

Physical Chemistry Seminar

solving physicochemical problems

1. Core basic concepts

1. Give the units of physical quantities defined by the expressions below

$$-\int_{V_1}^{V_2} p_{\text{prac}} dV; \quad \left(\frac{\partial U}{\partial T}\right)_V dT; \quad \left(\frac{\partial p}{\partial T}\right)_V; \quad \left[-p + T\left(\frac{\partial p}{\partial T}\right)_V\right] dV; \quad \frac{dn_i}{v_i}$$

gas constant, Boltzmann constant, Faraday constant

2. Calculate the indicated derivatives

a) $PV = nRT$; P with respect of V

b) $d = \frac{m}{V}$; $\left(\frac{\partial d}{\partial m}\right)_V = \left(\frac{\partial d}{\partial V}\right) =$

c) $\rho = \frac{PM}{RT}$; ρ with respect of T

d) $H = a + bT + cT^2 + \frac{d}{T}$; H with respect of T

e) $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$; P with respect of V

f) $V = \pi r^2 h$; $\left(\frac{\partial V}{\partial r}\right)_h = \left(\frac{\partial V}{\partial h}\right)_r =$

3. Sketch the curves of the coefficient of isothermal expansion and compressibility for an ideal gas.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{T,\xi}$$

4. Write an expression for the total differential of the following quantities:

$$V = f(r, h) = \pi r^2 h \quad c^2 \frac{2kT}{m} \quad V = 1001.93 + 111.5282m + 0.64698m^2$$

$$\ln p = \frac{-\Delta H}{Rt} + K \quad w = N \ln N - n_i \ln n_i$$

5. Calculation of errors of a complex function using the total differential method.

a) Calculate the absolute error of the measurement of the molar concentration of sodium hydroxide, knowing that a technical scale was used to weigh the mass, the volume was measured with a burette, and the mass numbers were read from the periodic table, rounded from integers.

Data: $m=100\text{g}$, $V=500\text{ml}$.

b) Calculate the absolute error of the measurement of the percentage concentration of potassium hydroxide, knowing that an analytical balance was used to weigh the KOH mass, and a technical balance was used to weigh the water.

Data: $m_{\text{KOH}}=10.0000\text{g}$, $m_{\text{water}}=500.0\text{g}$.

2. First law of thermodynamics

2.1. Gas laws, ideal gases

1. The air sample occupies a volume of 1 liter at a temperature of 25°C and a pressure of 1 atm. Calculate the pressure at which it will be compressed to 100 cm³ at this temperature.
2. The ideal gas undergoes isothermal compression, which reduces its volume by 2.20 L. The final pressure and volume of the gas are 3.78×10^3 Torr and 4.65 L, respectively. Calculate the initial pressure of the gas (in Torr and atmospheres).
3. To what temperature should a sample of ideal gas with a volume of 1.0 L and at room temperature be cooled in order to reduce its volume to 100 cm³?
4. A sample of neon weighing 255 mg occupies a volume of 3.00 L at a temperature of 122 K. Calculate the pressure of the sample, assuming that neon behaves as an ideal gas.
5. On a winter day, when the temperature was -5°C, a car tire was inflated to a pressure of 24 lb · in⁻² (pounds per square inch) (1 atm = 14.7 lb · in⁻²). What will the pressure be, assuming that the tire is airtight and its volume is constant, when the temperature is 35°C?
6. At a temperature of 500°C and a pressure of 0.92 atmospheres, 3.71 g of sulfur occupies a volume of 1 liter. What is the molar mass of a sulfur molecule under these conditions?
7. Calculate the mass of water vapor present in a room with a volume of 400 m³, containing air at a temperature of 27°C on a day with a relative humidity of 60%. The air pressure is 26.74 Tr.
8. Can a 131 g sample of xenon, behaving like an ideal gas in a 1.0 L vessel, exert a pressure of 20 atm at a temperature of 25°C? What pressure will it exert if it behaves like a van der Waals gas?
9.

A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 dm³. The final pressure and volume of the gas are 1.97 bar and 2.14 dm³, respectively. Calculate the original pressure of the gas in (a) bar, (b) Torr.
10.

A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23°C. What can its pressure be expected to be when the temperature is 11°C?
11.

A homeowner uses 4.00×10^3 m³ of natural gas in a year to heat a home. Assume that natural gas is all methane, CH₄, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20°C. What is the mass of gas used?
12.

What pressure difference must be generated across the length of a 15 cm vertical drinking straw in order to drink a water-like liquid of density 1.0 g cm⁻³?
- 13.

Calculate the mass of water vapour present in a room of volume 250 m^3 that contains air at 23°C on a day when the relative humidity is 53 per cent.

14.

A manometer like that described in Exercise 1.6a contained mercury in place of water. Suppose the external pressure is 760 Torr, and the open side is 10.0 cm higher than the side connected to the apparatus. What is the pressure in the apparatus? (The density of mercury at 25°C is 13.55 g cm^{-3} .)

15.

At 100°C and 16.0 kPa, the mass density of phosphorus vapour is 0.6388 kg m^{-3} . What is the molecular formula of phosphorus under these conditions?

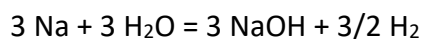
16.

A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.

2.2. Quantification of work, heat exchange, and heat capacity

1. A chemical reaction takes place in a tank with a cross-sectional area of 100 cm^2 . One side of the tank is closed with a freely movable piston. As a result of the reaction, the piston moved 10 cm, overcoming a pressure of 1 atmosphere. Calculate the work done by the system.

2. Calculate the work done as a result of the reaction of three moles of sodium with water at a temperature of 20°C .



3. In isothermal reversible compression of 52 mmol of gas at a temperature of 260 K, its volume decreased to one third of the initial volume. Calculate the work done in this process.

4. Calculate the heat required to melt 750 kg of metallic sodium at a temperature of 371 K, given that $\Delta H_{\text{fus}} = 2.60 \text{ kJ/mol}$.

5. How much heat must be used to bring 10 moles of water at a temperature of 20°C to boiling point under normal pressure, assuming that the specific heat of water is $4.18 \text{ J/(g}\cdot\text{K)}$?

6. Amount of 1747 J of heat was added to 100 g of benzene at a temperature of 293 K, after which the temperature of the sample rose to 303 K. Calculate the specific heat capacity and molar heat capacity of benzene at constant pressure.

7. Calculate how much heat must be supplied to heat 5 moles of nitrogen from 0°C to 200°C , assuming that nitrogen behaves like an ideal gas:

- a) at constant pressure,
- b) at constant volume.

8. The molar heat of vaporization of sulfur dioxide at a temperature of 263 K is 24.9 kJ/mol . Calculate the heat exchanged and the work done for the transformation during which 100 g of SO_2 evaporates at this temperature under a pressure of 105 Pa.

9. Calculate the amount of heat that must be supplied to convert 1 kg of ice at a temperature of -40°C into water vapor at a temperature of 200°C . The specific heats are: ice $2.02 \text{ J/(g}\cdot\text{K)}$, water $4.18 \text{ J/(g}\cdot\text{K)}$, water vapor $1.92 \text{ J/(g}\cdot\text{K)}$. The heat of fusion of ice is 334 J/g , and the heat of vaporization of water is 2259 J/g .

10. 1 mole of a diatomic ideal gas with an initial temperature of 10°C and a volume of 5 dm^3 expands against a constant external pressure of 1 atmosphere and reaches a temperature of -70°C and a volume of 12 dm^3 after the transformation. Calculate the work done and the heat exchanged with the environment.

11. A mass of $2 \cdot 10^{-3} \text{ kg}$ of Helium at a temperature of 273 K and a pressure of $2 \cdot 10^5 \text{ Pa}$ is expanded isothermally to a volume of $2 \cdot 10^{-3} \text{ m}^3$. Calculate the work done by the system.

12. A chemical reaction takes place in a tank whose cross-sectional area is 100 cm^2 . The tank is closed at one end by a free-moving piston. As a result of the reaction, the piston moves 10 cm, overcoming a pressure of 1.0 atm. Calculate the work done by the system.

13. In the isothermal reversible compression of 52.0 mmol of an ideal gas at 260 K, its volume is reduced to one third of its initial volume. Calculate the work W in this process.

14. When 229 J of heat is added to 3.0 moles of Ar(g) at constant pressure, the temperature of the sample increases by 2.55 K. Calculate the molar heat capacity of this gas at constant pressure and constant volume.

15. The mass of a typical sugar cube (sucrose) is 1.5 g. Calculate the amount of energy released when it burns in air. How high could a 65 kg person climb after eating such a sugar cube, assuming that 25% of the energy is used for work?

2.3. Heat balance

1. Calculate the amount of heat that must be supplied to convert 1 kg of ice at a temperature of -40°C into water vapor at a temperature of 200°C . The specific heats are: ice $2.02 \text{ J}/(\text{g}\cdot\text{K})$, water $4.18 \text{ J}/(\text{g}\cdot\text{K})$, water vapor $1.92 \text{ J}/(\text{g}\cdot\text{K})$. The enthalpy of fusion of ice is 334 J/g , and the enthalpy of vaporization of water is 2259 J/g .

2. A closed bottle with a volume of $V_0 = 500 \text{ cm}^3$ contains mineral water at a temperature of $t_0 = 20^{\circ}\text{C}$. After some time, the sun heated the bottle to a temperature of $t_k = 40^{\circ}\text{C}$. Calculate how much solar energy the bottle absorbed.

Given: mass of glass $m_{\text{glass}} = 300 \text{ g}$, specific heat of glass $c_{\text{glass}} = 0.75 \text{ kJ}/(\text{kg K})$, specific heat of water $c_w = 4.18 \text{ kJ}/(\text{kg K})$, density of water $d_w = 1 \text{ g/cm}^3$.

3. An ice cube with a mass of $m_L = 20 \text{ g}$ and a temperature of $t_L = -5^{\circ}\text{C}$ was placed in a polystyrene cup containing tea with a mass of $m_h = 100 \text{ g}$ and a temperature of $t_h = 80^{\circ}\text{C}$. The entire ice cube melted. Calculate the final temperature of the tea, assuming that the heat exchange between the system and the environment can be neglected. Data: specific heat of water $c_w = 4.18 \text{ J}/(\text{g deg})$, specific heat of ice $c_{wL} = 2.09 \text{ J}/(\text{g deg})$, heat of fusion of ice $q_{tL} = 332 \text{ J/g}$.

4. Estimate the cost of boiling water at a temperature of $t_0 = 150^{\circ}\text{C}$ in an electric kettle with a power of $P = 2000 \text{ W}$ and a capacity of 1.5 litres. Assumption: process efficiency $\eta = 80\%$, price of electricity per 1 kWh $p = 0.1 \text{ euro}$.

2.4. Internal energy, 1st law of thermodynamics

1. 4 moles of nitrogen were heated from 273 K to 473 K at a pressure of 1 atmosphere. Calculate the increase in internal energy in this process. The average specific heat capacity of nitrogen in the temperature range considered is $1021 \text{ J}/(\text{kg}\cdot\text{K})$.

2. Calculate the amount of heat absorbed by the system during isothermal reversible expansion of 50 grams of oxygen at a pressure of 1 atmosphere to a volume of 100 dm^3 at a temperature of 298 K.

3. 1 mole of a monatomic ideal gas with an initial temperature of 20°C and a volume of 4 dm^3 expands against a constant external pressure of 1 atmosphere and reaches a temperature of -80°C after the transformation. Calculate the change in internal energy in this process.

4. Calculate the change in internal energy during the evaporation of 50 grams of ethanol at boiling point under normal pressure. The molar enthalpy of vaporization of ethanol is 39.455 kJ/mol , and the molar volume of ethanol vapor is equal to $27.99 \cdot 10^{-3} \text{ m}^3/\text{mol}$.

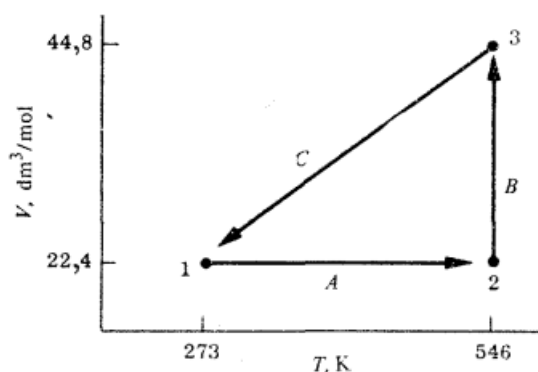
5. One mole of helium undergoes isothermal expansion from a volume of 11.2 dm^3 to a volume of 22.4 dm^3 at a temperature of 273 K in three ways: a) free expansion, b) expansion

under a constant external pressure of 1 atmosphere, c) reversible expansion. Calculate the work, heat, and change in internal energy for all cases.

6. Calculate the work done, heat exchanged, and change in internal energy in the following transformations of 2 moles of a monatomic ideal gas:

- isothermal reversible expansion from 10 dm^3 to 30 dm^3 at a temperature of 273 K ,
- isochoric increase in temperature from 273 K to 303 K .

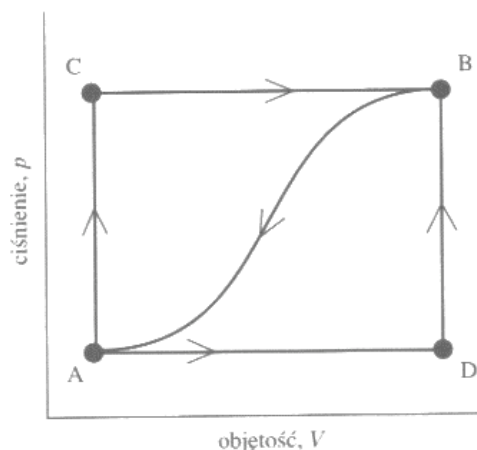
7. 1 mole of a monatomic ideal gas undergoes a closed cycle of three reversible transformations A, B, and C and reaches states 1, 2, and 3, respectively. Determine the missing values in the tables.



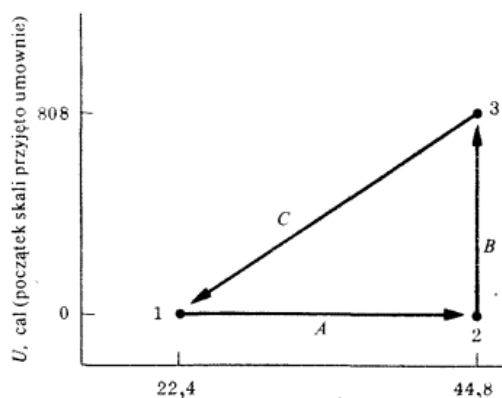
Stan	P		V, dm ³	T, K
	N/m ²	atm		
1			22,4	273
2			22,4	546
3			44,8	546

Przemiana	Nazwa przemiany	q		w		ΔU
		J	cal	J	cal	J
A						
B						
C						
Sumaryczna przemiana						

8. Gdy układ przechodzi od stanu A do B wzdłuż drogi ACB (rys. poniżej), 80 J ciepła przepływa do układu i wykonuje on pracę 30 J . a) Ile ciepła przepływa do układu wzdłuż drogi ADB, jeśli wykonana praca wynosi 10 J ? b) Gdy układ wraca ze stanu B do A wzdłuż zaznaczonej krzywej, praca wykonana na układzie wynosi 20 J . Czy układ pochłania, czy uwalnia ciepło i w jakiej ilości? c) Jeśli $U_d - U_a = +40 \text{ J}$, oblicz ciepło absorbowane w procesach AD i DB.



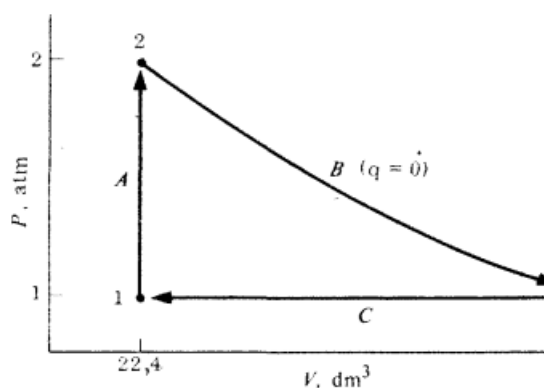
9. 1 mole of a monatomic ideal gas, initially under normal conditions, undergoes a cycle of reversible transformations, as shown in the figure below. Determine the missing values in the tables.



Stan	P		V, dm ³	T, K
	N/m ²	atm		
1	10^5	1	22,4	273
2			44,8	
3			44,8	

Przemiana	Nazwa przemiany	q		w		ΔU
		J	cal	J	cal	J
A						
B						
C						
Sumaryczna przemiana						

10. 1 mole of a monatomic ideal gas undergoes three reversible transformations in sequence, as illustrated in the figure below. Determine the missing values in the tables.



Stan	P		V, dm³	T, K
	N/m²	atm		
1	10⁵	1	22,4	
2	2 · 10⁵	2	22,4	
3	10⁵	1		

Przemiana	Nazwa przemiany	q		w	
		J	cal	J	cal
A					
B					
C					
Sumaryczna przemiana					

11. Three moles of water are evaporated isothermally at 373 K and isobarically at 101.3 kPa. The molar heat of vaporization of water is 40.66 kJ·mol⁻¹. Calculate the change in internal energy in this process.

12. A sample containing 1.00 mol H₂O (g) undergoes isothermal reversible condensation at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 kJ·mol⁻¹. Calculate w, q, ΔU, ΔH for this process.

2.5. Enthalpy, Hess's Law; Thermochemical Calculations, Kirchhoff's Law

1. Calculate the standard enthalpy of combustion of toluene, knowing that the standard enthalpies of formation are: toluene 12.4 kJ/mol; carbon dioxide -393.5 kJ/mol; water vapor -285.8 kJ/mol.

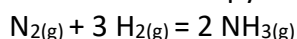
2. Calculate the enthalpy of combustion of glucose under standard conditions, knowing that the enthalpy of formation of glucose is -1268 kJ/mol, the enthalpy of formation of carbon dioxide is -393.5 kJ/mol, and the enthalpy of formation of water is -285.8 kJ/mol.

3. Calculate the standard enthalpy of combustion of ethane and the change in internal energy, knowing that the standard enthalpies of formation are: ethane -83.8 kJ/mol; carbon dioxide -393.5 kJ/mol; water vapor -285.8 kJ/mol.

4. Find the enthalpy of the methane formation reaction, knowing that the standard enthalpies of combustion of graphite, hydrogen, and methane are -394.069 kJ/mol, -286.218 kJ/mol, and -891.59 kJ/mol, respectively.

5. The standard enthalpy of combustion of dimethyl ether gas is -1460.3 kJ/mol. Calculate the standard enthalpy of formation of this compound.

6. Using the bond energy values, calculate the enthalpy of the reaction.



7. Knowing that the enthalpy of the synthesis reaction of carbon monoxide from elements at a temperature of 298K is -110.5 kJ, and knowing that the molar heat capacities of graphite, oxygen, and carbon monoxide are 8.5 J/mol·K, 29.4 J/mol·K, and 29.1 J/mol·K, respectively, calculate the enthalpy of this reaction at a temperature of 350K. (mol·K) ; 29.4 J/(mol·K) and 29.1 J/(mol·K), calculate the enthalpy of this reaction at a temperature of 350K.

8. The standard enthalpy of the reaction $2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$ at a temperature of 298K is -483.6 kJ. The heat capacities of the reactants are: water 33.6 J/(mol·K); hydrogen 28.8 J/(mol·K); oxygen 29.4 J/(mol·K). Calculate the enthalpy of this reaction at a temperature of 423K.

9. Knowing standard reaction enthalpies

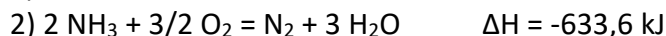


calculate the standard enthalpy of reaction

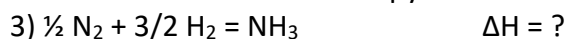


10.

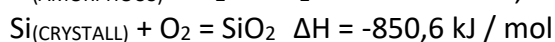
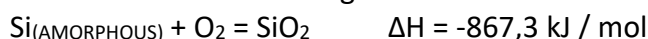
Knowing standard reaction enthalpies



calculate the standard enthalpy of reaction



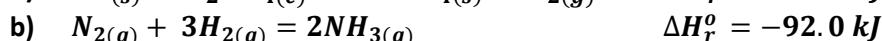
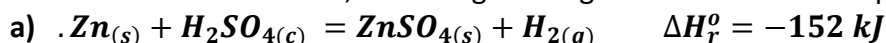
11. Based on the following data



Calculate how much heat will be released during the transition of 140 grams of amorphous silicon into crystalline silicon.

12. After burning 120 mg of naphthalene, the temperature in the calorimeter rose by 3.05 K. Calculate the calorimeter constant. How much will the temperature in the calorimeter rise if we burn 100 mg of phenol under the same conditions? The enthalpy of the naphthalene combustion reaction is -5157 kJ/mol, and the enthalpy of the phenol combustion reaction is -3054 kJ/mol.

13. Calculate the change in internal energy resulting from the following chemical reactions under standard conditions, according to the given stoichiometric equations:



14. Calculate the enthalpy change resulting from heating 5 moles of hydrogen sulphide from 373 K to 473 K at constant pressure, knowing that the molar specific heat of H_2S changes according to the equation:

$$C_p = 36.86 + 0.0079 T$$

15. The heat of formation of $\text{C}_2\text{H}_5\text{OH}_{(\text{l})}$ is -276 kJ/mol (-66 kcal/mol), while the heat of combustion of the isomer $\text{CH}_3\text{OCH}_{3(\text{g})}$ to $\text{CO}_{2(\text{g})}$ i $\text{H}_2\text{O}_{(\text{l})}$ is -1456 kJ/mol (-348 kcal/mol). Furthermore, it is known that the heat of formation of $\text{H}_2\text{O}_{(\text{l})}$ is -285 kJ/mol (-68 kcal/mol), and the heat of combustion of carbon to $\text{CO}_{2(\text{g})}$ is -393 kJ/mol (-94 kcal/mol). All data refer to a temperature of 25°C.

a) Calculate $\Delta H_{298\text{K}}$ of the isomerization reaction: $\text{C}_2\text{H}_5\text{OH}_{(\text{l})} = \text{CH}_3\text{OCH}_{3(\text{g})}$

b) Assuming that $\Delta H_{298\text{K}}$ of this reaction is -41.8 kJ (-10 kcal), calculate $\Delta U_{298\text{K}}$

16. As a result of combustion of 0.5 g of naphthalene ($M = 128.2 \text{ g}\cdot\text{mol}^{-1}$) in a bomb calorimeter, the temperature of the system increased by 1.92°C. The heat capacity of the calorimeter system is $K = 10.47 \text{ kJ}\cdot\text{K}^{-1}$, and the average measurement temperature is about 25°C. Calculate the molar heat of combustion of naphthalene at constant pressure and the given temperature.

- 17.** The value of $C_{p,m}$ for an ideal gas sample is found to vary with temperature according to the expression $C_{p,m} = 20.17 + 0.3665T$. Calculate q , w , ΔU , and ΔH for 1.00 mole of this gas as the temperature increases from 25°C to 200°C a) at constant pressure, b) at constant volume.
- 18.** From the standard enthalpy of combustion, calculate the standard enthalpy of formation of butane at 25°C.
- 19.** After burning 120 mg of naphthalene, $C_{10}H_8(s)$, the temperature in the bomb calorimeter increased by 3.05 K. Calculate the calorimeter constant. By how much will the temperature increase if we burn 100 mg of phenol, $C_6H_5OH(s)$, under the same conditions?
- 20.** After burning 0.3212 g of glucose in a bomb calorimeter with a constant of $641 \text{ J}\cdot\text{K}^{-1}$, the temperature increased by 7.793 K. Calculate: a) the standard molar energy of combustion, b) the standard internal energy of combustion, and c) the standard enthalpy of formation of glucose.

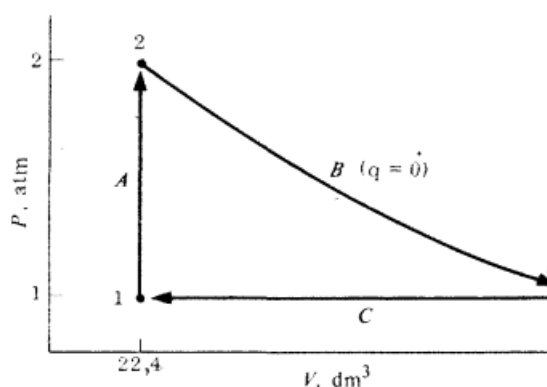
Assessment

Select three out of five

A1. A 15 g magnesium ribbon is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of this reaction. The atmospheric pressure is 1.0 atm and the temperature is 25°C.

A2. Steel hardening consists in rapid cooling of the heated metal. After throwing steel with a mass of $m_s = 5$ kg and a temperature of $t_s = 800^\circ\text{C}$ into water with a mass of $m_w = 20$ kg and a temperature of $t_w = 20^\circ\text{C}$, 1% of the water evaporated. Calculate the final temperature of the water together with the hardened element, assuming that the heat exchange of the system with the environment can be neglected. Given: specific heat of water $c_w = 4.18$ J/(g deg), heat of vaporization of water $q_v = 2260$ J/g, specific heat of steel $c_s = 0.46$ J/(g deg).

A3. mole of a monatomic ideal gas undergoes three successive reversible changes, as illustrated in the figure below. Determine the missing values in the tables.



point	P		V, dm³	T, K
	N/m²	atm		
1	10^5	1	22,4	
2	$2 \cdot 10^5$	2	22,4	
3	10^5	1		

transformation	name	q		w		J
		J	cal	J	cal	
A						
B						
C						
Total value: ABCA						

A4. A system consisting of 9 g of solid H_2O at 263 K is heated to form steam at 413 K. Calculate the enthalpy change ΔH for this change. The specific heat of ice is 2.09 J·g⁻¹·K⁻¹. The heat of fusion of ice is 333.94 J·g⁻¹, the heat of vaporization of water is 2261.34 J·g⁻¹, the specific heat of water vapor 33.98 J·mol⁻¹·K⁻¹.

A5. A sample containing 1.00 mol of Ar was subjected to isothermal expansion at 0°C from a volume of 22.4 L to 44.8 L assuming:

- in a reversible manner,
- under a constant external pressure equal to the final gas pressure,
- in a free manner (at zero external pressure).

Calculate q , w , ΔU and ΔH for all three cases.

3. Thermodynamics impulses (stimuli)

3.1. Second law of Thermodynamics

1. Calculate the change in entropy that occurs when 5 moles of hydrogen are cooled from 350 K to 270 K. The heat capacity of hydrogen at constant pressure is $C_p = 28.9 \text{ J}/(\text{mol}\cdot\text{K})$. Cooling occurs under the following conditions:

a) isobaric, b) isochoric.

2. What final volume corresponds to an entropy change of $38.28 \text{ J}/(\text{mol}\cdot\text{K})$ if 1 mol of an ideal gas occupying 0.02 m^3 under initial conditions undergoes isothermal expansion?

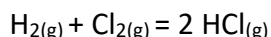
3. After heating 4 dm^3 of argon at a pressure of 2 atmospheres, the volume of the gas increased to 12 dm^3 . The initial temperature was 320 K. Calculate the change in entropy assuming that the gas behaves like an ideal gas.

4. The entropy of liquid ethanol at a temperature of 298 K is equal to $160.7 \text{ J}/(\text{mol}\cdot\text{K})$. The vapor pressure of ethanol is $7.87 \cdot 10^3 \text{ Pa}$. The heat of vaporization of ethanol at 298 K is 42.6 kJ/mol . Calculate the entropy of 1 mole of ethanol vapor at a pressure of $9.5 \cdot 10^3 \text{ Pa}$ at a temperature of 313 K. The molar heat capacity of ethanol vapor is $145 \text{ J}/(\text{mol}\cdot\text{K})$.

5. A tank with a volume of 30 dm^3 was divided into two parts with volumes of 20 dm^3 and 10 dm^3 . Two moles of helium were introduced into the larger part of the tank, and one mole of oxygen into the smaller part. The temperature was 298 K. Calculate the change in entropy that occurs when the partition separating the two parts of the tank is removed and the system is heated to 450 K.

6. 1.5 moles of water in the form of ice at a temperature of 263 K were added to 6 moles of water at a temperature of 323 K. Calculate the change in entropy associated with the processes taking place if the final temperature is 296 K. The molar heat capacity of ice is $36.4 \text{ J}/(\text{mol}\cdot\text{K})$; water is $75.3 \text{ J}/(\text{mol}\cdot\text{K})$; the enthalpy of fusion of ice is 6007 J/mol .

7. Using the standard entropies of the reactants, calculate the standard entropy of the reaction.



$S^\circ_{(\text{Cl}_2)} = 223,1 \text{ J}/(\text{mol}\cdot\text{K})$; $S^\circ_{(\text{H}_2)} = 130,7 \text{ J}/(\text{mol}\cdot\text{K})$; $S^\circ_{(\text{HCl})} = 186,9 \text{ J}/(\text{mol}\cdot\text{K})$.

8. Knowing that the molar entropy of helium at a temperature of 298 K is equal to $126.2 \text{ J}/(\text{mol}\cdot\text{K})$, calculate the entropy of 1 mole of this gas at a temperature of 700 K:

- a) at constant pressure,
b) at constant volume.

The heat capacity of helium at constant pressure is $20.8 \text{ J}/(\text{mol}\cdot\text{K})$.

9. Calculate the change in entropy when 2 moles of nitrogen are heated from 250 K to 450 K while being compressed from a volume of 40 L to 20 L. Treat nitrogen as an ideal gas.

10. Calculate the change in entropy of 9 g of ice when it melts at 273 K. The latent heat of fusion of ice is 333.6 J/g .

11. Calculate the increase in entropy when 1.00 mol of a monatomic ideal gas with $C_{p,m} = \frac{5}{2}R$ is heated from 300 K to 600 K while expanding from 30.0 L to 50.0 L.

- 12.** Calculate the entropy change when 50 g of water at 80°C is mixed with 100 g of water at 10°C in a thermally insulated container ($C_{p,m}$ of water is 75.5 J·K⁻¹·mol⁻¹).
- 13.** The molar heat capacity of hydrogen at constant pressure is given by the equation $C_p = 27.2 + 0.0037 T$. Calculate the change in entropy during the expansion of 1 mole of hydrogen as the temperature changes from $T_1 = 233$ K to $T_2 = 523$ K.
- 14.** What final volume does an entropy change of 38.28 J/(mol·K) correspond to if 1 mole of an ideal gas occupying 0.02 m³ initially undergoes an isothermal expansion?
- 15.** After heating 4 dm³ of argon at a pressure of 2 atmospheres, the volume of the gas increased to 12 dm³. The initial temperature was 320 K. Calculate the change in entropy, assuming that the gas behaves as an ideal gas.
- 16.** The entropy of liquid ethanol at 298 K is 160.7 J/(mol·K). The vapor pressure of ethanol is 7.87·10³ Pa. The heat of vaporization of ethanol at 298 K is 42.6 kJ/mol. Calculate the entropy of 1 mole of ethanol vapor at a pressure of 9.5·10³ Pa and a temperature of 313 K. The molar heat capacity of ethanol vapor is 145 J/(mol·K).
- 17.** A tank with a volume of 30 dm³ was divided into two parts with volumes of 20 dm³ and 10 dm³. 2 moles of helium were introduced into the larger part of the tank, and 1 mole of oxygen into the smaller part. The temperature was 298 K. Calculate the entropy change that occurs when the partition dividing the two parts of the tank is removed and the system is heated to 450 K.
- 18.** To 6 moles of water at 323 K are added 1.5 moles of water in the form of ice at 263 K. Calculate the entropy change associated with the processes occurring if the final temperature is 296 K. The molar heat capacity of ice is 36.4 J/(mol·K); of water 75.3 J/(mol·K); the enthalpy of fusion of ice is 6007 J/mol.

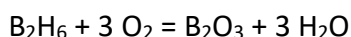
3.2. Gibbs free energy

1. Calculate the change in Gibbs free energy of the reaction $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$ occurring in gaseous form and under standard conditions, given the standard free enthalpies of formation of the reactants: $\text{C}_2\text{H}_4 = 68.1 \text{ kJ/mol}$; $\text{C}_2\text{H}_6 = -32.9 \text{ kJ/mol}$.

2. Calculate the change in Gibbs free energy of the ethane combustion reaction, given the standard free enthalpies of formation of the reactants: $\text{CO}_2 = -394.95 \text{ kJ/mol}$; $\text{H}_2\text{O} = -237.53 \text{ kJ/mol}$; $\text{C}_2\text{H}_6 = -82.93 \text{ kJ/mol}$.

3. Calculate the Gibbs free energy of the reaction $\text{CO}_2 + 4 \text{H}_2 = \text{CH}_4 + 2 \text{H}_2\text{O}$ occurring in the gas phase and under standard conditions, given the standard enthalpies and entropies of the reactants. Enthalpies: $\text{CH}_4 = -74.8 \text{ kJ/mol}$; $\text{H}_2\text{O} = -241.8 \text{ kJ/mol}$; $\text{CO}_2 = -393.5 \text{ kJ/mol}$
Entropies: $\text{CH}_4 = 186.1 \text{ J/(mol}\cdot\text{K)}$; $\text{H}_2\text{O} = 188.7 \text{ J/(mol}\cdot\text{K)}$; $\text{CO}_2 = 213.6 \text{ J/(mol}\cdot\text{K)}$; $\text{H}_2 = 130.6 \text{ J/(mol}\cdot\text{K)}$.

4. Using the information below, determine the standard Gibbs free energy of the reaction:



	B_2H_6	O_2	B_2O_3	H_2O
$\Delta H_{\text{tw}} [\text{kJ/mol}]$	35,6	0	-1273,5	-285,8
$S^\phi [\text{J/(mol}\cdot\text{K)}]$	232,1	205,2	54,0	70,0

5. Determine the temperature at which calcite decomposes according to the reaction



Enthalpies: $\text{CaCO}_3 = -1206,9 \text{ kJ/mol}$; $\text{CaO} = -635,9 \text{ kJ/mol}$; $\text{CO}_2 = -393,51 \text{ kJ/mol}$

Entropies: $\text{CaCO}_3 = 92,9 \text{ J/(mol}\cdot\text{K)}$; $\text{CaO} = 39,75 \text{ J/(mol}\cdot\text{K)}$; $\text{CO}_2 = 213,74 \text{ J/(mol}\cdot\text{K)}$.

6. Which of the allotropic forms of carbon, graphite or diamond, is more durable under standard conditions?

Combustion enthalpy: graphite = $-393,514 \text{ J/mol}$; diamond = $-395,405 \text{ J/mol}$

Molar entropy: graphite = $5.69 \text{ J/(mol}\cdot\text{K)}$; diamond = $2.439 \text{ J/(mol}\cdot\text{K)}$.

7. Assuming that 3 mmol of nitrogen occupying a volume of 36 cm^3 at a temperature of 300 K expands to 60 cm^3 , calculate the ΔG of this process.

8. Calculate the change in free enthalpy of an ideal gas compressed isothermally at a temperature of 40°C from 1.8 to 29.5 atmospheres.

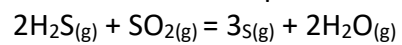
9. When 2 moles of gas at a temperature of 330 K and a pressure of 3.5 atm were subjected to isothermal compression, its free enthalpy increased by 8.25 kJ. Calculate the final pressure of the gas.

10. The chemical affinity value of pure components, A_o , for the isomerization reaction of 1 mole of cis-pent-2-ene to trans-pent-2-ene at a temperature of 400 K is 3.67 kJ. Calculate the equilibrium constant for the isomerization reaction.

11. Knowing the standard free enthalpy values of the reactants, determine the equilibrium constant of the reaction $\text{Al}_2\text{O}_3 + 3 \text{SO}_3 = \text{Al}_2(\text{SO}_4)_3$

$\Delta G^\ominus_{\text{Al}_2(\text{SO}_4)_3} = -3094,2 \text{ kJ/mol}$; $\Delta G^\ominus_{\text{Al}_2\text{O}_3} = -1692,88 \text{ kJ/mol}$; $\Delta G^\ominus_{\text{SO}_3} = -427,96 \text{ kJ/mol}$.

12. Calculate the equilibrium constant K_p at 298 K for the reaction:



Knownig: $\Delta G_{\text{H}_2\text{O}}^\ominus = -228.71 \text{ kJ/mol}$, $\Delta G_{\text{SO}_2}^\ominus = -300.8 \text{ kJ/mol}$, $\Delta G_{\text{H}_2\text{S}}^\ominus = -33.06 \text{ kJ/mol}$

3.3. Equilibrium and equilibrium constant

1. A mixture of gases obtained in the reaction: $2 \text{SO}_{2(g)} + \text{O}_{2(g)} = 2 \text{SO}_{3(g)}$ in equilibrium is placed in a 1-liter vessel at a temperature of 600°C. The composition of the mixture is as follows: 0.5 moles of SO_2 , 0.12 moles of O_2 , and 5 moles of SO_3 . At the start of the reaction, the vessel contained only SO_2 and O_2 . Calculate the concentration equilibrium constant and how many moles of oxygen must be pumped into the vessel so that the number of moles of SO_3 in equilibrium increases to 5.2.

2. At a temperature of 500 K and a pressure of 1 atmosphere, thermal dissociation of nitrosyl chloride occurs in the reaction: $2 \text{NOCl}_{(g)} = 2 \text{NO}_{(g)} + \text{Cl}_{2(g)}$. Calculate the pressure equilibrium constant if, at equilibrium, the pressure of NOCl is equal to $0.648 \cdot 10^5$ Pa.

3. At a temperature of 473 K and a pressure of 1 atmosphere, phosphorus pentachloride is dissociated by 48.5%. Calculate the pressure equilibrium constant of the reaction: $\text{PCl}_{5(g)} = \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$.

4. At a temperature of 25°C and a pressure of 1 bar, dinitrogen tetroxide dissociates by 18.46% according to the reaction: $\text{N}_2\text{O}_{4(g)} = 2 \text{NO}_{2(g)}$. Calculate the pressure equilibrium constant for this reaction.

5. At a temperature of 2257 K and a pressure of 1 atmosphere in equilibrium, water dissociates according to the reaction: $2 \text{H}_2\text{O}_{(g)} = 2 \text{H}_{2(g)} + \text{O}_{2(g)}$ to a degree of 1.77%. Calculate the pressure equilibrium constant, the chemical affinity value, and the chemical affinity of the pure components.

6. Reaction $2\text{A} + \text{B} = 3\text{C} + 2\text{D}$ proceeds in the gas phase. When 1.00 mol of A, 2.00 mol of B, and 1 mol of D were mixed, after equilibrium was established at 25°C and a total pressure of 1.00 bar, the mixture contained 0.90 mol of C. Calculate: a) the mole fractions of all reagents at equilibrium, b) K_x , c) K_p , and d) $A^\ominus$.

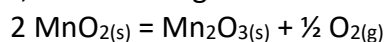
7. The equilibrium constant for a certain reaction is 4500 at a temperature of 298 K and 6000 at a temperature of 273 K. Calculate the heat effect of the reaction.

8. The equilibrium constant for a certain reaction is 1.6 at a temperature of 273 K and 0.018 at a temperature of 333 K. What is the equilibrium constant at a temperature of 353 K and what is the chemical affinity of the pure components at this temperature?

9. What is the standard enthalpy of a reaction whose equilibrium constant a) doubles, b) halves when the temperature increases by 10 K at 298 K?

10. It has been experimentally determined that the equilibrium constant of a certain reaction depends on temperature according to the function $\ln K = A/T + B + C \cdot \ln T$. At the same time, it has been found that the position of the equilibrium state does not change with changes in pressure. Find the temperature dependence of the standard enthalpy, standard entropy, and standard volume change of this reaction.

11. At temperatures above 750 K, the following reaction occurs:



The equilibrium oxygen pressures are: at 773 K, $p_{\text{O}_2} = 10^4$ Pa and at 873 K, $p_{\text{O}_2} = 10^5$ Pa. Calculate the average heat of reaction in this temperature range.

12. The mixture of gases obtained in the reaction: $2 \text{SO}_{2(g)} + \text{O}_{2(g)} = 2 \text{SO}_{3(g)}$ in equilibrium is placed in a vessel of volume of 1 liter at temperature of 600°C. The composition of the mixture is as follows: 0.5 moles of SO_2 , 0.12 moles of O_2 and 5 moles of SO_3 . At the moment of starting the reaction, the vessel contained only SO_2 and O_2 . Calculate the equilibrium concentration constant and how many moles of oxygen should be pumped into the vessel so that the number of moles of SO_3 in the equilibrium state increases to 5.2.

13. At a temperature of 500 K and a pressure of 1 atmosphere, thermal dissociation of nitrosyl chloride occurs in the reaction: $2 \text{NOCl}_{(g)} = 2 \text{NO}_{(g)} + \text{Cl}_{2(g)}$. Calculate the equilibrium pressure constant if the pressure of NOCl at equilibrium is equal to $0.648 \cdot 10^5 \text{ Pa}$.

14. At 473 K and 1 atmosphere pressure, phosphorus pentachloride is 48.5% dissociated. Calculate the pressure equilibrium constant of the reaction: $\text{PCl}_{5(g)} = \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$.

12.

The equilibrium constant of a certain reaction is 4500 at 298 K and 6000 at 273 K. Calculate the heat of the reaction.

13.

The equilibrium constant of a certain reaction is 1.6 at 273 K and 0.018 at 333 K. What is the equilibrium constant at 353 K and what is the value of the chemical affinity of the pure components at this temperature?

Assessment

Select three out of five

A1. Calculate the entropy change that occurs when 5 moles of hydrogen are cooled from 350 K to 270 K. The heat capacity of hydrogen at constant pressure is $C_p = 28.9 \text{ J}/(\text{mol}\cdot\text{K})$. Cooling occurs under: a) isobaric, b) isochoric conditions.

A2. The change in free enthalpy for a certain process taking place at constant pressure can be expressed by the formula $\Delta G/\text{J} = -85.40 + 36.5 (T/\text{K})$. Calculate the value of ΔS for this process.

A3. At a temperature of 2257 K and a pressure of 1 atmosphere in equilibrium, water dissociates according to the reaction: $2\text{H}_2\text{O}_{(\text{g})} = 2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$ to a degree of 1.77%. Calculate the equilibrium pressure constant, the value of chemical affinity and the chemical affinity of the pure components.

A4. The standard free energy of the isomerization reaction of cis-pent-2-ene to trans-pent-2-ene at 400 K is $-3.67 \text{ kJ}\cdot\text{mol}^{-1}$. Calculate the equilibrium constant of isomerization.

A5. The standard free enthalpy of the reaction of a certain metal $\text{M}(\text{s}) + \text{H}_2\text{O}(\text{g}) = \text{M}(\text{s}) + \text{H}_2(\text{g})$ is approximately constant in the temperature range from 920 K to 1280 K and is $+224 \text{ kJ}\cdot\text{mol}^{-1}$. At 1280 K the standard free enthalpy of this reaction is $+33 \text{ kJ}\cdot\text{mol}^{-1}$. Determine the temperature at which the equilibrium constant becomes greater than 1.

4. Physical transformations

4.1. Gibbs's Phase Rule

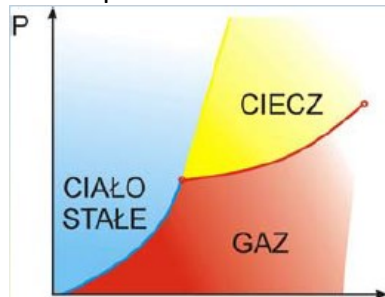
$$s = \alpha - \beta + 2$$

1.

Interpret the operation of a pressure cooker, the physicochemical mechanism of ice sheet movement, sliding on ice skates,

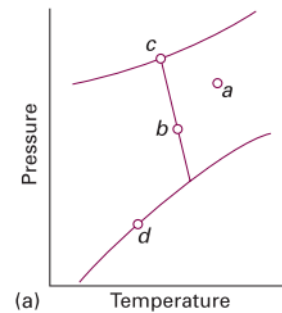
2.

Interpret the meaning of the slope angle of the liquid-ice equilibrium



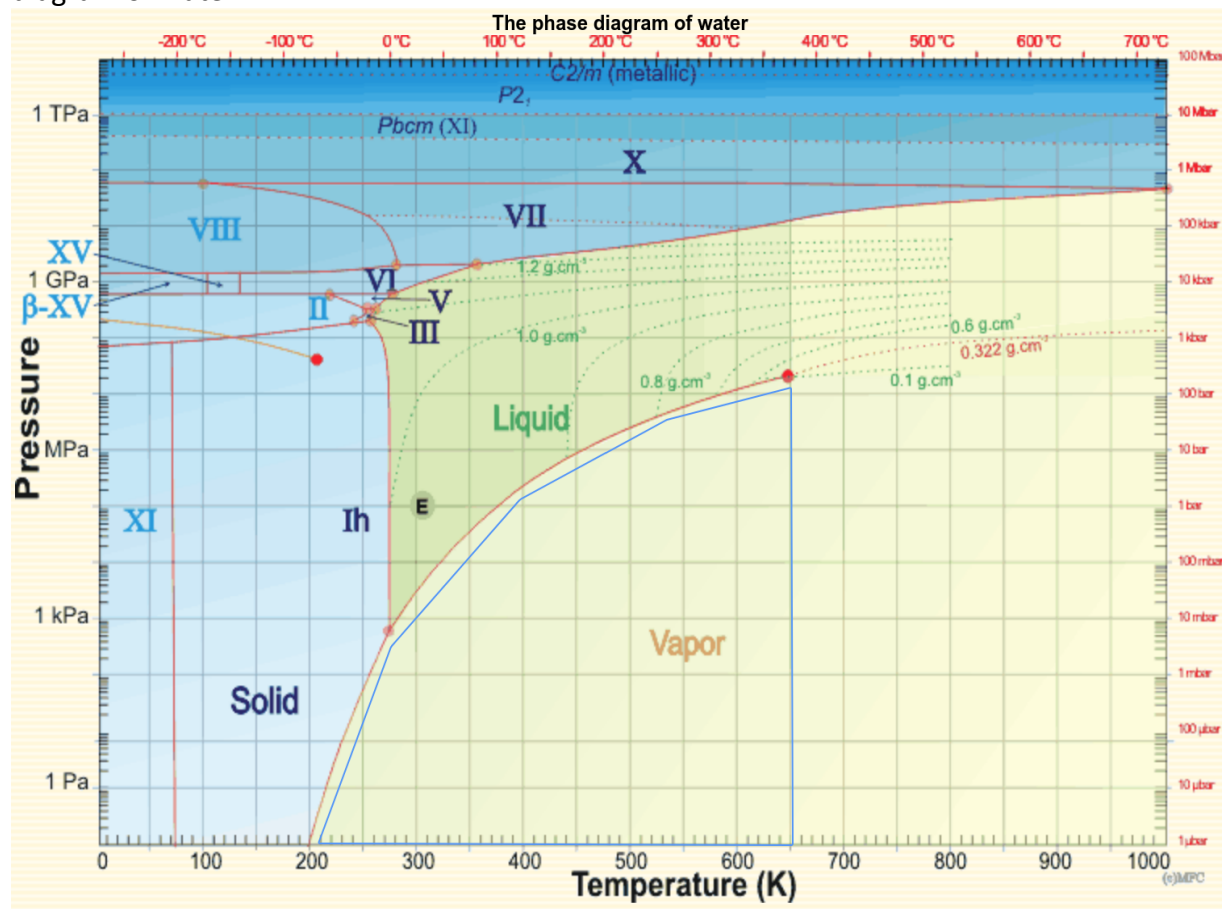
3.1.-3.

How many phases are present at each of the points marked in Fig.



3.

Using Gibbs' phase rule, interpret the indicated equilibrium points and lines on the phase diagram of water.



4.2. Clausius-Clapeyron equation

4.3. Phase diagrams

4.4. Raoult's law

Assessment