Study Guide

Thermodynamics

(NWI-MOL135) 2026/2027

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Literature

- Book: Physical Chemistry; P.W. Atkins; edition 11, Oxford University Press
- All information will be available via in Brightspace and **www.dullenslab.com/teaching**

Aim

- To introduce the basic principles of Thermodynamics and primarily how to use and apply these concepts in the context of (physical) chemistry, molecular life sciences and science in general.

Organisation

- **Lectures**

  During the lectures (Monday, 10:30 – 12:15, LIN 1) the main contents of this Thermodynamics course will (obviously) be discussed and explained. Please bring a notebook (and an active mindset) to the lectures so that you can write (and think) along. Note that the lectures and the book supplement each other, and some topics will be presented slightly differently than in the book.

- **Tutor Hour**

  Every week there will be a Tutor Hour, from 8:30 – 9:15 on Wednesday, in which the tutors will discuss the covered materials of the preceding lecture. Please note there are **no** problems attached to the Tutor Hours. The division into the 4 Tutor Groups will be the same as in the previous quarter, please see schedule below.

Location	HG00.310	Trans 00.005	Trans 00.012	HG00.308
Tutor	André Steenbergen	Vicky Mertens	Martin Waals	Els Heijmen

- **Problem Classes**

  The problems for the classes will appear online (**www.dullenslab.com/teaching/thermo-1/**); answers will be available online after the problem classes. There are 4 (parallel) problem classes on Wednesday from 9:30 – 12:15, i.e. straight after the Tutor Hour, please see schedule below. The answers do not have to be handed in.

Location	HG00.310	Trans 00.005	Trans 00.012	HG00.308
Tutors and TAs	André Steenbergen Marieke Reijneveld	Vicky Mertens Sjors Cornielje	Martin Waals Jan van Leeuwen	Els Heijmen Mara Bosman

  There will be a separate problem class for **premaster students** on Wednesdays from 13:30 – 15:15 in HG01.028, supervised by one of the tutors and a teaching assistant (Zuzanna Czarnobil).

- **Examination**

  The evaluation will consist of a 3-hour written exam. The 2023 exam (with answers) is available online. Note that a list of formulae (Appendix B), without further comments, will be provided at the exam. **Graphical calculators are NOT allowed during the exam (regular ones are).**

- **Video recordings**

  The lectures will be recorded and will be available on Brightspace. However, please note that this is not an adequate replacement of actually attending the lectures.

Contents of Thermodynamics 1

Lecture synopsis

1. Introduction to Thermodynamics, Gases and the First Law of Thermodynamics
2. Heat Capacities, Enthalpy and Thermochemistry
3. The Second Law of Thermodynamics
4. Free energies: Helmholtz and Gibbs Free Energies
5. Phase Transitions, Chemical Equilibrium
6. Chemical Equilibrium (cont.) and Electrochemistry
7. Condensation of Van der Waals Gas and recap

The above topics are covered in the following section of Atkins' Physical Chemistry (11th Edition):

Lecture	Sections (**11th edition, Atkins**)	Subject
1	1A + 1C + 2A	Gases, First Law of Thermodynamics
2	2B + 2C + 2E	Heat Capacities, Enthalpy, Thermochemistry
3	3A + 3B + 3C	Second Law of Thermodynamics
4	3D, 3E, 5A(p.145)	Free Energy: Helmholtz and Gibbs Free Energies
5	4A, 4B, 5A.1, 5A.2, 6A	Phase Transitions and Chemical Equilibrium
6	6A, 6B, 6C + 6D(p.224)	Chemical Equilibrium (cont.), Electrochemistry
7	1C(p.24-25)	Condensation

Problem set 1 – Gases and the First Law of Thermodynamics

Exercise Maths 1

Determine

$$\int_{x_1}^{x_2} f(x)\mathrm{d}x$$

with

a) $f(x) = abx^2$, where a and b are constants,

b) $f(x) = a$, where a is a constant,

c) $f(x) = \frac{1}{x}$,

d) $f(x) = \frac{nRT}{x}$, where n, R and T are constant,

e) $f(x) = \frac{a}{x^2}$, where a is a constant.

Exercise 1

Two moles of a perfect atomic gas are compressed isothermally and reversibly from 100 litre to 25.0 litre at a temperature of 50°C.

a) Calculate the work w. Is this work done by the surroundings on the system or the other way around?

b) Calculate the heat q. Is this heat supplied to the system or removed from it? Explain the sign of the result.

Exercise 2

Two moles of a perfect atomic gas are heated isochorically and reversibly from 27°C to 77°C.

a) Calculate the work. Is this work done by the surroundings on the system or the other way around?

b) Calculate the change in internal energy, ΔU.

Exercise 3

Two moles of a perfect atomic gas are compressed adiabatically and reversibly from 100 litres to 25.0 litres starting at a temperature of 50°C.

a) Show that for this process $-p\mathrm{d}V = \frac{3}{2}nR\mathrm{d}T$.
Hint: Use the internal energy of a perfect atomic gas, $U = \frac{3}{2}nRT$, to find an expression for $\mathrm{d}U$ for a closed system ($\mathrm{d}n = 0$).

b) Use the perfect gas law to show that $-\frac{1}{V}\mathrm{d}V = \frac{3}{2}\frac{\mathrm{d}T}{T}$.

c) After that, calculate the final temperature by integrating both sides of the equation of the result of part b) between the limiting values for the state variables in the process.

d) Calculate the work. Explain the difference when comparing the result with exercise 1.

Exercise 4

Two moles of a perfect atomic gas are isobarically and reversibly heated from 27°C to 77°C.

a) Calculate the work. Is this work done by the surroundings on the system or the other way around?

b) Calculate the change in internal energy. Compare your result with that obtained in exercise 2b and comment.

Exercise 5

The pressure of a non-perfect or real gas can be written as the virial equation of state

$$p = \frac{nRT}{V}\left(1 + B(T)\left(\frac{n}{V}\right) + C(T)\left(\frac{n}{V}\right)^2 + ...\right) = \frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ...\right),$$

where $V_m = \frac{V}{n}$ is the molar volume and B and C are the second and third ($T-$dependent) virial coefficients, respectively. For not too high pressures, the expansion can be truncated after B:

$$p = \frac{RT}{V_m}\left(1 + \frac{B}{V_m}\right).$$

One mole of argon at temperatures close to 273 K, where $B = -21.7$ cm^{3}mol^{-1} (and hence independent of T), is subjected to the following reversible and cyclic process:

From an initial state A, characterised by the state variables V_1, p_1, T_1, the gas is isothermally expanded to V_2 (state B), followed by the gas being isochorically cooled to a temperature T_2 (state C). Then, the gas is isothermally compressed to V_1 (state D) and before it is finally isochorically heated back to state A at temperature T_1.

a) Sketch the cyclic process in a $p - V$-diagram.

b) Express the work w for all four partial processes in terms of the relevant volumes, pressures and temperatures and B.

c) Use the First Law of Thermodynamics to express the net heat exchanged in terms of the state variables and B.

d) Find an expression for the net work exchanged for a perfect gas. Is this work done 'on the system (the perfect gas)' or 'by the system'? Graphically indicate this work in your sketch of part a).

Problem set 2 – Heat Capacties, Enthalpy and Thermochemistry

Exercise Maths 2

Determine

a) $\int_{T_1}^{T_2} \alpha \mathrm{d}T$, where α is a constant,

b) $\int_{x_1}^{x_2} \frac{1}{p} \mathrm{d}x$, where p is a constant,

c) $\int_{y_1}^{y_2} (g + hy) \mathrm{d}y$, where g and h are constants,

d) $\int_{z_1}^{z_2} \frac{C}{z} \mathrm{d}z$, where C is a constant,

e) $\frac{\mathrm{d}U}{\mathrm{d}T}$, where $U = \frac{3}{2}nRT$, with n and R constant. Hence, show that $\mathrm{d}U = \frac{3}{2}nR\mathrm{d}T$.

Exercise 6

When 3.0 mole of O_2 is heated at a constant pressure of 3.25 atm its temperature increases from 260 K to 285 K. Given that O_2 may be treated as a perfect (but not atomic!) gas and that its constant pressure molar heat capacity is 29.4 $\mathrm{JK^{-1}mol^{-1}}$, calculate q, ΔH and ΔU.

Exercise 7

Calculate the standard enthalpy of formation of N_2O_5 at 298 K from the data below (note that the $\Delta_r H^{\ominus}$ are given in kJ per mole oxygen).

$$\begin{aligned} 2\mathrm{NO(g)} + \mathrm{O_2(g)} &\rightarrow 2\mathrm{NO_2(g)} \qquad \Delta_r H^{\ominus}(298) = -114.1 \text{ kJ mol}^{-1} \\ 4\mathrm{NO_2(g)} + \mathrm{O_2(g)} &\rightarrow 2\mathrm{N_2O_5(g)} \qquad \Delta_r H^{\ominus}(298) = -110.2 \text{ kJ mol}^{-1} \\ \mathrm{N_2(g)} + \mathrm{O_2(g)} &\rightarrow 2\mathrm{NO(g)} \qquad \Delta_r H^{\ominus}(298) = +180.5 \text{ kJ mol}^{-1} \end{aligned}$$

Exercise 8

At 298 K, the standard enthalpy of formation ($\Delta_{\mathrm{f}} H^{\ominus}$) of $NH_3(g)$ is -46.11 kJ $\mathrm{mol^{-1}}$. Assuming that the molar heat capacities can be represented by expressions of the form $\mathrm{C}_{p,m} = A + BT$, with the coefficients A and B given below, calculate $\Delta_{\mathrm{f}} \mathrm{H}^{\ominus}$ at 1000 K.

	N_2	H_2	NH_3
A/J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$	28.58	27.28	29.75
B/J $\mathrm{K^{-2}}$ $\mathrm{mol^{-1}}$	$3.77 \cdot 10^{-3}$	$3.26 \cdot 10^{-3}$	$25.1 \cdot 10^{-3}$

Exercise 9

One mole of a perfect monatomic gas (with $C_V = \frac{3}{2}R$) is expanded adiabatically and reversibly to twice its initial volume, from an initial temperature of 298 K. Calculate

a) the final temperature of the gas;

b) the work done during the expansion.

Exercise 10

A 0.825 g sample of benzoic acid was ignited in a bomb calorimeter (constant V) in the presence of excess oxygen. The temperature of the calorimeter rose by 1.940 K from 298 K. The internal energy of combustion of benzoic acid is -3251 kJ mol^{-1} and its relative molecular mass is 122.

a) Calculate the heat capacity of the bomb calorimeter, $C_{V,bomb}$.

In two separate experiments in the same apparatus, 0.498 g of fumaric acid ($C_4H_4O_4$) and 0.509 g of its isomer maleic acid were ignited and gave temperature rises of 0.507 K and 0.528 K, respectively.

Te combustion reaction is $C_4H_4O_4$ (s) + $3O_2$ (g) $\rightarrow$ $4CO_2$ (g) + $2H_2O$ (l) and the relative molecular mass of fumaric and maleic acid is 116.

Calculate, for (i) fumaric acid and (ii) maleic acid,

b) the molar internal energy of combustion, $\Delta_r U$;

c) the molar enthalpy of combustion, $\Delta_r H$;

Hint: use $\Delta_r H = \Delta_r U + \Delta n_g RT$, where Δn_g is the change in the number of moles of gas. We can use this since we approximate the gases as perfect gases and ignore the effect due to the small increase in temperature (so that $T = 298$ K).

d) the molar enthalpy of formation, $\Delta_f H$, using Hess's Law;

The standard enthalpy of formation of water is -285.8 kJ mol^{-1} and of CO_2 -393.5 kJ mol^{-1} .

e) Comment on the difference between the enthalpies of formation of the two isomers.

Problem set 3 – The Second Law of Thermodynamics

Exercise Maths 3

a) Determine $\int_{x_1}^{x_2} \left(\frac{a}{x} + b + cx\right) \mathrm{d}x$, where a, b and c are constants,

b) Show that $\frac{(T_1+T_2)^2}{4T_1T_2} = 1 + \frac{(T_1-T_2)^2}{4T_1T_2}$,

c) Determine $\left(\frac{\partial f}{\partial x}\right)_y$ with $f(x, y) = hy^2x^2 \ln(gx)$, where g and h are constants,

d) Integrate on both sides: $\frac{3}{2}\int_{T_1}^{T_2} \frac{1}{T}\mathrm{d}T = -\int_{V_1}^{V_2} \frac{1}{V}\mathrm{d}V$, to show that $\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{3/2}$.

Exercise 11

a) How is entropy defined (i) thermodynamically and (ii) statistically?

b) What role does ΔS play in determining the direction of spontaneous change?

c) On cold nights, water spontaneously freezes to form ice. How is this change consistent with your answer to (b)?

d) Given that $C_p(\mathrm{H_2O})$= 75.3 J K^{-1} mol^{-1} and $\Delta_{\mathrm{fus}}H^{\ominus}(\mathrm{H_2O})$= 6.00 kJ mol^{-1} , calculate the change in entropy of a system comprising 1 mole of water at 10 °C that is cooled to 0 °C and then freezes to form ice at 0 °C.

e) Comment on the sign of ΔS you obtained in (d) in light of the microscopic changes occurring in the system.

Exercise 12

a) Calculate the molar entropy of a constant volume sample of 1 mole of Ne(g) at 500 K, given that it is 146.22 J K^{-1} at 298 K. Assume Ne(g) is a perfect gas.

b) Calculate the entropy change of 3 moles of CH_4 that is heated from 298 K to 1098 K at a pressure of 1 atm, given that

$$C_p(\mathrm{CH_4})/\mathrm{J\ K^{-1}\ mol^{-1}} = 23.64 + 4.79 \times 10^{-2}\,T - 1.93 \times 10^{-5}\,T^2$$

over the temperature range 298–2000 K.

c) The entropy change of 2 moles of a perfect gas when it was expanded isothermally from V_A to V_B was found to be 5.595 J K^{-1}. Calculate the ratio V_B/V_A.

Exercise 13

a) Starting from the thermodynamic definition of entropy show that the entropy change ΔS when n moles of a perfect mono-atomic gas expands isothermally from volume V_1 to volume $V_2 = 2V_1$ is given by

$$\Delta S = nR \ln 2.$$

b) Write the answer to part a), $\Delta S = nR\ln 2$, in the form of Boltzmann's statistical definition of entropy, $S = k_{\mathrm{B}} \ln W$, hence, whow that $\frac{W_2}{W_1} = 2^N$. How does the number of possible ways to realise a given configuration change due to the expansion?

Exercise 14

Two equal amounts of the *same* liquid are brought in thermal contact with each other (without mixing) at constant pressure and without loss of heat (i.e. adiabatically) to the surroundings. The initial temperatures are T_1 and T_2, with $T_1 < T_2$. We assume that the constant pressure heat capacity of the liquids C_P is constant between T_1 and T_2 and the final temperature T_f of both liquids will be equal.

a) By considering the transfer of heat between the two liquids, i.e. $q_{1\to 2}$ and $q_{2\to 1}$, show that the final temperature T is given by $T_f = \frac{1}{2}(T_1 + T_2)$.

b) Show that the entropy change during this process is given by $\Delta S = C_p \ln \frac{T_f^2}{T_1 T_2}$.

c) **Bonus**: Use the Second Law of Thermodynamics to show that this process proceeds spontaneously, as one would expect.

Exercise 15

In a Carnot cycle a system is first expanded reversibly and isothermally, then expanded reversibly and adiabatically, after that compressed reversibly and isothermally, and finally compressed reversibly and adiabatically to the initial state. Sketch the Carnot cycle, including the direction of the process, in a

a) $p - V$ diagram b) $p - T$ diagram c) $T - S$ diagram d) $U - S$ diagram

Note that the exact shape of the 'curved' processes in these figures does not have to be determined.

Problem set 4 – Gibbs and Helmholtz free energies

Exercise Maths 4

a) With $f = f(x)$, use the product rule (or otherwise) to show that $\left(\frac{\partial(f/x)}{\partial x}\right)_y = \frac{1}{x}\left(\frac{\partial f}{\partial x}\right)_y - \left(\frac{f}{x^2}\right)$.

b) Write down the total differential of $z(x, y)$ in terms of the partial derivatives.

c) Given that $z(x, y) = x^4 e^{3y}$. Compute the partial derivatives $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial z}{\partial y}\right)_x$.

d) Use your answer from part c) to show that $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$ (as is the case when z is a state function).

Exercise 16

Consider 1.0 mole of an atomic perfect gas at an initial temperature of 25°C and pressure of 5.0 bar.

a) Calculate the values for the following quantities for an isothermal and reversible expansion to a final pressure of 1.0 bar:

- the final temperature,
- the work done,
- the change in internal energy,
- the change in heat ,
- the entropy change,
- the change in the Helmholtz free energy and
- the change in the Gibbs free energy.

b) Discuss (without calculation) whether you expect a different answer for all quantities listed in part a) for an isothermal expansion from an initial pressure of $p = 5$ bar to a final pressure of $p = 1$ bar, but now against a constant external pressure of 1.0 bar. Note that this is an *irreversible* process.

c) Determine the values of the quantities listed in part a) for the irreversible process.

Exercise 17

a) Starting from the First Law of Thermodynamics (including expansion and chemical work), the thermodynamic definition of the entropy and the definition of the Gibbs free energy (G), show that the fundamental equation for the Gibbs free energy is given by

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}n.$$

b) Write down the total differential for $G(T, p, n)$ and compare it to the answer in part a) to show that the temperature variation of the Gibbs free energy is given by

$$\left(\frac{\partial G}{\partial T}\right)_{p,n} = -S.$$

c) The temperature variation of G in terms of the enthalpy H is given by the Gibbs-Helmholtz equation

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{p,n} = -\frac{H}{T^2}.$$

Derive the Gibbs-Helmholtz equation using the answer to part b) and the definition of the Gibbs free energy ($G = H - TS$).

Exercise 18

At $T = 298$ K the enthalpy change of the graphite (G) $\rightarrow$ diamond (D) phase transition is $\Delta_r H = 1.8961$ kJ mol^{-1} and the entropy change is $\Delta_r S = -3.2552$ J K^{-1} mol^{-1}.

a) Determine whether the graphite $\rightarrow$ diamond transition takes place spontaneously at 25°C?

b) Which direction ($G \rightarrow D$ or $D \rightarrow G$) is favoured by a rise in temperature?

c) Starting from the fundamental equation for G, derive an expression for the pressure dependence of G assuming that V is independent of the pressure. Write down the resulting expressions for both diamond, $G_D(p)$, and graphite, $G_G(p)$, and hence, show that the change in Gibbs free energy for the transition from graphite to diamond is given by

$$\Delta_r G = G_D(p) - G_G(p) = \Delta_r G^{\ominus} + \Delta V \left(p - p^{\ominus} \right).$$

d) For the $G \rightarrow D$ transition, $\Delta V = V_D - V_G = -1.92$ cm^{3}mol^{-1}, and $\Delta_r G^{\ominus} = 2.9$ kJ mol^{-1} . At what pressure would diamond become stable at 298 K?

Exercise 19

a) From the fundamental equation for the Helmholtz free energy, derive the following Maxwell-relation

$$\left(\frac{\partial S}{\partial V} \right)_{T,n} = \left(\frac{\partial p}{\partial T} \right)_{V,n}.$$

b) Use the Maxwell-relation from part a) to derive an expression for the entropy change for an isothermal expansion of n moles of a perfect monatomic gas from volume V_1 to volume $V_2 = 2V_1$.

Note that the same expression was obtained in Exercise 13 (problem set 3), but then starting from the thermodynamic definition of the entropy.

Exercise 20

Consider a system consisting of 1 mole sodium, Na, at standard pressure $p^{\ominus}$. In the table below a number of thermodynamic parameters is given.

	T_{fus}	$\Delta_{fus}H$	T_{vap}	$\Delta_{vap}H$
Na	371.0 K	2.601 kJ/mol	1156 K	98.01 kJ/mol

The heat capacity at constant pressure for all phases is given by (T is the temperature in K)

$$C_p(\text{J/molK}) = A + BT + CT^2,$$

in which the parameters A, B and C, for temperatures $10\ K \leq T \leq 1500\ K$, in the three phases s(olid), l(iquid) and g(as) are given in the table below

Na	A(J/molK)	B(J/molK^2)	C(J/molK^3)
solid	72.6	$-9.49 \cdot 10^{-3}$	$-731 \cdot 10^{-6}$
liquid	40.3	$-28.2 \cdot 10^{-3}$	$20.7 \cdot 10^{-6}$
gas	20.8	$-0.277 \cdot 10^{-3}$	$-0.392 \cdot 10^{-6}$

a) At very high temperature the system behaves like an atomic perfect gas. What are the values of A, B and C in that case?

b) Which of the following quantities have the same value for both phases (melt and solid) at constant pressure, at $T = T_{fus}$, where the melt and the solid are in equilibrium?

- the entropy,
- the chemical potential,
- the enthalpy,
- the Gibbs free energy,
- the Helmholtz free energy.

c) Calculate the entropy change $\Delta_{vap}S$ at the evaporation temperature T_{vap}.

d) Calculate the entropy of this system at 1000 K; you can neglect the contributions for $T < 10$ K.

Problem set 5 – Phase and Chemical Equilibrium

Exercise Maths 5

a) Show that $\int_{T_1}^{T_2} \frac{A}{T^2} \mathrm{d}T = -A\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, where A is a constant,

b) By differentiating $\ln p$ with respect to p, show that $\frac{1}{p}\mathrm{d}p = \mathrm{d}\ln p$.

c) Determine $\int_{p_1}^{p_2} \mathrm{d}\ln p$.

The Clausius-Clapeyron equation (in integrated form) is given by

$$\ln \frac{p}{p^{\ominus}} = -\frac{\Delta_{trs}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where T_1 is the transition temperature at $p^{\ominus}$ (and thus constant). Rearrange the Clausius-Clapeyron equation to show that in a plot of $\ln(p/p^{\ominus})$ as a function of $\frac{1}{T_2}$ (hence, T_2 is the 'running variable')

d) the slope is given by $-\frac{\Delta_{trs}H}{R}$,

e) and the intercept is $\frac{\Delta_{trs}H}{RT_1}$.

Exercise 21

a) Starting from the Gibbs-Duhem equation, $\mathrm{d}\mu = -S_m\mathrm{d}T + V_m\mathrm{d}P$, derive the Clapeyron equation,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_m}{\Delta V_m}. \tag{1}$$

b) Sketch the phase diagram of water near the triple point and label the phases, indicate the triple and critical points, and discuss the slopes of the phase boundaries with reference to the Clapeyron equation.

c) Why is the solid-liquid boundary negative and the solid-gas boundary always steeper than the liquid-gas boundary?

d) Starting from the Clapeyron equation and stating any approximations, derive the Clausius-Clapeyron equation for the vapour pressure of a liquid

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{vap}H}{RT^2}.$$

Exercise 22

a) The enthalpy of vaporization of water is 44.0 kJ mol^{-1} . Estimate the vapour pressure of water at 120 °C.

b) Show that the Clapeyron equation for an equilibrium between a solid and its liquid is given by

$$p_2 - p_1 = \frac{\Delta_{\mathrm{fus}}H}{\Delta_{\mathrm{fus}}V}\ln\frac{T_2}{T_1}.$$

The enthalpy of fusion (melting) is 6.01 kJ mol^{-1} , the vapour pressure at the triple point is 533.29 Pa and the mass densities of ice and water at 0°C are 0.917 g cm^{-3} and 1.0 g cm^{-3} respectively. The molar mass of water is 18 g mol^{-1}.

c) Calculate the difference between the melting point of ice at 1 atm pressure and at the temperature of the triple point of water and comment on the small value you (should) obtain.

Exercise 23

The vapour pressure of CO_2 at different temperatures are as follows:

T (K)	p (bar))
186	0.526
196	1.132
206	2.447
226	7.605
236	11.065
246	15.579

a) Determine $\Delta_{\text{vap}}H$ and $\Delta_{\text{sub}}H$ of CO_2 in this temperature range.

b) Determine $\Delta_{\text{fus}}H$ of CO_2.

Exercise 24

The reaction Gibbs energy is defined by

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p}. \tag{2}$$

a) Sketch a graph of $G_{T,p}$ (Gibbs energy at constant T and p) vs. ξ (extent of the reaction) and

- explain the shape of the curve,
- indicate where the forward and backward reactions are spontaneous,
- and where equilibrium is reached.

The standard enthalpy and entropy of formation of methane (CH_4) at 298 K are given by $\Delta_f H^{\ominus}$(CH_4,g) = -74.85 kJ/mol and $\Delta_f S^{\ominus}$(CH_4,g) = -80.67 J/molK.

b) Calculate the equilibrium constant at 298 K for the decomposition of methane CH_4(g) into the elements H_2(g) and graphite C(s).

c) What does this result imply for the position of the equilibrium (to the left hand side or the right hand side of the reaction)?

d) Write down the expression for the equilibrium constant K_p in terms of the partial pressures for the decomposition reaction of methane.

Exercise 25

NO_2 is in equilibrium with its dimer at room temperature:

$$2\ NO_2(g) \quad \rightleftharpoons \quad N_2O_4(g)$$

Use the following data for the (partial) pressures of NO_2 and N_2O_4 at equilibrium

	$p(NO_2)$ (bar)	$p(N_2O_4)$ (bar)
298 K	0.061	0.031

to calculate:

a) the equilibrium constant for the reaction, and

b) the standard molar Gibbs free energy.

Problem set 6 – Chemical Equilibrium and Electrochemistry

Exercise 26

For the following cell at 25°C:

$$\mathrm{Al(s)} \mid \mathrm{Al^{3+}(aq)} \parallel \mathrm{Sn^{2+}(aq)} \mid \mathrm{Sn(s)}$$

the standard electrode potentials are $E^{\ominus}_{\mathrm{Sn/Sn^{2+}}} = -0.136\mathrm{V}$ and $E^{\ominus}_{\mathrm{Al/Al^{3+}}} = -1.61\mathrm{V}$.
State or calculate:

a) the cell reaction and the standard cell potential,

b) the cell potential when the activities of the ions in solution are

   i) 1,

   ii) 0.1.

c) $\Delta_r G^{\ominus}$ and the equilibrium constant for the cell reaction.

Exercise 27

For the reaction, $\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)}$, it is found that between 400 and 500 K, the standard reaction Gibbs free energy, $\Delta_r G^{\ominus}$ (in J mol^{-1}), varies with the temperature according to

$$\Delta_r \mathrm{G}^{\ominus} = 83680 - 14.52T \ln T - 72.26T.$$

a) Calculate $\Delta_r G^{\ominus}$, K_p, $\Delta_r S^{\ominus}$ and $\Delta_r H^{\ominus}$ for the reaction at 450 K.

b) The reaction is started with n moles of $\mathrm{PCl_5}$ and at equilibrium, a fraction α of this amount has dissociated to give a final total pressure of p. Complete the following table:

	$\mathrm{PCl_5}$	$\mathrm{PCl_3}$	$\mathrm{Cl_2}$	total
no. moles at start	n	0	0	
no. moles at equilibrium	$n(1-\alpha)$			$n(1+\alpha)$
mole fraction (x_i)		$\frac{\alpha}{1+\alpha}$		
partial pressure (p_i)				p

c) Show that the equilibrium constant can be expressed as

$$K_p = \frac{\alpha^2}{(1+\alpha)(1-\alpha)} \frac{p}{p^{\ominus}}.$$

d) Given that the reaction takes place in a container of volume V and assuming the gases behave as perfect gases, show that p and, hence, K_p can be expressed as

$$p = \frac{n(1+\alpha)RT}{V}, \qquad \text{and} \qquad K_p = \frac{\alpha^2}{(1-\alpha)} \frac{nRT}{p^{\ominus} V}.$$

e) Calculate the degree of dissociation α of $\mathrm{PCl_5}$ when 0.01 mole of $\mathrm{PCl_5}$ is introduced into a container of volume 1 dm^3 at 450 K and allowed to come to equilibrium.

Exercise 28

The following electrochemical cell,

$$\mathrm{Pt} \mid \mathrm{H_2(g)}\ (p = 1\ \mathrm{bar}) \mid \mathrm{H^+(a = 10^{-4}), Br^-}\ (\mathrm{a} = 10^{-4}) \mid \mathrm{CuBr(s)} \mid \mathrm{Cu}$$

has a cell potential of 0.559 V at 25°C.

a) Make a sketch of the experimental set-up of this cell and explain why no salt bridge is needed.

b) Determine the standard electrode potential for the Cu/CuBr couple.

The solubility product of a salt is defined as the equilibrium constant K_s for a solid salt dissolving in an aqueous solution. For example, for the reaction $\mathrm{Ag_2CO_3(g) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)}$, the solubility product is given by $K_s = a^2_{\mathrm{Ag^+}} a_{\mathrm{CO_3^{2-}}}$.

Now, the standard hydrogen electrode has been replaced by the $\mathrm{Cu/Cu^+}$ couple, whose standard electrode potential is +0.522 V.

b) Write down the correct half reactions and the overall cell reaction.

c) Calculate the solubility product of CuBr(s).

Exercise 29

a) Starting from $\Delta_r G^{\ominus} = -RT \ln K_p$, use the Gibbs-Helmholtz equation, $\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$, to derive the Van 't Hoff equation,

$$\frac{\mathrm{d} \ln K_p}{\mathrm{d}T} = \frac{\Delta_r H^{\ominus}}{RT^2},$$

which describes the temperature dependence of K_p.

b) Integrate the result of part a) to obtain the Van 't Hoff equation in its integrated form:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^{\ominus}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where K_1 and K_2 are K_p at T_1 and T_2, respectively.

c) For a given reaction, the value of K_p doubles on changing the temperature from 298 K to 308 K. Calculate $\Delta_r H^{\ominus}$ for the reaction.

Problem set 7 – Electrochemistry, Chemical equilibrium and condensation of Van der Waals gas

Exercise 30

The temperature dependence of the standard potential of the cell,

$$\mathrm{Pt} \mid \mathrm{H_2(g)}\ (p = 1\ \mathrm{atm}) \mid \mathrm{H^+(a = 1), Cl}\ (\mathrm{a} = 1) \mid \mathrm{AgCl(s)} \mid \mathrm{Ag}$$

can be expressed in the form (with T the temperature in K):

$$E^{\ominus}_{\mathrm{cell}}/\mathrm{V} = 0.2366 - 4.856 \times 10^{-4}(T - 273) - 3.421 \times 10^{-6}(T - 273)^2$$

Write down the cell reaction and calculate $\Delta G^{\ominus}$, $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ at 298 K.

Exercise 31

Consider the following reaction

$$\frac{1}{2}\mathrm{N_2(g)} + \frac{3}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{NH_3(g)}.$$

The standard reaction Gibbs energy of formation of $\mathrm{NH_3(g)}$ is -16.49 kJ mol^{-1} at 298 K and the standard reaction enthalpy is -46.11 kJ mol^{-1} . Assuming that $\Delta_r H^{\ominus}$ is independent of temperature, calculate the equilibrium constant, K_p, for the reaction at

a) i) 298 K,
   ii) 1000 K.

Then find

c) the temperature at which $K_p = 1$,

d) **(bit more challenging)** the amounts of $\mathrm{N_2}$, $\mathrm{H_2}$ and $\mathrm{NH_3}$ present when 1 mole of $\mathrm{NH_3}$ is allowed to come to equilibrium at this temperature (where $K_p = 1$) and 1 atm pressure.
Hint: make a table like in Exercise 26.

Exercise 32

The Van der Waals equation of state for one mole ($n = 1$) is given by

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

a) Explain the physical significance of the Van der Waals parameters a and b.

Below a critical temperature T_c the Van der Waals equation of state predicts condensation, and this critical point of the van der Waals gas is defined by the conditions

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0.$$

b) Apply the first condition to the perfect gas law, and explain that a perfect gas will never exhibit a critical point, i.e. will never condense into a liquid.

c) Apply both of the above conditions to the Van der Waals equation of state to find the critical volume $V_c = 3b$, and hence, the critical temperature $T_c = \frac{8a}{27Rb}$.

d) Finally, substitute the expressions for V_c and T_c back into the Van der Waals equation of state to obtain the critical pressure $p_c = \frac{a}{27b^2}$.

(e) Due to intermolecular interactions carbon dioxide cannot be treated as a perfect gas, but does obey the Van der Waals equation. Given that $a = 0.361$ $\mathrm{Jm^3mol^{-2}}$ and $b = 42.9 \cdot 10^{-6}$ $\mathrm{m^3mol^{-1}}$ for CO_2, calculate the V_c, T_c and p_c for carbon dioxide. How does it compare to the actual critical temperature (304.2 K) and critical pressure (72.9 atm) of CO_2?

A Glossary

Microscopic On an atomic or molecular scale.

Macroscopic Seen from an helicopter view, in such a way that we can forget about microscopic processes (averaging).

System That part of the universe in which we are interested; we only consider macroscopic systems with many particles in thermodynamics.

Surroundings The rest of the universe we need to allow exchange of matter or energy with the system; is also a system, but not *the* system.

Thermal bath A heat reservoir (usually as surroundings), from which you can extract heat or to which you can deliver heat, without changing the temperature of the reservoir.

State variables Macroscopic quantities $(p, V, T, n, \cdots)$ that describe the thermodynamic state of a system. For a complete description a minimal amount of (independent) state variables is required.

Equation of state Relation between state variables that determines the possible states of the system in thermodynamic equilibrium.

Thermodynamic equilibrium A system is in thermodynamic equilibrium if the state variables of the system do not change spontaneously.

State function A (thermodynamic) single valued function of the (independent) state variables; The value of a state function is independent of the way the system has reached a certain state.

Reversible process A process during which the system is in thermodynamic equilibrium at every moment; with that a reversible process is also reversible.

Irreversible process A process that is not necessarily reversible.

Isothermal process A process that proceeds at constant temperature ($\mathrm{d}T = 0$ for the system).

Isobaric process A process that proceeds at constant pressure ($\mathrm{d}p = 0$ for the system).

Isochoric process A process that proceeds at constant volume ($\mathrm{d}V = 0$ for the system).

Adiabatic process A process that proceeds without heat exchange with the environment ($\mathrm{d}q = 0$).

Isolated system No exchange between system and surroundings ($\mathrm{d}w = \mathrm{d}q = \mathrm{d}n = 0$).

Closed system No exchange of matter between system and surroundings ($\mathrm{d}n = 0$); there can be exchange of work ($\mathrm{d}w \neq 0$) and/or heat ($\mathrm{d}q \neq 0$).

Open system There can be exchange of matter ($\mathrm{d}n \neq 0$), work ($\mathrm{d}w \neq 0$) and/or heat ($\mathrm{d}q \neq 0$) between system and surroundings.

Homogeneous system A system in which every (macroscopic) subsystem has the same properties.

Isotropic system A system that has the same properties in all directions, such as an homogeneous fluid. A crystal is not isotropic.

Intensive quantity Does not change if we enlarge the system; e.g. T and p.

Extensive quantity Doubles if we make the system twice as large; e.g. V and n.

B Formulae

$$pV = nRT = Nk_\mathrm{B}T$$
$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_\mathrm{B}T$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \quad \text{or} \quad \Delta U = q + w$$
$$\mathrm{d}q_\mathrm{V} = C_\mathrm{V}\mathrm{d}T \quad \text{and} \quad C_\mathrm{V} = \left(\frac{\partial U}{\partial T}\right)_V$$
$$\mathrm{d}q_\mathrm{p} = C_\mathrm{p}\mathrm{d}T \quad \text{and} \quad C_\mathrm{p} = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\mathrm{d}S = \frac{\mathrm{d}q_\mathrm{rev}}{T} \geq \frac{\mathrm{d}q}{T}$$
$$\mathrm{d}S_\mathrm{tot} = \mathrm{d}S + \mathrm{d}S_\mathrm{surr} \geq 0$$
$$S = k_\mathrm{B}\ln W$$

$$H = U + pV$$
$$A = U - TS$$
$$G = H - TS$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \Delta_r G^\ominus + RT\ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$
$$\Delta_r G^\ominus = -RT\ln K_p \quad \text{with} \quad K_p = \prod_i a_i^{\nu_i}$$

$$\Delta_r G = -\nu F E$$
$$E = E^\ominus - \frac{RT}{\nu F}\ln Q$$

C List of constants

Elementary charge	e	1.602×10^{-19} C
Faraday's constant	F	9.648×10^{4} C mol^{-1}
Boltzmann's constant	k_{B}	1.381×10^{-23} J K^{-1}
Planck's constant	h	6.626×10^{-34} J s
Atomic mass constant	m_{u}	1.661×10^{-27} kg
Avogadro's constant	N_{A}	6.022×10^{23} mol^{-1}
Gas constant	R	8.314 J K^{-1} mol^{-1}
Gravitational acceleration	g	9.807 m s^{-2}
Unit of energy		1 cal = 4.184 J
Standard pressure	$p^{\ominus}$	1 bar = 1×10^{5} Pa = 0.9869 atm
Unit of pressure		1 atm = 101.3 kPa