Physical Chemistry I. practice

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II.: Ideal gases

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http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/practice_class_requirements.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: $V_1/V_2 = T_1/T_2$

Adiabatic reversible:

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

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

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

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

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

$$pV = nRT$$

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 ?

Argon

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

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

$$p_2 \;=\; 10^6 Pa\ \left(\frac{1\ m^3}{2\ m^3}\right)^{\frac{5}{3}} \;=\; 3.15 \cdot 10^6 Pa$$

$$n \;=\; \frac{10^6 Pa}{R\ 298K} \;=\; 403.62\ mol$$

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

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

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

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?

($\kappa = 1.4$, $M_{O_2} = 32\ g/mol$)

Thermodynamic cycle

- Plot the thermodynamic cycle on a p–V diagram and denote the known T, p, and V values!
- Collect the equations needed to answere the questions! Which W, Q, ΔU, ΔH, or ΔS values are zero? What are the unkown p, T, and V values we have to calculate?
- Calculate W, Q, ΔU, ΔH, and ΔS for the subprocesses and the whole cycle!
- Check yourself!

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 $4 \rightarrow 1$

$W_4 = -nR(T_1 - T_4)$

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

$\Delta U_4 = W_4 + Q_4$

$\Delta H_4 = Q_4$

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

$\sum \Delta U_i = 0$, $\sum \Delta H_i = 0$, $\sum \Delta S_i = 0$

Thermodynamic cycle

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

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

$$\kappa = 1.4 \rightarrow C_{m,p} = 1.4\ C_{m,v}$$

$$\rightarrow 0.4\ C_{m,v} = R \rightarrow C_{m,v} = \frac{5}{2}R\ ,\ C_{m,p} = \frac{7}{2}R$$

Ad. rev.: $T_2 = 293\ K \left(\frac{10^5 Pa}{2{\cdot}10^6 Pa}\right)^{\frac{1-1.4}{1.4}} \hat{\simeq} 690\ K$

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. $1 \rightarrow 2$

$W_1 = nC_{m,v}(T_2 - T_1) = 41.3kJ$

$Q_1 = 0\ J$

$\Delta U_1 = W_1$

$\Delta H_1 = nC_{m,p}(T_2 - T_1) = 57.8kJ$

$\Delta S_1 = 0\ J/K$

2. Isochor $2 \rightarrow 3$

$W_2 = 0\ J$

$Q_2 = nC_{m,v}(T_3 - T_2) = 8.6kJ$

$\Delta U_2 = Q_2$

$\Delta H_1 = nC_{m,p}(T_3 - T_2) = 12.0kJ$

$\Delta S_2 = nC_{m,v}ln(T_3/T_2) = 11.8J/K$

3. Isothermal $3 \rightarrow 4$

$W_3 = nRT_3ln(p_4/p_3) = -99.9kJ$

$Q_3 = -W_3$

$\Delta U_3 = 0\ J$

$\Delta H_3 = 0\ J$

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

$= 129.2J/K$

4. Isobaric $4 \rightarrow 1$

$W_4 = -nR(T_1 - T_4) = 19.9kJ$

$Q_4 = nC_{m,p}(T_1 - T_4) = -69.8kJ$

$\Delta U_4 = W_4 + Q_4$

$\Delta H_4 = Q_4$

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

$= -141.1J/K$

$\sum W = -34.8kJ$, $\sum Q = 34.8kJ$

Thermodynamic cycle

- Sum of the change of functions of state is 0!
- $\sum Q_i + \sum W_i = 0$

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?

Plot the process on the p–V diagram!

Different routes

1. Isochor $1 \rightarrow 2$

$W_1 = 0\ J$

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

$\Delta U_1 = Q_1$

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

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

2. Isothermal $2 \rightarrow 3$

$W_2 = nRT_2ln(p_3/p_2)$

$Q_2 = -W_2$

$\Delta U_2 = 0\ J$

$\Delta H_2 = 0\ J$

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

Only p_2 is unknown

Isochor $1 \rightarrow 2$

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

$$\hat{=}\ 1.25 \cdot 10^5 Pa$$

$$\sum W = 4294\ J$$

$$\sum Q = -3359\ J$$

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

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

$$\sum \Delta S = -8.71\ J/K$$

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 $2 \rightarrow 3$

$$W_2 = nRT_2ln(p_3/p_2)$$

$$Q_2 = -W_2$$

$$\Delta U_2 = 0\ J$$

$$\Delta H_2 = 0\ J$$

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

Every variable is known

$$\sum W = 4367\ J$$

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

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

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

$$\sum \Delta S = -8.71\ J/K$$

Argon II

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?

Argon II

In sum, it is an isochor process

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

$n = \frac{p_1 V_1}{RT_1} = 40.36\ mol$

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

$\Delta S = 348.88\ J/K$