Edlisefnafrædi 2

Lokapróf, 12. des. 2005

Leyfileg hjálpargögn: Reiknivélar og stærdfrædihandbækur
Prófid samanstendur af 5 spurningum sem eru mislangar, samtals 100 punktar. Aftast er listi yfir jöfnur.

Problem 1: (15 pts)

In English:

(a) One mole of a perfect, monatomic gas expands reversibly and isothermally at $25°C$ from an initial pressure of 5 atm to 1 atm. Determine the value of q, w, ΔU, ΔH, ΔS, ΔS_{surr}, and ΔS_{tot} for this process.

(b) One mole of a perfect, monatomic gas expands reversibly and adiabatically from 5 atm to 1 atm. The initial temperature is $25°C$. Determine the final temperature of the gas, as well as q, w and ΔU.

(c) The enthalpy change is $\Delta H_{vap} = 40\ kJ/mol$ when water boils at 100 $°C$. This accounts for both the increase in internal energy as the molecules go from the liquid to vapour phase, as well as the expansion of the volume when water vapor forms. What fraction of the enthalpy change is due to the volume expansion?

Á Íslensku:

(a) Rúmmál eins móls af einatóma kjörgasi eykst vid jafnan hita, $25°C$, á afturkræfan hátt og samtímis lækkar P úr 5 atm í 1 atm. Ákvardadu gildi q, w, ΔU, ΔH, ΔS, ΔS_{surr}, og ΔS_{tot} fyrir ferlid.

(b) Rúmmál eins móls af einatóma kjörgasi eykst adíabatískt á afturkræfan hátt og samtímis lækkar P úr 5 atm í 1 atm. Upphafshitastigid er $25°C$. Hvert er lokahitastigid, og hvad er q, w og ΔU fyrir ferlid?

(c) Varmagildisbreytingin vid sudu vatns vid 100 $°C$ er $\Delta H_{vap} = 40\ kJ/mol$. Hún ákvardast bædi af breytingu innri orkunnar er sameindir fara úr vökvafasa í gasfasa svo og rúmmálsaukningu kerfisins vid myndun vatnsgufunnar. Hvada hlutfall af varmagildisbreytingunni er vegna rúmmálsaukningarinnar?

Problem 2: (15 pts)

In English:

Consider a gas that can be described by the following equation of state:

$$P(V_m, T) = R\left(\frac{T}{V_m} + q\left(\frac{T}{V_m}\right)^2\right)$$

where q is a constant that is characteristic for the gas.

(a) Find an expression for the compression factor, Z, of this gas.

(b) Give an expression that can be used to calculate the fugacity coefficient as a function of pressure and simplify as much as possible.

(c) What is the value of the fugacity coefficient in the limit as P$\rightarrow$ 0?

Á Íslensku:

Gefid er gasefni sem lýst er med ástandsjöfnunni

$$P(V_m, T) = R\left(\frac{T}{V_m} + q\left(\frac{T}{V_m}\right)^2\right)$$

Hér er q fasti sem hádur er eiginleikum gassins.

(a) Finndu líkingu fyrir sampjöppunarstudul gassins, Z.

(b) Skrifadu nidur líkingu fyrir "fugacity"-studli gassins sem fall af P. Einfaldadu eins og hægt er.

(c) Hvada gildi hefur "fugacity" studullinn í markgildinu P$\rightarrow$ 0?

Problem 3: (30 pts)

In English:

A measurement of the vapor pressure of water was carried out over the temperature range 5 $^\circ C$ to 80 $^\circ C$. The results are shown in the graph below where the pressure is plotted as a function of temperature in degrees K. A linear least squares fit to the data is also shown. The equation for the fit is $P(T) = 67.54 - 0.3109\,T + 4.036 \cdot 10^{-4}\,T^2 - 9.507 \cdot 10^5\,T^{-2}$. The heat capacity of the liquid and the vapor can to a good approximation be taken to be constant over the temperature range 25 $^\circ C$ to 100 $^\circ C$, namely 74 $J/Kmol$ for the liquid and 35 $J/Kmol$ for the vapor.

(a) Use the Clausius-Claperon approximation to estimate the enthalpy change upon evaporation, ΔH_{vap}, at a temperature of 20 $^\circ C$ (in units of kJ/mol).

(b) By how many percent would the value you obtained in part (a) be changed if the molar volume of the liquid was taken into account? Explain.

(c) Sketch roughly the molar volume of the vapor (assuming ideal gas behaviour) as a function of temperature in the measured range along the liquid/vapor coexistence line.

(d) Estimate from your result in (a) and the change in enthalpy with temperature the value of ΔH_{vap} at the boiling temperature, 100 $^\circ C$.

(e) Use the combined first and second law expression for enthalpy, $dH = TdS + VdP$, to obtain an expression for the change in enthalpy as the pressure is changed.

(f) Rewrite your expression from part (e) in terms of the experimentally measureable quantities V, T and P, using a Maxwell relationship. Estimate the change in ΔH_{vap} in going from $P_{vap}(20\ ^\circ C)$ to $1atm$ and 20 $^\circ C$ assuming ideal gas behaviour. Explain.

Á Íslensku:

Mæling á gufuprýstingi vatns var gerd á bilinu 5 $^{\circ}C$ til 80 $^{\circ}C$. Nidurstödurnar eru gefnar á grafinu hér ad ofan (sjá enska textann) sem sýnir P/atm sem fall af T/K. Mátun med adferd minnstu kvadrata hefur verid gerd og gaf líkinguna $P(T) = 67.54 - 0.3109\,T + 4.036 \cdot 10^{-4}\,T^2 - 9.507 \cdot 10^5\,T^{-2}$. Varmarýmd vökvans og gufunnar er hægt ad nálga sem fasta á hitastigsbilinu 25 $^{\circ}C$ til 100 $^{\circ}C$ og eru gildin 75 $J/Kmol$ fyrir vökvann og 34 $J/Kmol$ fyrir gufuna.

(a) Notadu Clausius-Claperon nálgunina til ad meta enthalpíubreytinguna vid uppgufun vatns, ΔH_{vap}, vid 20 $^{\circ}C$ (í einingunni kJ/mol).

(b) Hvad myndi svarid í lid (a) breytast um margar prósentur ef mólrúmmál vökvans væri tekid med í reikninginn? Útskýrdu.

(c) Skissadu gróflega mólrúmmál gufunnar sem fall af hitastigi (innan kjörgasnálgunarinnar) sem fall af hitastigi á hitastigsbilinu sem mælingarnar ná yfir (eftir vökva/gufu jafnvægiskúrvunni).

(d) Notadu nidurstödurnar úr lid (a) og breytingu enthalpíunnar med hitastigi til ad meta gildi ΔH_{vap} vid sudumark, 100 $^{\circ}C$.

(e) Notadu samtengt fyrsta og annad lögmál varmafrædinnar fyrir enthalpíu, $dH = TdS + VdP$, til ad leida út líkingu fyrir breytingu enthalpíunnar vid breytingu á P.

(f) Umritadu líkinguna úr lid (e) med Maxwell jöfnu til ad geta reiknad út breytinguna í enthalpíunni eingöngu út frá mælistærdunum V, T and P. Gefdu mat á breytingu ΔH_{vap} vid ad fara frá $P_{vap}(20\ ^{\circ}C)$ til 1 atm og 20 $^{\circ}C$ innan kjörgasnálgunarinnar. Útskýrdu.

Problem 4: (20 pts)

In English:

The constant volume heat capacity of a gas consisting of $P_4(g)$ molecules has been measured to be 67.15 $J/Kmol$. The P_4 molecules are non-linear.

(a) Assuming ideal gas behaviour, what is the expected heat capacity ratio, $\gamma = C_P/C_V$, based on the experimental data?

(b) What value of the heat capacity ratio, γ, would one expect from the high temperature approximations to translational, rotational and vibrational partition functions (the "equipartition theorem" results)?

(c) Often, the vibrational degrees of freedom are not active at room temperature and are therefore skipped when the heat capacity is estimated. What is the heat capacity ratio, γ, one would expect from the high temperature approximations if vibrational degrees of freedom are skipped? Which is more accurate in this case: (i) including vibration or (ii) skipping it? Explain briefly the results you obtain for $P_4(g)$.

(d) Explain carefully (with equations) how you would go about predicting the constant volume heat capacity of $P_4(g)$ using information obtained from spectroscopy (you do not

need to carry out the calculations).

Á Íslensku:

Varmarýmd vid fast rúmmál $P_4(g)$ gasefnis hefur mælst vera 67.15 $J/Kmol$. P_4 sameindirnar eru ólínulegar.

(a) Ef gert er rád fyrir kjörgasi, hvert er varmarýmdarhlutfallid, $\gamma = C_P/C_V$, samkvæmt mælingunum?

(b) Hvada gildi á varmarýmdarhlutfallinu, γ, myndi madur búast vid út frá háhitanálgunum á dreifisummu færslu, snúnings og titrings ("jafnskiptingarlögmálinu")?

(c) Oft eru frelsisgrádur sem samsvara titringi sameinda ekki virkar vid herbergishita og er gjarnan sleppt vid mat á varmarýmd. Hvada gildi á varmarýmdarhlutfallinu mætti búast vid út frá háhitanálgununum ef titringi er sleppt? Hvort er nákvæmara hér (i) ad telja titring med, eda (ii) sleppa titringi? Útskýrdu stuttlega nidurstödurnar sem fást fyrir $P_4(g)$.

(d) Útskýrdu vandlega (med jöfnum) hvernig hægt væri ad spá fyrir um varmarýmd $P_4(g)$ út frá nidurstödum litrófsgreiningar (en ekki framkvæma reikningana).

Problem 5: (20 pts)

In English:

Consider a gas of N identical molecules which have two accessible electronic energy levels separated by an energy gap $\delta\epsilon$. The energy of the lower level is ϵ_1. Make the approximation that higher energy levels cannot be reached and that the gas can be approximated as an ideal gas. The lower level is non-degenerate but the higher level is three-fold degenerate (see figure below).

(a) What is the molecular electronic partition function and what is the canonical partition function of the system? Simplify as much as possible.

(b) Give an expression for the number of molecules in the excited state as a function of temperature and state explicitly the limit as the temperature goes to zero and the limit as the temperature becomes very high.

(c) Give an expression for the electronic contribution to the internal energy of the gas as a function of temperature and state explicitly the limit as the temperature goes to zero and the limit as the temperature becomes very high.

(d) Give an expression for the entropy of the system as a function of temperature and state explicitly the limit as the temperature goes to zero and the limit as the temperature becomes very high.

Á Íslensku:

Verkefnid fjallar um gas med N sameindum sem allar eru eins, og hafa tvö adgengileg orkustig fyrir rafeindirnar, med orkumun $\delta\epsilon$. Orka lægra stigsins er ϵ_1. Gerdu rád fyrir ad enn hærri rafeindaástönd séu ekki adgengileg og ad gasid megi nálga sem kjörgas. Margfeldni lægra orkugildisins er 1, en hærra orkugildid hefur 3 ástönd (sjá mynd hér ad nedan).

(a) Hver er dreifisumma sameindanna (hvad rafeindirnar snertir) og hver er kórdreifisumma kerfisins? Einfaldadu eins og unt er.

(b) Skrifadu líkingu fyrir fjölda sameinda í örvada ástandinu sem fall af hitastigi og tilgreindu hvert markgildid er vid alkul og hvert markgildid er vid hátt hitastig.

(c) Skrifadu líkingu fyrir framlag rafeindaörvunar til innri orku kerfisins sem fall af hitastigi og tilgreindu hvert markgildid er vid alkul og hvert markgildid er vid hátt hitastig.

(d) Skrifadu líkingu fyrir entrópíu kerfisins sem fall af hitastigi og tilgreindu hvert markgildid er vid alkul og hvert markgildid er vid hátt hitastig.