Physical Chemistry Examples Class for Second Year Students

Compiled by Judit Zádor

2005

1. Tricks and tips

> *What I hear, I forget,*
> *What I see, I remember,*
> *What I do, I know.*
>
> old Chinese proverb

1. Read the question carefully from the beginning to the end. Try to figure out the specific problem or topic you have to deal with.
2. When reading for the second time, write down all data, and convert them to the required units.
   (a) If you have to calculate ratio of values, conversion is not necessary, but make sure that you have the data in the same units. You can save time in this way.
   (b) Temperature must always be changed to Kelvin, except when you need temperature differences only. In that case, ∘C is also applicable.
   (c) Do not forget about the prefixes (mega-, milli-, micro-, etc.) of the units.
3. If it is appropriate, draw a diagram or a figure. This might help a lot.
4. Choose the right formula(e) (see the Appendix).
5. If applicable, check, whether you have the same number of equations as unknowns. If not, you need to find more relations among your variables.
6. Before substituting your numerical data, express the unknown(s) from the equation(s) you have. Even if you miscalculate something, it will be clear that you are aware of the underlying relations.
7. Give a correct numerical answer, if possible. Never forget to state its units. The number of significant digits[1] of the solution should not be greater than those of the original data.
8. Check if your answer is physically and chemically meaningful.
9. Check if you answered the questions that were asked, and if you have answered all questions.
10. If you can think of an alternative way of solution, at least sketch it. These are always warmly welcome and rewarded with extra points in an exam or homework.

---

[1] 1.2 has two significant digits, 1.2000 has 5

2. Problems

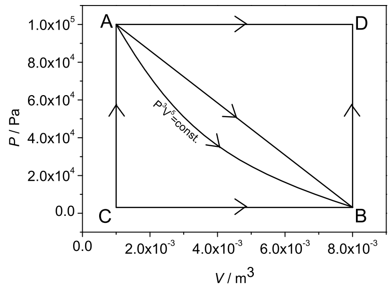
The source of the problems in this compilation are the book of Callen, the book of Atkins, the Web, and there are own problems as well. They are compiled to be used during the second year physical chemistry course in English.

2.1 Heat and work

1. A particular gas is enclosed in a cylinder with a moveable piston. It is observed that if the walls are adiabatic, a quasi-static increase in the volume results in a decrease in pressure according to the equation:

$$P^3V^5 = \text{constant} \qquad (\text{for} \quad Q = 0)$$

   (a) Find the quasi-static work done on the system and the net heat transfer to the system in each of the three processes (ADB, ACB, and the direct linear process AB) as shown in the figure ($P_\mathrm{C} = 3125$ Pa).



   (b) A small paddle is installed inside the system and is driven by an external motor (by means of a magnetic coupling through the cylinder wall). The motor exerts a torque, driving the paddle at an angular velocity ω, and the pressure of the gas (at constant volume) is observed to increase at a rate given by

$$\frac{dP}{dt} = \frac{2\,\omega}{3\,V} \cdot \text{torque}$$

   Show that the energy difference of any two states of equal volumes can be determined by this process. In particular, evaluate $U_C - U_A$ and $U_D - U_B$. Explain why this process can proceed only in one direction (vertically upward rather than downward in the $P-V$ plot).

   (c) Show that *any* two states (any two points in the $P-V$ plane) can be connected by a combination of the processes in (a) and (b). In particular, evaluate $U_D - U_A$.

   (d) Calculate the work W_{AD} in the process A $\longrightarrow$ D . Calculate the heat transfer Q_{AD}. Repeat for D $\longrightarrow$ B , and for C $\longrightarrow$ A . Are these results consistent with those of (a)?

2. For a particular gaseous system it has been determined that the energy is given by

$$U = 2.5PV + \text{constant}$$

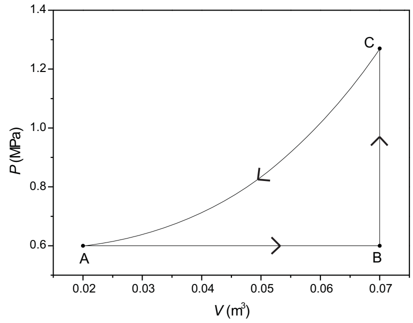
   (a) Calculate Q and W along the parabola $P = 10^5 + 10^9 \cdot (V - 0.02)^2$ between the points A(0.2 MPa, 0.01 m^3) and B(0.2 MPa, 0.03 m^3).

   (b) Find the equation of the adiabats in the $P - V$ plane (i.e. find the form of the curves $P = P(V)$ such that $đQ = 0$ along the curves).

3. For a particular gaseous system it has been determined that the energy is given by:

$$U = 3.50PV + \text{constant}$$

The system is initially in the state $P = 0.60\,\text{MPa}$, $V = 0.02\,\text{m}^3$; designated as point A in the figure. The system is taken through the cycle of three processes (A $\longrightarrow$ B , B $\longrightarrow$ C , C $\longrightarrow$ A), shown in the figure. The system between points C and A moves along the curve $P = 0.584 + 2000 \times V^3$; B: 0.60 MPa, 0.07 m^3; C: 1.27 MPa, 0.07 m^3.



   (a) Calculate Q, W and ΔU for each of the processes.

   (b) Find the equation of the adiabats in the $P - V$ plane (i.e. find the form of the curves $P = P(V)$ such that $đQ = 0$ along the curves).

4. A mixture of two different types ($f_1 = 3, f_2 = 6$) of ideal gases ($n_1 = 1$ mol, $n_2 = 2$ mol) is taken through a cycle of four known quasi-static processes ($A \to B \to C \to D$). The internal energy function of the system is:

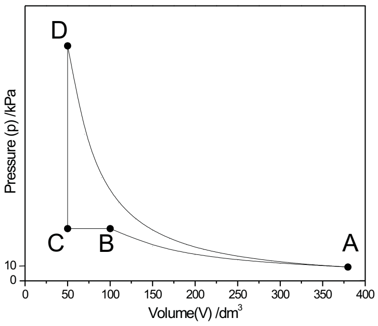
$$U = U_1 + U_2 \qquad U_i = \frac{f_i}{2} n_i RT$$

Calculate all the missing quantities in the tables below.

State	T/K	P/kPa	V/dm^3
A		10	$(3/2)^5 * 50$
B			100
C			50
D			

Process		ΔU / kJ	W / kJ	Q / kJ
$A \to B$	Isothermal compression			
$B \to C$	Isobaric cooling			
$C \to D$	Isochoric heating			
$D \to A$	Adiabatic expansion			

Homework: Callen 1.8-1, 1.8-2



2.2 Fundamental equation and equations of state

1. Two moles of a particular single-component system are found to have a dependence of internal energy U on pressure and volume given by:

$$U = APV^2 \qquad (\text{for } N = 2)$$

Note that doubling the system doubles the volume, energy, and mole number, but leaves the pressure unaltered. Write the complete dependence of U on P, V, and N for arbitrary mole number.

2. Find the three equations of state for a system with the fundamental equation

$$U = \left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{NV}$$

   (a) Corroborate that the equations of state are homogeneous zero order (i.e., that T, P, and μ are intensive parameters).

   (b) Find μ as a function of T, V, and N.

3. Find the three equations of state for a system with the fundamental relation

$$\frac{S}{R} = \frac{UV}{N} - \frac{N^3}{UV}$$

   (a) Show that the temperature is intrinsically positive.

   (b) Find the "mechanical equation of state" $P = P(T, v)$.

   (c) Find the form of the adiabats in the $P - v$ plane. (An "adiabat" is a locus of constant entropy, or an "isentrope").

4. It is found that a particular system obeys the relations

$$U = PV$$

and

$$P = BT^2$$

where B is constant. Find the fundamental equation of the system.

5. A particular system obeys the relation

$$u = Av^{-2}\exp(s/R)$$

N moles of this substance, initially at temperature T_0 and pressure P_0 are expanded isentropically ($s =$constant) until the pressure is halved. What is the final temperature?

6. Show that, in analogy with equation $du = Tds - Pdv$, for a system with r components

$$du = Tds - Pdv + \sum_{j=1}^{r-1}(\mu_j - \mu_r)dx_j$$

where the x_j are the mole fractions ($= N_j/N$).

7. The following equation is purported to be the fundamental equation of an idealized solid body (A, B, D, s_0, v_0, u_0 are positive constants):

$$S = Ns_0 + NB\ln\left(\frac{U}{Nu_0} - \frac{D}{2}\left(\frac{V}{Nv_0} - 1\right)^2\right) + AV$$

   (a) Is it consistent with Postulates II-IV? (Check them all.)
   (b) Give the fundamental equation in the energy representation.

8. The following equation is purported to be the fundamental equation of a well-known, idealized thermodynamic system.

$$U(S, V, N) = AN^{\frac{f+2}{f}}V^{-\frac{2}{f}}e^{\frac{2S}{fNR}}$$

The quantities A and f are positive constants. R is the gas constant.

   (a) Is this fundamental equation consistent with Postulate III-IV?
   (b) Find the three equations of state in entropy representation.
   (c) What can be the system described by the equation above?

9. Find the three equations of state in the entropy representation for a system with the following fundamental equation(Θ, R and v_0 are constants):

$$u = \frac{\Theta}{R}s^2e^{-v^2/v_0^2}$$

Give the corresponding Euler form of the fundamental equation, also in entropy representation.

10. A system obeys the two equations $u = 3/2Pv$ and $u^{1/2} = BTv^{1/3}$. Find the fundamental equation of the system (B is a constant).

Homework: Callen 2.2-4

2.3 Thermal, mechanical, and chemical equilibrium

1. Two particular systems have the following equations of state:

   $$\frac{1}{T^{(1)}} = \frac{3}{2}R\frac{N^{(1)}}{U^{(1)}}$$

   and

   $$\frac{1}{T^{(2)}} = \frac{5}{2}R\frac{N^{(2)}}{U^{(2)}}$$

   where R is the gas constant. The mole number of the first system is $N^{(1)} = 2$ and that of the second is $N^{(2)} = 3$. The two systems are separated by a diathermal wall, and the total energy of the composite system is 2.5×10^3 J. What is the internal energy of each system in equilibrium?

2. Two systems with the equations of state given in Problem 1 are separated by a diathermal wall. The respective mole numbers are the same as in that problem. The initial temperatures are $T^{(1)} = 250$ K and $T^{(2)} = 350$ K. What is the equilibrium temperature?

3. Three cylinders containing gases are fitted with four pistons (see blackboard). The cross-sectional areas of the cylinders are in the ratio $A_1 : A_2 : A_3 = 1 : 2 : 3$. Pairs of pistons are coupled so that their displacements (linear motions) are equal. The walls of the cylinders are diathermal and are connected by a heat conducting bar. The entire system is isolated (so that, for instance, there is no pressure exerted on the outer surfaces of the pistons). Find the ratios of the of pressures in the three cylinders in equilibrium.

4. The hypothetical problem of equilibrium in a closed composite system with an internal moveable *adiabatic* wall is a unique *indeterminate* problem. Physically, release of the piston would lead it to perpetual oscillation in the absence of viscous dumping. With viscous dumping the piston would eventually come to rest at such a position that the pressures on either side would be equal, but the temperatures in each subsystem would then depend on the relative viscosity in each subsystem. The solution of this problem depends on *dynamical* considerations. Show that the application of the entropy maximum formalism is correspondingly indeterminate with respect to the temperatures (but determinate with respect to the pressures).

5. The hydrogenation of propane to form methane proceeds by the reaction

   $$C_3H_8 + 2\,H_2 \rightleftharpoons 3\,CH_4$$

   Find the relationship among the chemical potentials and show that both the problem and the solution are formally identical to that of the following mechanical equilibrium: three cylinders of identical cross-sectional areas fitted with a piston, and each contains a gaseous system (not necessarily of the same composition). The pistons are connected to a rigid bar hinged on a fixed fulcrum (see blackboard). The "moment arms", on the distances from the fulcrum, are in the ratio of 1:2:3. The cylinders rest on a heat conductive table of negligible mass. The entire system is isolated and no pressure acts on the external surfaces of the pistons.

6. Two particular systems have the following equations of state:

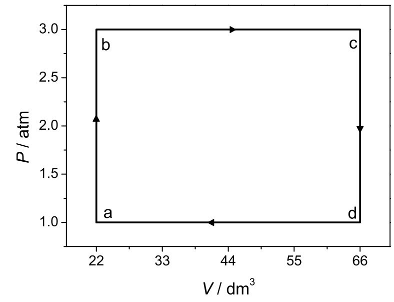
   $$\frac{1}{T^{(1)}} = \frac{3}{2}R\frac{N^{(1)}}{U^{(1)}} \qquad \text{and} \qquad \frac{1}{T^{(2)}} = \frac{5}{2}R\frac{N^{(2)}}{U^{(2)}}$$

where R is the gas constant. The mole number of the first system is $N^{(1)} = 5$ and that of the second is $N^{(2)} = 2$. The two systems are initially separated by an adiabatic and rigid wall. Initially $T^{(1)} = 300$ K and $U^{(2)} = 1.5 \times 10^3$ J. What is the equilibrium temperature, if the wall becomes permeable with respect to heat (becomes diathermal)?

7. Two isolated cylinders (A and B) are separated by a wall, which is diathermal, moveable, but impermeable with respect to matter. Cylinder A is filled with a monatomic ideal gas, while cylinder B is filled with a diatomic ideal gas. Initially the two systems are at equilibrium: U_A=10 kJ, V_A=5 dm^3, N_A=3, and N_B=2.
   (a) Calculate the volume of cylinder B.
   (b) Subsequently 3 kJ heat is introduced in cylinder A by means of an electric wire. Calculate the temperature and the pressure at the new equilibrium.

2.4 Engine, refrigerator and heat pump

1. For the P–V diagram shown you can calculate the ratio $\frac{\text{work done}}{\text{heat taken in}-\text{heat dumped}}$[1], which is in a cycle to be equal to unity, independent of the type of gas used in the engine.
   (a) Why is it equal to unity?
   (b) As you might know, a more important ratio is the efficiency of the engine, $\mu = \frac{\text{work done}}{\text{heat taken in}}$, since the amount of fuel used to produce the work depends on (heat taken in) and not on (heat taken in)-(heat dumped). What is the efficiency of the engine if the working substance of the engine is one mole of ideal monatomic gas?
   (c) One mole of ideal diatomic gas?



2. An engine goes through states $1 \longrightarrow 2 \longrightarrow 3 \longrightarrow 4 \longrightarrow 1$, in a manner that the states are connected with straight lines in the T–S plane. The engine uses water as an auxiliary media.

State	T/ K	P / kPa	v / dm^{3}mol^{-1}	u / kJ mol^{-1}	h / kJ mol^{-1}	s / kJ mol^{-1}K^{-1}	Comp
1	500	2367	0.02165	17.52	17.57	0.0465	L
2	500	2367	1.367	46.91	50.51	0.1124	V
3	300	3.536	506.8	31.84	33.63	0.1124	L+V
4	300	3.536	189.7	13.19	13.86	0.0465	L+V

What cycle does the engine use? Draw both the P–V and the T–S diagram and label the processes. Also, indicate schematically the phases on the T–S graph. Calculate the quasi-static heat and work for all processes. What is the efficiency of the engine? How does it compare to the theoretical efficiency for this cycle?

---

[1] heat dumped=hőveszteség

3. Water is used as a working fluid in a power plant. It goes through the states, listed in the table below. Sketch the processes in a P–V, and also in a T–S diagram. (Hint: If for a state a value is the same as in the preceeding one, the system moves on a straight line on the appropriate graph). Calculate the reversible work and heat for processes $1 \rightarrow 2, 2 \rightarrow 3$ and $3 \rightarrow 4$ if 2 kg of water is used, and explain briefly the reason for the data chosen. If there are more than one way to calculate an answer, compare the different solutions.

state and phase	t °C	P MPa	v $\mathrm{m^3kg^{-1}}$	u $\mathrm{kJ\ kg^{-1}}$	h $\mathrm{kJ\ kg^{-1}}$	s $\mathrm{kJ\ kg^{-1}K^{-1}}$
1: liquid(40%)+vapour(60%)	300	8.581	0.01357	2071	2187	4.724
2: saturated vapour	300	8.581	0.02167	2563	2749	5.704
3: overheated vapour	300	1.000	0.2579	2793	3051	7.123
4: saturated vapour	120.5	0.2017	0.8788	2530	2707	7.123

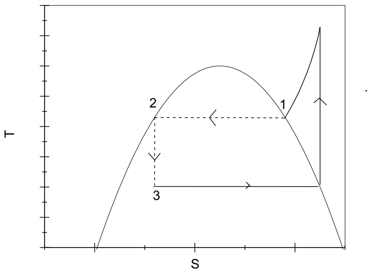
4. A Rankine cycle using a liquid and its vapour as the working media (see figure) is characterised by the following data (subscripts: v: vapour, l liquid).

T/ °C	P_v / MPa	v_v / $\mathrm{dm^3mol^{-1}}$	v_l / $\mathrm{dm^3mol^{-1}}$	u_v / kJ $\mathrm{mol^{-1}}$	u_l / kJ $\mathrm{mol^{-1}}$
10	0.0602	38.03	0.09089	29.0	5.831
-18	0.01733	121	0.08723	27.3	2.543

(a) Label the diagram for processes $1 \longrightarrow 2$ and $2 \longrightarrow 3$. Draw and label a P–V diagram for the two processes as well.

(b) Calculate $\Delta S, \Delta U$, W and Q for processes $1 \longrightarrow 2$ and $2 \longrightarrow 3$, if the vapour to liquid *ratio* is 0.1163 in state 3 and 1 mole of substance is used. Temperature in state 1 and 2 is 10°C, in state 3 it is -18 °C. Present the final results in a table. Hint: the properties of a system of liquid and vapour can be calculated by taking the percentage values of each component. For example the internal energy of a system containing 30% liquid can be calculated as:

$$u = 0.3 * u_l + 0.7 * u_v \tag{2.1}$$



5. In old time refrigerators, ammonia was the working fluid. In the table below, the states of ammonia are listed in a refrigeration cycle, $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$.

No.	T °C	P MPa	v $\mathrm{m^3kg^{-1}}$	u $\mathrm{kJ\ kg^{-1}}$	h $\mathrm{kJ\ kg^{-1}}$	s $\mathrm{kJ\ kg^{-1}K^{-1}}$	composition	phase
1	–24	0.1587	0.7385	1295	1413	5.679	1	Saturated Vapor
2	40	0.4247	0.3466	1395	1542	5.679	-	Superheated Vapor
3	40	1.555	0.01801	563.2	591.2	2.059	0.2	Liquid Vapor Mixture
4	–24	0.1587	0.2431	472.2	510.8	2.059	0.3278	Liquid Vapor Mixture

(a) Calculate the quasi-static heat and work for *each step* of the complete cycle. Sketch the system in T–S plane (using straight lines only). Present your final answers in a table.

(b) Calculate the efficiency of the cycle: $\eta = \frac{\text{heat withdrawn by ammonia at } -24^\circ\text{C}}{\text{work done } on \text{ ammonia}}$

2.5 Measurable quantities

1. Show that $c_P/c_v = \kappa_T/\kappa_S$

2. The density of mercury at various temperatures(°C) is given in g cm^{-3}:

ρ	t	ρ	t	ρ	t
13.6202	-10	13.5217	30	13.3283	110
13.5955	0	13.4973	40	13.1148	200
13.5708	10	13.4729	50	12.8806	300
13.5462	20	13.3522	100	12.8572	310

Calculate α at 0°C, at 45°C, at 105°C, and at 305°C.

Should the stem of a mercury-in-glass thermometer be marked off in equal divisions for equal temperature intervals if the coefficient of the thermal expansion of glass is assumed to be strictly constant?

3. Express α, κ_T, c_P and c_V functions of the system, described in problem 4 of 2.1.

4. Compute the coefficient of expansion and the isothermal compressibility in terms of P and v for a system with the van der Waals equation of state ($P = \frac{RT}{v-b} - \frac{a}{v^2}$).

5. Show that $\alpha = 1/T$ and $\kappa = 1/P$ for an ideal gas.

6. Show that $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$ for an ideal gas.

7. Show that $\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$

8. 50 g liquid is evaporating adiabatically at constant pressure. Calculate the decrease in the liquid's temperature, if 1 g of the liquid has already evaporated. The molar heat of evaporation of the liquid is 36 kJ mol^{-1}, its isobar molar heat capacity is 112 J K^{-1}mol^{-1}, both are assumed to be independent of temperature. The molar weight of the liquid is 32 g mol^{-1}.

9. Show that $đQ = c_p dT - Tv\alpha dP$.

2.6 Maxwell relations

1. Show that $đQ = c_p\, dT - Tv\alpha\, dP$.

2. In the immediate vicinity of a state T_0, v_0 the volume of a particular system of 1 mole is observed to vary according to the relationship

$$v = v_0 + a(T - T_0) + b(P - P_0)$$

Calculate the transfer of heat $đQ$ to the system if the molar volume is changed by a small increment $dv = v - v_0$ at constant temperature T_0.

3. Prove the validity of the form of the Gibbs-Helmholtz equation: $H = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P$ using the total differential of G and standard differentiation rules.

4. Derive a general expression for dS as a function of temperature and pressure using Maxwell relations. The resulting equation should contain measurable quantities.

5. How can you transform the following derivatives?
   (a) $\left(\frac{\partial U}{\partial V}\right)_T$
   (b) $\left(\frac{\partial U}{\partial V}\right)_S$
   (c) $\left(\frac{\partial G}{\partial P}\right)_S$
   (d) $\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial P}{\partial S}\right)_V$
   (e) $\left(\frac{\partial S}{\partial T}\right)_V / \left(\frac{\partial S}{\partial P}\right)_V$

6. Prove that the following relation applies for any thermodynamic system:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha}{\kappa_T}T - p$$

   where α a is the thermal expansion coefficient, and κ_T is the coefficient of isothermal compressibility.

7. Show that $\left(\frac{\partial c_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$

8. For a particular system of 1 mole, in the vicinity of a particular state, a change of pressure dP at constant T is observed to be accompanied by a heat flux $dQ = AdP$. What is the value of the coefficient of thermal expansion of this system, in the same state?

2.7 Phase transition pure substances

1. The heat of fusion of Hg at its normal melting point, –38.9°C, is 2.82 cal g^{-1}. The densities of Hg(s) and Hg(l) at the normal melting point are 14.193 and 13.690 g cm^{-3}, respectively. Estimate the melting point of Hg at (a) 65 atm, and (b) 465 atm.

2. Construct the phase diagram for benzene near its triple point at 36 Torr and 5.50°C using the following data: $\Delta_{fus}H = 10.6$ kJ mol^{-1}, $\Delta_{vap}H = 30.8$ kJ mol^{-1}, $\rho(s) = 0.891$ g cm^{-3}, $\rho(l) = 0.879$ g cm^{-3}.

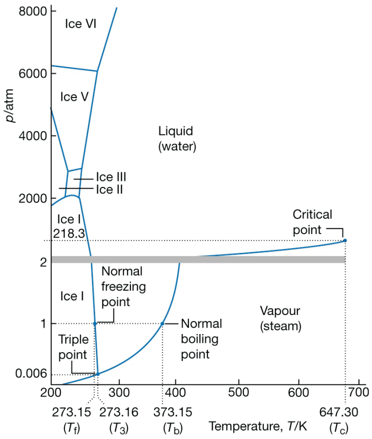
3. It is found that a certain liquid boils at a temperature of 95°C at the top of a hill, whereas it boils at a temperature of 105°C at the bottom. The latent heat is 1000 kJ mol^{-1}. What is the approximate height of the hill?

4. In the vicinity of the triple point the vapor pressure of liquid ammonia (in Pascals) is represented by

$$\ln P = 24.38 - \frac{3063}{T}$$

   This is the equation of the liquid-vapor boundary curve in the P–T diagram. Similarly, the vapor pressure of solid ammonia is

$$\ln P = 27.92 - \frac{3754}{T}$$



What are the temperature and pressure at the triple point? What are the latent heats of sublimation and vaporization? What is the latent heat of fusion at the triple point?

5. Show that, for a transition between two incompressible solid phases, ΔG is independent of pressure.

6. Why does the latent heat of vaporization vanishes at the critical point for a simple, pure substance?

7. It has been snowed, and the relative humidity of air is 60% at –2°C. In what temperature range will all of the snow remain for a long time? (Let's forget about wind and other unpredictable meteorological conditions). At the triple point of water $P = 0.0060$ atm and $T = 273.16$ K. The latent heat of vaporisation is 45.05 kJ mol^{-1}, and that of freezing is –6.01 kJ mol^{-1}. Assume that thermodynamical data are independent of temperature.

8. Find the approximate temperature at which HgO decays. Assume that thermodynamical data are independent of temperature.

	$\Delta_f H^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J mol^{-1}K^{-1}
Hg(g)	61.3	175.5
HgO(s)	–90.8	70.3
Hg(l)	0	76.0
O_2(g)	0	205.1

9. The freezing point of water decreases with increasing pressure until $P = 0.22$ GPa. At this solid-solid-liquid triple point, a new phase of ice, known as Ice-III, appears, and the freezing point of water from this pressure on increases with pressure. (This is the lowest temperature at which liquid water is a stable equilibrium phase.) Let us assume that the latent heat of melting at 273.15 K (333 J g^{-1}), and the densities of ice and water (0.917 g cm^{-3}and 1.00 g cm^{-3}, respectively) are constant up to 0.22 GPa. Estimate the temperature of the high-pressure solid-solid-liquid triple point.

10. Show that the vaporisation line and sublimation line for water do not have the same slopes at the triple point in the P–T plane. (Which of them has the greater slope?)

11. What pressure is required to convert graphite into diamond at 25°C? The following data apply to 25°C and 100 kPa. Assume the specific volume, v_s and κ_T are constant with respect to pressure changes.

	Graphite	Diamond
$\Delta_f G^\ominus$ / kJ mol^{-1}	0.	2.8678
v_s / cm^3 g^{-1}	0.444	0.284
κ_T / kPa	3.04×10^{-8}	0.18710^{-8}

12. (a) An adiabatic system, open to the atmosphere, which has a pressure of 10^5 Pa, consists of 1 mol water at 0°C and 6 mol water at 25°C. Assuming a constant specific heat $c_P = 75.3$ J K^{-1}mol^{-1} for water, determine the final temperature of the system and the change in entropy for the spontaneous adiabatic process. Comment your results.
    (b) Repeat your calculation with 1 mol of ice instead of 1 mol of water. The latent heat of melting for ice is 6020 J mol^{-1}.
    (c) Repeat your calculation with 6 mol ice and 1 mol water vapor, which has a temperature of 100°C. The latent heat of vaporisation is 41.4 kJ mol^{-1}.

13. The variation of the melting point of acetic acid with pressure is given by the following expression, which is valid up to 2×10^8 Pa:

$$t/C = 16.66 + 0.231 \times 10^{-6}(P/\text{Pa}) - 2.25 \times 10^{-16}(P/\text{Pa})^2$$

What is the melting point and the molar heat of melting of acetic acid at 100 MPa, if the specific volume change is 0.115 dm^3 kg^{-1}? $M_{\text{CH}_3\text{COOH}} = 60$ g mol^{-1}.

14. Consider the vapour pressure of caesium in equilibrium with liquid caesium. The vapour pressure of caesium is so low that it behaves as an ideal gas. Also, the molar volume of the vapour is much larger than the molar volume of the liquid. The latent heat of vaporization varies with temperature approximately as $\Delta_{vap}H = a(T_0 - T)^2$, where a is a positive constant and T_0 is a reference temperature. Using the above information and the differential form of the Clausius-Clapeyron equation, obtain an expression for the vapour pressure of caesium at a temperature T, that is an explicit $P = P(T)$ function. The vapour pressure of Cs at 500°C is 104 Pa.

15. The freezing point of water is 273.15 K at p=1 atm. At what temperature does Lake Baikal freeze to the bottom, if the deepest point of the lake is 1940 m below the surface of the water? Some useful data: $\rho_{\text{H}_2\text{O}} = 1.00$ g cm^{-3}, $\Delta_f H = 6.02$ kJ mol^{-1}, $\Delta_f v = 0.09$ cm^3 g-1, $M_{\text{H}_2\text{O}} = 18.0$ g mol^{-1}.

16. The vapour pressure of water, P, may be approximately represented by the equation, $\ln P = B - 4884/T$, where B is a constant whose value depends on the units used for P.
    (a) Based on the vapour pressure of water at its normal boiling point, 373.15 K, evaluate B.
    (b) 10 g of water is introduced into an evacuated chamber of constant volume, $V = 0.010$ m^3. At a temperature of 373.15 K, what will be the mass of liquid water in the chamber? Assume the liquid density is constant (1 g cm^{-3}). The molecular weight of water is 18 g mol^{-1}. You can use the ideal gas law for the water vapour where appropriate.

17. An experimental vapour pressure expression: $\ln(P/\text{Torr}) = 16255 - \frac{2501.8}{T/\text{K}}$. Calculate the latent heat for the corresponding phase transition.

Homework: Atkins Problem 6.2, Additional problem 6.18 [N.B. Pay attention: there are Exercises, Problems, Theoretical problems and Addtitional problems … in the Atkins book]

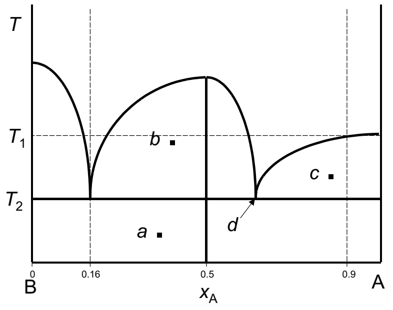
2.8 Ideal mixtures

1. At 20°C the vapour pressures of pure n-octane and pure benzene are 2.66 kPa and 13.3 kPa, respectively. To a close approximation these two compounds form ideal liquid and gaseous mixtures.
   (a) In what pressure range is a mixture of them, in which the mole fraction of benzene is 0.4, biphase in equilibrium?
   (b) In what composition range is a mixture of them, which has a total vapour pressure of 6 kPa biphase in equilibrium?
2. The vapour pressure of a pure liquid A at 293 K is 68.6 kPa and that of the pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture, in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of a liquid mixture.
3. Benzene and toluene form nearly ideal solutions. At 20°C the vapour pressures of pure benzene and toluene are 22 Torr and 74 Torr, respectively. A solution consisting of 1.00 mol of each component is boiled by reducing the external pressure below the vapour pressure. Calculate the pressure when boiling begins, the composition of each component in the vapour, and the vapour pressure when only a few drops of liquid remain. Assume that the rate of vaporization is low enough for the temperature to remain constant at 20°C.
4. At 20°C the vapour pressure of pure A is 2.66 kPa and that of pure B is 13.3 kPa. The system is ideal and $z_B = 0.4$. In what pressure range form this mixture a biphase system?
5. It is found that the boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96°C at 1 atm. At this temperature the vapour pressures of pure A and B are 110.1 kPa and 94.93 kPa, respectively.
   (a) Is this solution ideal?
   (b) What is the composition of the vapour when boiling begins?
6. Find the book called "Physico-Chemical Constants of Binary Systems" in the library and draw a phase diagram based on real data. Label the diagram and try to assign it to one of the types you have learned in the class.
7. Dibromoethene (DE) and dibromopropene (DP) form nearly ideal solutions. At 358 K, the vapour pressures of pure DE and PE are 172 Torr and 128 Torr, respectively. A solution consisting of 1.00 mol of each component is in equilibrium with its vapour. Assume that the rate of vaporisation is low enough for the temperature to remain constant at 358 K.
   (a) Calculate the equilibrium vapour pressure above the original liquid mixture.
   (b) Calculate the equilibrium vapour pressure when only a little drop of liquid remains in equilibrium with the (nearly) completely vaporised mixture.
   (c) Calculate the equilibrium vapour pressure when half of the mixture is in the vapour phase.

Homework: Atkins Exercise 8.4(a), 8.13(a),

2.9 Phase diagrams

1. Diborane (B_2H_6, melting point 131 K) and dimethylether (CH_3OCH_3, melting point 135 K) form a compound $(CH_3)_2OB_2H_6$ that melts at 133 K. The system exhibits one eutectic at $x(B_2H_6)$=0.25 and 123 K, and another at $x(B_2H_6)$=0.90 and 104 K.
   (a) Sketch the T vs $x(B_2H_6)$ phase diagram of this system and label it with the name of the appropriate compounds and phases. Indicate all known values in the graph.
   (b) Sketch the cooling curves for the compositions $x(B_2H_6)$=0.25, 0.5 and 0.75. Assume that the heat capacity of the liquid is greater than that of the solid. Indicate all known values in the graph.
2. Two partially immiscible liquids (A and B) have an upper critical temperature of 89°C at composition $x_B = 0.4$, and a lower critical temperature of 17°C at composition x_B=0.5. The lowest and highest mole fractions where the mixture forms two phases are $x_b = 0.07$ and $x_B = 0.91$, respectively, both at 52°C.
   (a) Sketch the T–x phase diagram and label appropriate areas with the name of the phases. Indicate all known values in the graph.
   (b) Below $x_b = 0.07$, the mixture can be considered as an ideal two-component mixture. Calculate the composition of the vapour phase at $x_B = 0.05$, if the vapour pressures of pure A and B are 56.7 kPa and 120 kPa, respectively.
3. Consider the phase diagram, which represents a solid-liquid equilibrium.
   (a) Indicate the number of species and phases present at the points/regions labelled a, b, c and d.
   (b) Sketch cooling curves for composition $x_A = 0.16$ and 0.90 (put the appropriate temperatures on the vertical axes).



2.10 Colligative properties

1. The vapour pressure of benzene is 400 Torr at 60.6°C, but it fell to 386 Torr when 19.0 g of an involatile organic compound was dissolved in 500 g of benzene. Calculate the molar mass of the compound.
2. The osmotic pressure of an aqueous solution at 300 K is 120 kPa. Calculate the freezing point of the solution.

3. Calculate the molality of an aqueous solution, whose boiling point is 373.57 K at a pressure of 101068 Pa. (Water boils at 100.0°C at atmospheric pressure. 1 atm = 101 325 Pa, the molar enthalpy of evaporation of pure water is 40.670 kJ mol^{-1}, its density is 1.00 g cm^{-3}.)

4. Water (T_f=0°C, K_f=1.86°C kg/mol) is not a very good substance to do accurate freezing point depression measurements and hence to obtain the molality of a compound. If we want more accurate measurements, camphor is an excellent solvent (T_f=179.8°C, K_f=40.0°C kg/mol).
    (a) Why can we do more accurate measurements in camphor?
    (b) For example, if the freezing point of a water solution of some substance is −0.186°C, what is the freezing point of a camphor solution of the same molality?

5. Calculate the freezing point of a glass of water of volume 250 cm^{3}sweetened with 7.5 g of sucrose. The standard enthalpy of fusion of water is 6.008 kJ mol^{-1}at the transition temperature. The standard enthalpy of vaporization of water is 44.016 kJ mol^{-1}near the standard freezing point. The molar mass of sucrose is 342 g mol^{-1}and that of water is 18 g mol^{-1}. The standard freezing point of water is 273.15K. Near the standard freezing point the enthalpies can be considered independent of the temperature and the pressure.

Homework: Atkins Exercise 7.7(a), 7.16(b), 8.4(a), 8.8(a)

2.11 Molar quantities

1. The volume of an aqueous solution of NaCl at 25°C was measured at a series of molalities b, and it was found that the volume fitted the expression

$$V/\mathrm{cm}^3 = 1003 + 16.62b + 1.77b^{3/2} + 0.12b^2$$

where b is the volume of the solution formed from 1.000 kg of water and b is to be understood as $b/b^{\ominus}$. Calculate the partial molar volume of the components in a solution of molality 0.100 mol kg^{-1}.

2.12 Liquid surfaces

1. Calculate the work of creating a spherical cavity of radius r = 2 mm in a liquid of surface tension γ = 427 mN m^{-1}.

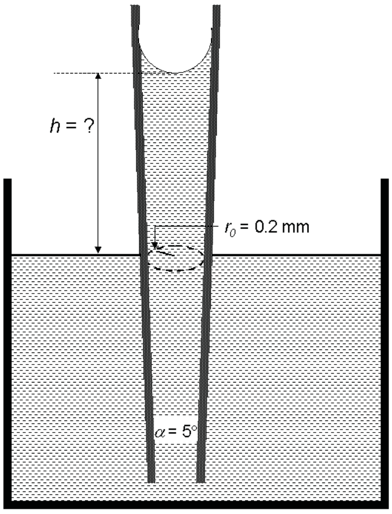
2. Two soap bubbles of different radii are blown on opposite ends of a tube with a stopcock in the middle. When the stopcock is opened what happens to the radii of the bubbles? Write down the equations your answer is based on and explain your answer with a few words.

3. We have a tube with two pipes containing water: the diameter of the first is 2 mm, the other has a radius of 0.1 mm. What is the difference between the water level of the pipes? Assume hemispherical surfaces. γ = 72.75 mN m^{-1}, g = 9.81 m s^{-2}.

4. A closed vessel contains two droplets of different size but of the same substance. What will be the equilibrium size of the two droplets? Explain your answer.

5. Calculate the radius of a cavity, which is stable at 10 cm below the surface of water. The surface tension of water is γ = 72.75 mN m^{-1}, ρ = 1.0 g cm^{-3}.

6. A physical chemist drinking champagne observes a spherical cavity of r=0.2 mm in his glass.
    (a) What is the pressure difference across the surface of the cavity? The surface tension of champagne is 60.5 mN m^{-1}.
    (b) What is the pressure inside the cavity, if it is 10 cm deep below the level of the champagne? Assume $\rho_{\text{champagne}} = 1$ g cm^{-3}.
    (c) After sipping from the glass, the cavity comes closer to the surface level of champagne with 1 cm. Provided that the pressure inside remains constant, what is the radius of the cavity?
    (d) Calculate the work corresponding to the change of cavity surface from its initial value to the value calculated in 6c.
7. The technician did not manage to pull a capillary with parallel sides, only a cone of an angle of 5° (see figure).



    (a) Give the capillary rise for water in the cone ($\gamma = 7.275 \cdot 10^{-2}$ Nm^{-1}), if the bottom of the capillary is the narrow edge, and the radius at the outer water level is 0.2 mm. As a first approximation, assume a hemispherical surface. ($\rho_{water} = 1$ g cm^{-3})
    (b) Is the assumption valid? (Hint: calculate r at height h.)

2.13 Chemical equilibrium

1. Dinitrogen tetroxide is 18.46 per cent dissociated at 25°C and 1.00 bar in the equilibrium $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$. Calculate (a) K, (b) $\Delta_r G^\ominus$, (c) K at 100°C given that $\Delta_r H^\ominus$=57.2 kJ mol^{-1} over the temperature range.
2. In the gas-phase reaction $2\,A + B \longrightarrow 3\,C + 2\,D$, it was found that, when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^\ominus$.

3. The standard reaction enthalpy of $Zn(s) + H_2O(g) \longrightarrow ZnO(s) + H_2(g)$ is approximately constant at 224 kJ mol^{-1} from 920 K up to 1280 K. The standard reaction Gibbs energy is 33 kJ mol^{-1} at 1280 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

4. The equilibrium constant of the reaction $2\,C_3H_6(g) \longrightarrow C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088}{T/\mathrm{K}} \cdot \frac{1.51 \cdot 10^5}{(T/\mathrm{K})^2}$$

between 300 K and 600 K. Calculate the standard reaction enthalpy and standard reaction entropy at 400 K.

5. What is the standard enthalpy of a reaction for which the equilibrium constant is (a) doubled, (b) halved when the temperature is increased by 10 K at 298 K?

6. Estimate the temperature at which $CaCO_3$ (calcite) decomposes.

7. The equilibrium constant for the reaction, $I_2(s) + Br_2(g) \rightleftharpoons 2\,IBr(g)$ is 0.164 at 25°C. (a) Calculate $\Delta_r G^{\ominus}$ for this reaction. (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25°C. Find the partial pressure of IBr(g) at equilibrium. Assume that all the bromine is in the liquid form and that the vapour pressure of iodine is negligible. (c) In fact, solid iodine has a measurable vapour pressure at 25°C. In this case, how would the calculation have to be modified?

8. The dissotiation vapour pressure of NH_4Cl at 427°C is 608 kPa but at 459°C it has risen to 1115 kPa. Calculate for 427°C

   (a) the equilibrium constant
   (b) the standard reaction Gibbs energy
   (c) the standard enthalpy of dissociation
   (d) the standard entropy of dissociation

   Assume that the vapour behaves as an ideal gas and that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are independent of temperature in the range given.

9. The percentage (α) of dissociated $CO_2(g)$ into CO(g) and $O_2(g)$ at high temperatures was found to vary as follows:

T/K	1395	1498
α/%	$1.44 \cdot 10^{-2}$	$4.71 \cdot 10^{-2}$

   Assuming the standard reaction enthalpy to be constant over this temperature range, calculate at both temperatures: the equilibrium constant, the standard Gibbs energy, the standard reaction enthalpy and the reaction entropy.

10. Calculate the percentage change in the equilibrium constant K_x of the reaction

    $H_2CO(g) \rightleftharpoons CO(g) + H_2(g)$

    when the total pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

11. The standard Gibbs energy of formation of $NH_3(g)$ is –16.5 kJ mol^{-1}at 298 K.

(a) What is the reaction Gibbs energy when the partial pressures of N_2, H_2 and NH_3 (treated as perfect gases) are 3.0 bar, 1.0 bar and 4.0 bar, respectively?

(b) What is the spontaneous direction of the reaction in this case?

2.14 Transport

1. A solid surface with dimensions 2.5 mm × 3.0 mm is exposed to argon gas at 90 Pa and 500 K. What is the collision frequency? How many collisions do the Ar atoms make with this surface in 15 s? $M_{Ar} = 39.95$ g mol^{-1}.

2. The space between two surfaces is filled with Ar gas at 25°C and 1.00 bar. The area of each of the surfaces is 25 cm^2, and the distance between them is 3 mm. One surface is at 35°C, and the other is at 15°C. What is the heat flow between the two surfaces? $\kappa = 1.75 \times 10^{-2}$ J K^{-1}s^{-1} and is independent of temperature in this region.

3. The body-temperature viscosity and density of human blood are 4 cP (centipoise) and 1.0 g cm^{-3}. The flow rate of blood from the heart through the aorta is 5 L/min in a resting human. The aorta's diameter is typically 2.5 cm. Find the pressure gradient along the aorta.

4. The times that a steel ball ($\rho_{ball} = 7.8 \times 10^3$ kg m^{-3}) required to drop through water and commercial shampoo were 1 s and 7 s, respectively. Given that the densities of water and the shampoo are 1000 and 1030 kg m^{-3}, respectively, find $\eta_{shampoo}/\eta_{water}$. Assume that the velocity of the ball is constant (true, if $t \to \infty$).

5. The diffusion coefficient of sucrose in water at 25°C is 5.2×10^{-6} cm^2 s^{-1}. What is the value of the root mean distance after 1 day, if we pour some sugar into a glass and then add some water very slowly and carefully (in order to avoid direct mixing) on the top?

6. In a spherical infinite diffusion scheme the root mean square distance travelled by a sulphate ion (SO_4^{2-}) in water at 25°C in 250 minutes is 1 cm.
   (a) What is the diffusion coefficient of SO_4^{2-} in water at 25°C.
   (b) What is the approximate hydrodynamic radius of SO_4^{2-} in water at 25°C if the viscosity of water at this temperature is 0.891 cP.
   (c) Calculate the concentration of SO_4^{2-} after 250 min at a distance of 1 cm from the centre if 0.1 mmol of SO_4^{2-} was in the centre initially. (Diffusion-potential has been eliminated.)
   (d) What is the mobility of SO_4^{2-} in water at 25°C?
   (e) Calculate the concentration gradient of SO_4^{2-} and the thermodynamic force acting on a single sulphate ion at the time and position defined under point 6c.
   (f) Derive the (time-dependent) curvature of the spatial concentration profile of SO_4^{2-} at 25°C using Fick's 2nd law.

7. The viscosity of a chlorofluorocarbon (CFC) was measured by comparing its rate of flow through a long narrow tube with that of argon. For the same pressure difference, the same volume of the CFC passed through the tube in 72.0 s, and that of argon in 18 s. The viscosity of argon at 25°C is 208 μP. What is the viscosity of the CFC? M_{CFC}=200 g mol^{-1}.

3. Constants and relations

3.1 Constants and unit conversion

$R = 8.314 \frac{\mathrm{J}}{\mathrm{mol\,K}}$ $\qquad N_A = 6.022 \cdot 10^{23}$ $\qquad k = 1.38 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}$ $\qquad g = 9.81\mathrm{m\,s^{-2}}$

1P [1] $= 0.1\mathrm{Pa\ s^{-1}}$ $\qquad 1\,\mathrm{atm} = 101325\,\mathrm{Pa}$ $\qquad 1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$

3.2 Relations

internal energy of monatomic ideal gas: $U = \frac{3}{2}NRT$ $\qquad$ of diatomic: $U = \frac{5}{2}NRT$

ideal gas law: $PV = NRT$

$dU = đW + đQ$ $\qquad$ quasi-static work: $đW = -P\,dV$ $\qquad$ quasi-static heat: $đQ = T\,dS$

Carnot efficiency: $\eta = 1 - \frac{T_c}{T_h}$

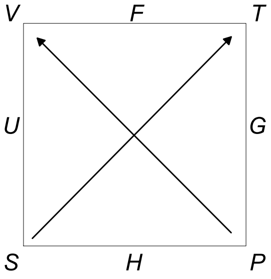
$dU = T\,dS - P\,dV + \sum_i \mu_i\,dN_i$ $\qquad dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \sum_i \frac{\mu_i}{T}\,dN_i$

Gibbs-Duham relations: $S\,dT - V\,dP + \sum_i N_i\,d\mu_i = 0$ $\qquad U\,d\frac{1}{T} + V\,d\frac{P}{T} - \sum_i N_i\,d\frac{\mu_i}{T} = 0$

enthalpy: $H = U + PV$ $\qquad$ free energy: $F = U - TS$ $\qquad$ Gibbs energy: $G = U - TS + PV$

Gibbs-Helmholtz equation: $H = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P$

Maxwell relations (**V**alid **F**acts and **T**heoretical **U**nderstanding **G**enerate **S**olutions to **H**ard **P**roblems)



$\left(\frac{\partial\mu}{\partial T}\right)_P = -s$ $\qquad \left(\frac{\partial\mu}{\partial P}\right)_T = v$

isobaric coefficient of thermal expansion: $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

---

[1] Poise

isothermal compressibility: $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ adiabatic compressibility: $\kappa_s \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

heat capacity at constant pressure: $c_P \equiv \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{N}\left(\frac{\partial Q}{\partial T}\right)_P$

heat capacity at constant volume: $c_v \equiv \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{N}\left(\frac{\partial Q}{\partial T}\right)_V$

$c_P = c_v + \frac{TV\alpha^2}{N\kappa_T}$ $\kappa_T = \kappa_s + \frac{TV\alpha^2}{Nc_P}$

$\frac{dP}{dT} = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}$ Clapeyron equation: $\frac{dP}{dT} = \frac{\Delta_{\mathrm{melt}}H}{T\Delta_{\mathrm{melt}}V}$

external pressure effect on vapour pressure: $P = P^* e^{v_f \Delta P/RT} \approx P^*\left(1 + \frac{v_f \Delta P}{RT}\right)$

Clausius-Clapeyron equation: $\frac{dP}{dT} = \frac{\Delta_{\mathrm{vap/subl}}Hp}{RT^2}$ or: $\frac{d\ln P}{dT} = \frac{\Delta_{\mathrm{vap/subl}}H}{RT^2}$

Gibbs phase rule: $F = C - P + 2$

barometric formula: $P = P_0 e^{-Mgh/RT}$

$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ $\Delta_r G^\ominus = -RT\ln K$ $\sum_j N_j d\mu_j = 0$ $Q = \prod_j a_j^{\nu_j}$

van't Hoff equation: $\frac{d\ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$ or: $\frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^\ominus}{R}$ $\left(\frac{\partial K}{\partial P}\right)_T = 0$

$\Delta_{\mathrm{mix}}G^{\mathrm{ideal}} = NRT\sum_j N_j \ln x_j$

excess thermodynamic functions: $G^{\mathrm{E}} = \Delta_{\mathrm{mix}}G - \Delta_{\mathrm{mix}}G^{\mathrm{ideal}}$ $S^E = \Delta_{\mathrm{mix}}S - \Delta_{\mathrm{mix}}S^{\mathrm{ideal}}$

chemical potential of ideal solution: $\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^\ominus + RT\ln P_{\mathrm{A}}$

Raoult's law: $P_A = x_A P_A^*$ Henry's law: $P_A = K_A P_A^*$

liquid composition: $P = x_A P_A^* + x_B P_B^*$ vapour composition: $\frac{1}{P} = \frac{y_A}{P_A^*} + \frac{y_B}{P_B^*}$

freezing point depression: $\Delta T = K_f b = \frac{RT^{*2}}{\Delta_{\mathrm{fus}}H}x_B$ boiling point elevation: $\Delta T = K_b b = \frac{RT^{*2}}{\Delta_{vap}H}x_B$

osmotic pressure: $\Pi = cRT(1 + Bc + \ldots)$

partial molar volume: $V_j = \left(\frac{\partial V}{\partial N_j}\right)_{P,T,\overline{N}}$ $V = \sum_j N_j V_j$

Laplace equation: $P_{\mathrm{concave}} = P_{\mathrm{convex}} + \frac{2\gamma}{r}$ capillary action: $h = \frac{2\gamma}{\rho g r}\cos\Theta$

work done to create surface: $dw = \gamma\, d\sigma$ contact angle: $\gamma_{\mathrm{sg}} = \gamma_{\mathrm{sl}} + \gamma_{\mathrm{lg}}\cos\Theta$

hydrostatic pressure: $P = \rho g h$ Kelvin equation: $P = P^* \cdot e^{2\gamma V_m/rRT}$

collision flux: $Z_w = \frac{P}{(2\pi m k T)^{1/2}}$

Fick's first law: $J_{\mathrm{matter}} = -D\frac{dc}{dz}$ energy flux: $J_{\mathrm{energy}} = -\kappa\frac{dT}{dz}$ momentum flux: $J_{I_x} = -\eta\frac{dv_x}{dz}$

Fick's second law: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$

Poisuille equation for liquids: $\frac{dV}{dt} = \frac{(P_1 - P_2)\pi r^4}{8l\eta}$ for gases: $\frac{dV}{dt} = \frac{(P_1^2 - P_2^2)\pi r^4}{16l\eta p_0}$

diffusion in 1D: $c(x,t) = \frac{N_0}{2A(\pi Dt)^{1/2}} e^{-x^2/4Dt}$ semi-1D: $c(x,t) = \frac{N_0}{A(\pi Dt)^{1/2}} e^{-x^2/4Dt}$

in 3D $c(r,t) = \frac{N_0}{8(\pi Dt)^{3/2}} e^{-r^2/4Dt}$

root mean square distance, 1D: $\langle x^2 \rangle^{1/2} = \sqrt{2Dt}$ 2D: $\langle \rho^2 \rangle^{1/2} = \sqrt{4Dt}$ 3D: $\langle r^2 \rangle^{1/2} = \sqrt{6Dt}$