION OF THE CONCENTRATION EQUILIBRIUM CONSTANT FOR METHYL ORANGE DISSOCIATION REACTION

At pH < 3 the reaction take place:



Let the equilibrium concentration of the yellow form is *x* and the equilibrium concentration of the red form is (C - x). Then optical density of these solutions can be calculated using this equation:

$$D = \varepsilon_1 (C - x)l + \varepsilon_2 xl \tag{1}$$

where ε_1 is molar absorbance coefficient of red form; ε_2 is molar absorbance coefficient of yellow form; *l* is absorbance layer thin, cm; *C* is concentration of methyl orange, mol/l.

Using the optical density D_1 of red form and the optical density D_2 of yellow form solutions, ε_1 and ε_2 can be calculated using these equations, respectively:

$$D_1 = \varepsilon_1 C l \,, \tag{2}$$

$$D_2 = \varepsilon_2 C l . \tag{3}$$

Work execution. Measure 5 ml 0,0001 mol/1 methyl orange and 5 ml buffer solution with pH 3,2–3,8 into a flask; 5 ml 0,0001 mol/1 methyl orange and 5 ml 0,1 mol/1 HCl; 5 ml 0,0001 mol/1 methyl orange and 5 ml 0,1 mol/1 KOH. Then optical density of these solutions is measured. Optical density measuring is carried out at the wavelength 540 nm.

Equilibrium concentration of hydroxyl ions $C(H^+)$ is calculated from equation $pH = - \lg C(H^+)$. Concentration equilibrium constant is

$$K_{c} = \frac{C_{\mathrm{H}^{+}} \cdot C_{\mathrm{yellow form}}}{C_{\mathrm{red form}}} = \frac{C_{\mathrm{H}^{+}} \cdot x}{C - x}.$$
(4)

Examination questions

Level A

1. Define or explain the following terms:

(*a*) Chemical equilibrium;

(b) Equilibrium constant; (d) Heterogeneous equilibrium.

2. (a) Why chemical equilibrium is called a dynamic equilibrium?

(b) In what direction the following equilibrium will be shifted if some chlorine gas is introduced into the system at equilibrium?

 $\operatorname{COCl}_2(g) \leftrightarrow \operatorname{CO}(g) + \operatorname{Cl}_2(g).$ (*c*) Calculate the ratio of K_p to K_c at 27°C for the equilibrium reaction: $\operatorname{C}_2\operatorname{H}_6(g) \leftrightarrow \operatorname{C}_2\operatorname{H}_4(g) + \operatorname{H}_2(g)$

3. (*a*) What is standard free energy change? Derive a relationship between standard free energy change and equilibrium constant of a reaction at a given temperature.

(b) The equilibrium constant K_p for the reaction:

 $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

is $1.64 \cdot 10^{-4}$ at 673 K and $0.144 \cdot 10^{-4}$ at 773 K. Calculate the mean heat of formation of ammonia from its elements in this temperature range.

4. Calculate ΔG° and K_p for the following reaction at 298 K $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

5. Derive van't Hoff equation showing the variation of equilibrium constant K with temperature. Also obtain its integrated form.

6. Derive a mathematical relation to calculate the temperature dependence of equilibrium constant of a chemical reaction.

7. Derive the relation between K_c and K_p .

8. Prove that $\Delta G^{\circ} = - \operatorname{RT} \ln K_{p}$.

9. For a reaction $K_p = K_c$. What do you infer from this?

10. Write a short note on "Le Chatelier's Principle".

11. What is Le Chatelier's principle? Discuss its applications.

12. Derive the relationship between K_c and K_p . Calculate K_c for the following reaction at 673 K: 2H₂O(g) + 2Cl₂(g) \leftrightarrow 4HCl(g) + O₂(g) (Given $K_p = 0.035$; $R = 8.314 \text{ J} \cdot \text{K}^{-1} \text{mol}^{-1}$).

13. What is the value of K_p : K_c for the equilibrium $N_2(g) + O_2(g) \leftrightarrow 2NO(g)$ at 27°C?

14. How are K_p , K_c and K_a related?

15. Consider the reaction: $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$ How would the equilibrium be affected by the addition of Cl_2 ? **16.** (*a*) Derive van't Hoff equations. (*b*) Write expression for K_p and K_c for the following equilibrium: $N_2O_4(g) \leftrightarrow 2NO_2(g)$

17. For the reaction $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ $K_p = 1.60 \cdot 10^{-4}$ at 400°C. Calculate ΔG° for the reaction.

18. The value of K_p for the water gas reaction is CO + H₂O ↔ CO₂ + H₂ is 1.06 · 10⁵ at 25°C. Calculate the standard state free energy change ΔG° of the reaction at 25°C.

19. Calculate the equilibrium constant of the reaction $A + B \leftrightarrow 2C$ from the data given below. The reaction was started with 2.0 moles litre⁻¹ of A and 2.0 moles litre⁻¹ of B and the equilibrium concentration of C was found to be 0.32 mole litre⁻¹.

20. The value of K_c for the following reaction at 1173K is 0.28. $CS_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2 S(g)$ Calculate the value of K_p at this temperature.

21. Calculate the value of K_c for the following reaction $N_2O_4(g) \leftrightarrow 2NO_2(g)$ when K_p is 0.113 atm at 25 °C.

Level B (multiple choice questions)

1. A chemical system is at equilibrium

(a) when the rate of the forward reaction becomes zero;

(b) when the rates of the forward reaction and the reverse reaction are equal;

(c) when all of the reactants have been used up;

(d) when the rates of the forward reaction and the reverse reaction are both zero.

2. If the equilibrium constant for a reaction is large, what can be said about the reaction?

(*a*) very little product is formed;

(b) very little reactant remains at equilibrium;

(*c*) the reaction goes to completion;

(d) large quantities of reactants will remain at equilibrium.

3. A reaction is at equilibrium. What happens to the value of the equilibrium constant if an additional quantity of reactant is added to the reaction mixture?

(a) the equilibrium constant is shifted to favour production of more reactant;

(b) the equilibrium constant is shifted to favour production of more product;

(c) the equilibrium constant is increased;

(d) the equilibrium constant stays the same.

4. Which of the following can change the value of the equilibrium constant for a reaction *(a)* changing the concentration of the reactants;

(b) adding a catalyst;

(c) changing the solvent;

t (d) removing the products as they are formed.

5. Which of the following changes the value of K_c ?

(*a*) adding reactant; (*b*) adding product;

(c) changing temperature; (d) adding a catalyst.

9. Which one of the following statements is incorrect?

(a) adding products shifts the equilibrium to the left;

(b) adding reactants shifts the equilibrium to the right;

(c) exothermic reactions shift the equilibrium to the left with increasing temperature;

(d) adding a catalyst shifts the equilibrium to the right.

10. Which one of the following is incorrect?

(a) equilibrium is dynamic, as some molecules are always reacting;

(b) the equilibrium constant is just the ratio of forward to reverse rate constants;

(c) at equilibrium the concentrations no longer change with time;

(*d*) the equilibrium constant is not affected by temperature changes.

11. The yield of AB(g) A(g) + B(g) \leftrightarrow AB(g) + heat

 $A(g) + B(g) \leftrightarrow AB(g) + 1$

would be increased by

(*a*) decreasing the pressure

(b) adding additional AB to the reaction mixture

(c) decreasing the temperature

(d) adding a non-reactive liquid to the reaction mixture

12. $N_2 + 3H_2 \leftrightarrow 2NH_3 + heat$

In this reversible reaction, the equilibrium shifts to the right because of all the following factors except:

(a) adding heat; (b) adding reactant amounts;

(c) formation of ammonia gas; (d) increasing pressure on reactants.

13. Which statement is true for a liquid/gas mixture in equilibrium?

(*a*) the equilibrium constant is dependent on temperature;

(b) the amount of the gas present at equilibrium is independent of pressure;

(c) all interchange between the liquid and gas phases has ceased;

(*d*) all of the above.

14. Why doesn't catalyst shift the equilibrium position?

(a) it speeds up both the forward and reverse reaction;

(b) it is recoverable unchanged at the end of a reaction;

(c) it increases the concentration of both the reactants and products equally;

(d) it provides a surface site at which the reaction can occur.

15. $H_2 + S \leftrightarrow H_2S + energy$

In this reversible reaction, select the factor that will shift the equilibrium to the right.

(a) adding heat; (b) adding H_2S ;

(c) blocking hydrogen gas reaction; (d) removing hydrogen sulphide gas.

16. To an equilibrium mixture of $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$, some helium, an inert gas, is added at constant volume. The addition of helium causes the total pressure to double. Which of the following is true?

(a) The concentrations of all three gases are unchanged

(b) [SO₃] increases

(c) The number of moles of SO3 increases

(d) [SO₂] increases

17. For the endothermic reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, which of the following actions would favour shifting the equilibrium position to form more CO_2 gas?

(a) decreasing the system temperature;

- (b) both decreasing the system temperature and increasing the system pressure;
- (c) increasing the system pressure;
- (d) increasing the system temperature.

18. Consider the following exothermic reaction:

 $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g).$

Which of the following changes would not increase the amount of NH_3 produced from given quantities of N_2 and H_2 ?

(*a*) decrease in *V*; (*b*) increase in *p*;

(c) remove some NH_3 and re-establish equilibrium; (d) increase in T.

19. For which one of the following equilibrium equations will K_p equal K_c ?

(*a*) $PCl_5 \leftrightarrow PCl_3 + Cl_2$;

(b) $\operatorname{COCl}_2 \leftrightarrow \operatorname{CO} + \operatorname{Cl}_2$;

(c) $H_2 + I_2 \leftrightarrow 2HI$;

(d) $3H_2 + N_2 \leftrightarrow 2NH_3$.

20. Which of the following shifts the equilibrium of the following reaction to the right? $A(g) + B(g) + C(g) \leftrightarrow A(g) + BC(g)$ (*a*) addition of more A;

(*b*) removal of B;

(c) increasing the pressure;

(d) decreasing the temperature.

21. In the reaction below, how could we cause the equilibrium to shift to the left? $CH_4(g) + 2H_2S(g) \leftrightarrow CS_2(g) + 4H_2(g)$ ($K = 2.5 \cdot 10^{-3}$)

(a) increasing the pressure by adding an inert gas at constant volume;

(b) increasing the pressure by decreasing the volume;

(c) increasing the volume by adding an inert gas at constant pressure;

(d) increasing the pressure and the volume by adding an inert gas.

22. The equilibrium expression, $K_p = P(CO_2)$ represents the reaction :

(a) $C(s) + O_2(g) \leftrightarrow CO_2(g);$

(b) $CO(g) + \frac{1}{2}O_2(g) \leftrightarrow CO_2(g);$

(c) $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g);$

(d) $CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s)$.

23. Equilibrium is established in the reversible reaction 4HCl(g) + O₂(g) ↔ 2H₂O(g) + 2Cl₂(g) (ΔH° = -114.4 kJ).
Which one of the following changes will not increase the amount of Cl₂ present at equilibrium? (*a*) removing H₂O(g);
(*b*) increasing the total gas pressure in the system;

(c) decreasing the volume of the container;

(d) raising the temperature.

24. For the equilibrium $N_2(g) + 3H_2(g) = 2NH_3(g)$, the value of K_c at 227°C is 152. What is the value of K_p at 227°C? Assume that pressures are measured in atmospheres.

 $(a)^{9.03} \cdot 10^{-2};$

(*b*) 12.5;

(c) 347; (d) $2.79 \cdot 10^{-4}$

25. Of the following equilibriums, which one will shift to the left in response to a decrease in volume?

(a) $CO_2(g) + H_2O(1) \leftrightarrow H_2CO_3(aq);$ (b) $P_2(g) + Cl_2(g) \leftrightarrow 2HCl(g)$ (c) $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g);$ (d) $2SO_3(g) \leftrightarrow 2SO_2(g) + O_2(g).$

26. For the following reaction at 500 K

 $C(s) + CO_2(g) \leftrightarrow 2CO(g)$

the equilibrium mixture contained CO_2 and CO at partial pressures of 7.6 atm and 3.2 atm respectively.

The value of the K_p is (*a*) 2.4 atm; (*b*) 18.1 atm; (*c*) 0.6 atm; (*d*) 1.0 atm.

27. If the equilibrium concentrations found in the reaction

 $2A(g) + B(g) \leftrightarrow C(g)$ are $[A] = 2.4 \cdot 10^{-2} \text{ M}$, $[B] = 4.6 \cdot 10^{-3} \text{ M}$, and $[C] = 6.2 \cdot 10^{-3} \text{ M}$, calculate the value of K_c .

(a) $2.3 \cdot 10^3$; (b) $1.8 \cdot 10^{-2}$; (c) $4.3 \cdot 10^{-4}$; (d) $5.8 \cdot 10^2$.

28. For the reaction $2NO(g) + Br_2(g) \leftrightarrow 2NOBr(g)$ $K_c = 1.32 \cdot 10^{-2}$ at 1000 K. Determine the value of K_p that corresponds to this value of K_c at that temperature. (a) 1.08; (b) 0.161; (c) 1.61 \cdot 10^{-4}; (d) 2.39 \cdot 10^{-8}.

29. At 25°C, for $3O_2(g) \leftrightarrow 2O_3(g) K_c = 2.9 \cdot 10^{-59}$. If at equilibrium, the concentration of O_2 is 0.040 M, what is the concentration of O_3 ? (*a*) $1.9 \cdot 10^{-63}$ M; (*b*) $4.3 \cdot 10^{-32}$ M; (*c*) $2.3 \cdot 10^{31}$ M; (*d*) $1.2 \cdot 10^{21}$ M.

30. Equilibrium is established in a sealed 1.75 L vessel at 250°C in the reaction $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$ The quantities found at equilibrium are 0.562 g PCl₅, 1.950 g PCl₃, and 1.007 g Cl₂. (*a*) Kc = 3.49; (*b*) Kc = 0.0139; (*c*) Kc = 2.00; (*d*) Kc = 0.0427.

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