Physical Chemistry I. practice

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II.: Ideal gases

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http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Requirements.pdf
http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Important_dates.pdf

Equations for the state changes of ideal gases

	W	Q	ΔU	ΔH	ΔS
Isobaric	$-nR\Delta T$	$nC_{m,p}\Delta T$	$nC_{m,v}\Delta T$	$nC_{m,p}\Delta T$	$nC_{m,p}ln\frac{T_2}{T_1}$
Isochor	$\emptyset$	$nC_{m,v}\Delta T$	$nC_{m,v}\Delta T$	$nC_{m,p}\Delta T$	$nC_{m,v}ln\frac{T_2}{T_1}$
Isothermal	$nRTln\frac{p_2}{p_1}$	$-nRTln\frac{p_2}{p_1}$	$\emptyset$	$\emptyset$	$-nRln\frac{p_2}{p_1}$
Ad. rev.	$nC_{m,v}\Delta T$	$\emptyset$	$nC_{m,v}\Delta T$	$nC_{m,p}\Delta T$	$\emptyset$

Isothermal: $p_1/p_2 = V_2/V_1$

Isochor: $p_1/p_2 = T_1/T_2$

Isobaric: $V_1/V_2 = T_1/T_2$

$C_{m,p} - C_{m,v} = R$

Adiabatic reversible:

$T_1/T_2 = (V_2/V_1)^{\kappa-1}$

$p_1/p_2 = (V_2/V_1)^{\kappa}$

$T_1/T_2 = (p_2/p_1)^{\frac{1-\kappa}{\kappa}}$

$\kappa = \frac{C_{m,p}}{C_{m,v}}$

Thermodynamic cycle

We perform a cycle process with 160 g of O_2 (ideal gas)

- From 20 °C and 0,1 MPa we compress it to 2 MPa in an adiabatic reversible process
- Then we heat it to 500 °C in an isochor process
- Then we expand it to 0,1 MPa in an isothermal process
- Finally we cool it to 20 °C in an isobaric process

What are W, Q, ΔU, ΔH, and ΔS

- in the four subprocesses?
- in the overall process?

$(\kappa = 1,4)$

Thermodynamic cycle

1. Ad. rev. $1 \rightarrow 2$

$W_1 = nC_{m,v}(T_2 - T_1)$

$Q_1 = 0\ J$

$\Delta U_1 = W_1$

$\Delta H_1 = nC_{m,p}(T_2 - T_1)$

$\Delta S_1 = 0\ J/K$

2. Isochor $2 \rightarrow 3$

$W_2 = 0\ J$

$Q_2 = nC_{m,v}(T_3 - T_2)$

$\Delta U_2 = Q_2$

$\Delta H_1 = nC_{m,p}(T_3 - T_2)$

$\Delta S_2 = nC_{m,v}ln(T_3/T_2)$

3. Isothermal $3 \rightarrow 4$

$W_3 = nRT_3ln(p_4/p_3)$

$Q_3 = -W_3$

$\Delta U_3 = 0\ J$

$\Delta H_3 = 0\ J$

$\Delta S_3 = -nRln(p_4/p_3)$

Isobaric $4 \rightarrow 1$

$W_4 = -nR(T_1 - T_4)$

$Q_4 = nC_{m,p}(T_1 - T_4)$

$\Delta U_4 = W_4 + Q_4$

$\Delta H_4 = Q_4$

$\Delta S_4 = nC_{m,p}ln(T_1/T_4)$

Thermodynamic cycle

n, $C_{m,p}$, $C_{m,v}$, T_2, p_3 ?

$$n = \frac{160g}{32g/mol} = 5\ mol$$

$$C_{m,p} = 1,4\ C_{m,v}$$

$$\rightarrow 0,4\ C_{m,v} = R \rightarrow C_{m,v} = \frac{5}{2}R\ ,\ C_{m,p} = \frac{7}{2}R$$

Ad. rev.: $T_2 = 293\ K \left(\frac{10^5 Pa}{2\cdot 10^6 Pa}\right)^{\frac{1-1,4}{1,4}} \simeq 690\ K$

Isochor: $p_3 = 2 \cdot 10^6 Pa \left(\frac{773\ \ K}{690\ \ K}\right)\ =\ 2,24 \cdot 10^6 Pa$

Thermodynamic cycle

1. Ad. rev. $1 \to 2$

$W_1 = nC_{m,v}(T_2 - T_1) = 41,3kJ$

$Q_1 = 0\ J$

$\Delta U_1 = W_1$

$\Delta H_1 = nC_{m,p}(T_2 - T_1) = 57,82kJ$

$\Delta S_1 = 0\ J/K$

2. Isochor $2 \to 3$

$W_2 = 0\ J$

$Q_2 = nC_{m,v}(T_3 - T_2) = 8,6kJ$

$\Delta U_2 = Q_2$

$\Delta H_1 = nC_{m,p}(T_3 - T_2) = 12,0kJ$

$\Delta S_2 = nC_{m,v}ln(T_3/T_2) = 11,8J/K$

3. Isothermal $3 \to 4$

$W_3 = nRT_3ln(p_4/p_3) = -99,9kJ$

$Q_3 = -W_3$

$\Delta U_3 = 0\ J$

$\Delta H_3 = 0\ J$

$\Delta S_3 = -nRln(p_4/p_3)$

$= 129,2J/K$

4. Isobaric $4 \to 1$

$W_4 = -nR(T_1 - T_4) = 19,9kJ$

$Q_4 = nC_{m,p}(T_1 - T_4) = -69,8kJ$

$\Delta U_4 = W_4 + Q_4$

$\Delta H_4 = Q_4$

$\Delta S_4 = nC_{m,p}ln(T_1/T_4)$

$= -141,1J/K$

$\sum W = -34,8kJ$, $\sum Q = 34,8kJ$

Sum of the functions of state is 0!

Different routes

We have 1 mol of argon (ideal gas) that is 25 °C and 10^5 Pa.

We heat and compress it to 100 °C and $5 \cdot 10^5$ Pa.

$C_{m,p} = 5/2R$ and $C_{m,v} = 3/2R$.

What is the total W, Q, ΔU, and ΔH if

a)

- We first heat it to 100 °C on constant volume
- Then increase the pressure to $5 \cdot 10^5$ Pa on constant temperature?

Different routes

1. Isochor $1 \to 2$

$W_1 = 0\ J$

$Q_1 = nC_{m,v}(T_2 - T_1)$

$\Delta U_1 = Q_1$

$\Delta H_1 = nC_{m,p}(T_2 - T_1)$

$\Delta S_1 = nC_{m,v}ln(T_2/T_1)$

2. Isothermal $2 \to 3$

$W_2 = nRT_2ln(p_3/p_2)$

$Q_2 = -W_2$

$\Delta U_2 = 0\ J$

$\Delta H_2 = 0\ J$

$\Delta S_2 = -nRln(p_3/p_2)$

Only p_2 is unknown

Isochor $1 \to 2$

$$p_2 = 10^5 Pa \left(\frac{373\ K}{298\ K}\right)$$

$$\hat{\approx} 1,25 \cdot 10^5 Pa$$

$\sum W = 4294\ J$

$\sum Q = -3359\ J$

$\sum \Delta U = 935\ J$

$\sum \Delta H = 1559\ J$

$\sum \Delta S = -8,71\ J/K$

Different routes

We have 1 mol of argon (ideal gas) that is 25 °C and 10^5 Pa.

We heat and compress it to 100 °C and $5 \cdot 10^5$ Pa.

$C_{m,p} = 5/2R$ and $C_{m,v} = 3/2R$.

What is the total W, Q, ΔU, and ΔH if

b)

- We first heat it to 100 °C on constant pressure
- Then increase the pressure to $5 \cdot 10^5$ Pa on constant temperature?

Different routes

1. Isobaric $1 \rightarrow 2$

$$W_1 = -nR(T_2 - T_1)$$

$$Q_1 = nC_{m,p}(T_2 - T_1)$$

$$\Delta U_1 = W_1 + Q_1$$

$$\Delta H_1 = Q_1$$

$$\Delta S_1 = nC_{m,p} ln(T_2/T_1)$$

2. Isothermal $2 \rightarrow 3$

$$W_2 = nRT_2 ln(p_3/p_2)$$

$$Q_2 = -W_2$$

$$\Delta U_2 = 0\ J$$

$$\Delta H_2 = 0\ J$$

$$\Delta S_2 = -nRln(p_3/p_2)$$

Every variable is known

$$\sum W = 4367\ J$$

$$\sum Q = -3432\ J$$

$$\sum \Delta U = 935\ J$$

$$\sum \Delta H = 1559\ J$$

$$\sum \Delta S = -8,71\ J/K$$

Different routes

We have 1 m^3 argon (ideal gas) with 298 K temperature and 10^5 Pa pressure.

We compress it in an adiabatic reversible process, then expand it to its original volume in an isothermal process.

Its pressure becomes $2 \cdot 10^5$ Pa.

$C_{m,p} = 5/2R$, $C_{m,v} = 3/2R$

What is the total change in entropy?

Different routes

In sum, it is an isochor process

$\Delta S = nC_{m,v}ln(T_3/T_1)$

$n = \frac{p_1 V_1}{RT_1} = 40,36\ mol$

$T_3 = \frac{p_3 V_3}{nR} = 596\ K$

$\Delta S = 348,88\ J/K$

More argon

We have 1 m^3 argon (ideal gas) with 298 K temperature and 10^6 Pa pressure.

We expand it in an adiabatic reversible process to 2 m^3.

$C_{m,p} = 5/2R$, $C_{m,v} = 3/2R$

What is the new T and p ?

What is the W, ΔU, and ΔH ?

More argon

$$\kappa = \frac{5}{3}$$

$$T_2 \;=\; 298\;K\left(\frac{1\;m^3}{2\;m^3}\right)^{\frac{2}{3}} \;=\; 188\;K$$

$$p_2 \;=\; 10^6 Pa\left(\frac{1\;m^3}{2\;m^3}\right)^{\frac{5}{3}} \;=\; 3,15 \cdot 10^6 Pa$$

$$n \;=\; \frac{10^6 Pa}{R\;298K} \;=\; 403,62\;mol$$

$$W \;=\; n\;C_{m,v}\;\Delta T \;=\; -554\;kJ$$

$$\Delta U \;=\; W$$

$$\Delta H \;=\; n\;C_{m,p}\;\Delta T \;=\; -923\;kJ$$