

EXAM 1

24 September 1993

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation. If possible, please write on one side of the paper only.

Give units for all quantities!

Some information: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$

(1) *20 points*

$\Delta H_{f,298}$ for $\text{NH}_3(g)$, $\text{N}(g)$ and $\text{H}(g)$ are -46 , 473 and 218 kJ mol^{-1} , respectively. Calculate the average N-H bond dissociation enthalpy in ammonia ($\text{NH}_3(g)$).

(2) *25 points*

Consider a sample of 1 mol of ideal gas at 300 K that occupies a volume of 1 m^3 .

- What is its pressure?
- Imagine the sample absorbs 1 kJ of heat, while the volume is held constant. What are q , w and ΔU for the gas?
- The final temperature of the gas is 350 K: what is C_v ?

(3) *25 points*

- Write out the equation of state for one mole of a Van der Waals gas. Explain what the 'b' parameter corresponds to physically.
- Derive a general expression for the work done on this gas if it is compressed from an initial volume V_1 to a final volume V_2 , isothermally at a temperature T .
(If you have no answer for (a), use the Berthelot eq. shown below instead)

$$p = \frac{RT}{V-b} - \frac{a}{TV^2}$$

(4) *30 points*

The enthalpies of combustion at 298 K for ethanol ($\text{C}_2\text{H}_5\text{OH}(l)$) and dimethyl ether ($\text{CH}_3\text{OCH}_3(l)$) are -1368 and $-1454 \text{ kJ mol}^{-1}$, respectively. C_p for ethanol and dimethyl ether are 111 and $129 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

- Use this information to find ΔH_{298} for the reaction $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{CH}_3\text{OCH}_3(l)$.
- What is ΔH for the reaction in part a at 200 K?
- What is ΔU_{298} for the combustion of ethanol?

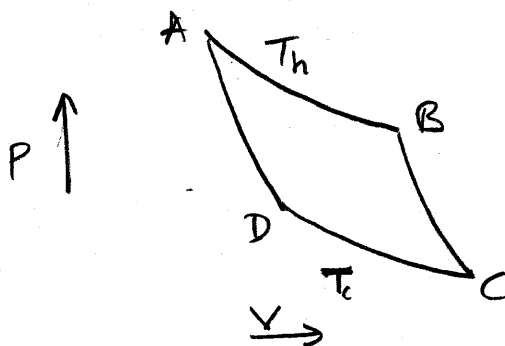
EXAM 2
25 October 1993

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation. If possible, please write on one side of the paper only. Give units for all quantities!

Some information: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$

(1) 35 points.

Here is a reversible Carnot cycle where the working fluid is one mole of ideal gas.
 $T_c = 350 \text{ K}$.



- i) When 60 J are absorbed at T_h , 35 J of work are obtained from the engine. Calculate the efficiency ϵ and T_h .
- ii) What can you say about the work obtained if the engine was operating irreversibly?
- iii) What can you say about the sum of the entropy changes for the engine for the four processes $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$, and why?
- iv) What can you say about ΔS for $B \rightarrow C$, and why?

(2) 30 points.

Imagine that 1 mol of an ideal gas, the system, is heated from 400 to 600 K while at a constant volume. $C_v = 12 \text{ J K}^{-1}$ here. Calculate q , w , ΔU and ΔH . *Clearly state any extra results or relations you use in your work.*

(3) 35 points.

Consider one mole of ideal gas, the system. Initially the volume is 2 m^3 , and $T = 400 \text{ K}$. The gas is reversibly and adiabatically compressed to 0.5 m^3 . Calculate q , ΔS , ΔU , w and ΔH for the system. You may assume $C_p = 20 \text{ J K}^{-1}$ here, and that pV^γ is constant along an adiabat. *Clearly state any extra results or relations you use in your work.*

EXAM 3

27 October 1993

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation. If possible, please write on one side of the paper only.

Give units for all quantities!

Some information: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$

$C_p(\text{liquid H}_2\text{O}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{H}_2\text{O vapor}) = 33.6 \text{ J K}^{-1} \text{ mol}^{-1}$

ΔH_{vap} for H_2O at T_b (373 K) = 40.6 kJ mol^{-1} .

(1) *40 points.*

- i) One mole of water (the system) evaporates spontaneously at 378 K. What is ΔS (for the system)?
- ii) What can you say about ΔS for the universe?
- iii) What can you say about ΔG for the system?

(2) *30 points.*

- i) Starting with dH , derive a Maxwell relation involving $(\partial V/\partial S)_p$.
- ii) 4 mol of ideal gas (the system) are confined in 1.5 m^3 at 350 K. What is $(\partial H/\partial p)_s$?

(3) *30 points.*

Find $(\partial U/\partial V)_T$ for one mole of a Berthelot gas, where

$$p = \frac{RT}{V-b} - \frac{a}{TV^2}$$

HINT: You may assume that $(\partial A/\partial V)_T = -p$ and

$$\left\| \frac{\partial p}{\partial T} \right\|_V = \left\| \frac{\partial S}{\partial V} \right\|_T.$$

without proof.

EXAM 4

19 November 1993

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation. If possible, write on one side of the paper only.

Give units for all quantities!

Some information: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
 $p^\ominus = 10^5 \text{ Pa}$.

(1) *20 points.*

Imagine a liquid for which $\Delta H_{\text{vap}} = 30 \text{ kJ mol}^{-1}$ and whose vapor pressure at 298 K is $1 \times 10^4 \text{ Pa}$. Estimate the boiling temperature. [*Hint: use the Clausius-Clapeyron equation or just consider liquid \rightarrow vapor as a regular equilibrium problem*].

(2) *20 points.*

Consider the dissociation of water vapor at high temperatures:



for which $\Delta G^\ominus = +50 \text{ kJ mol}^{-1}$ at 3000 K.

- Is the reaction spontaneous (from left to right) if the initial activity of each species is 1?
- Is the reaction spontaneous (from left to right) if the initial activity of each species is 0.01?

(3) *20 points.*

Consider samples of He (molar mass 0.004 kg) and Ar (molar mass 0.040 kg) at the same temperature and pressure.

- What is the ratio of the mean kinetic energies of the atoms in each sample?
- What is the ratio of the root mean square speeds of the atoms in each sample?
- If the samples were allowed to effuse through a small hole, what would be the ratio of the rates of effusion of the two samples?

(4) *10 points.*

1 mole of ideal gas is expanded isothermally to 3 times the initial volume at 400 K. Calculate ΔG .

(5) *30 points.*

At 1000 K, ΔG_f for atomic chlorine is 50 kJ mol^{-1} . Calculate the degree of dissociation for 10^5 Pa of initially pure Cl_2 at 1000 K.