Name ___________solutions_____ ___ ___________

Thermal Physics 224 **Final exam** **8.25 am, Wednesday December 12, 2007**
Autumn 2007 Instructor: David Cobden

You have 2 hours. Begin at 8.25 and hand your exam to me by the time I leave the room at 10.25.

Attempt all the questions.

Please write your name on every page and your SID on the first page.

Write all your working on these question sheets. Use this front page for extra working. It is important to show your calculation or derivation. Some of the marks are given for showing clear and accurate working and reasoning.

Watch the blackboard for corrections or clarifications during the exam.

This is a closed book exam. ***No books, notes or calculators allowed.***

$dU = TdS - pdV + \mu dN.$

$N_A \approx 6 \times 10^{23}$ $k_B = 1.4 \times 10^{-23}$ JK^{-1} $R = N_A k_B = 8.3$ JK^{-1} $e = 1.6 \times 10^{-19}$ C

1 mole of gas occupies 24 liters (= 0.024 m^3) at T = 300 K and p = 1 bar (= 10^5 Pa)

Name Solutions

1. [5] Two possible energies of a molecule in surroundings at temperature T are E_1 and E_2. What is the ratio of the respective probabilities P_1 and P_2 of finding it with these energies?

$$\frac{P_1}{P_2} = e^{-(E_1-E_2)/kT}$$

2. [12] Assume that the earth's atmosphere is an ideal gas with a uniform temperature T. Write down the form of the probability distribution $P(z)$ that a given molecule of mass m will be found at a height z. (Think of comparing the probabilities of being at two different heights. Use the gravitational constant g). Deduce an expression for the variation of density, and therefore pressure with height, if the pressure at ground level ($z = 0$) is p_0.

$$E = mgz \quad \rightarrow \quad P(z) \propto e^{-mgz/kT}$$

Independent molecules $\rightarrow \rho(z) \propto P(z) \propto e^{-mgz/kT}$

Ideal gas: $p = \frac{\rho}{m}kT \propto Te^{-mgz/kT}$

$\therefore$ For uniform T, $p = p_0 e^{-mgz/kT}$

3. [15] A dipole has two energy levels, $E_1 = +\Delta$ and $E_2 = -\Delta$. Find its partition function at temperature T and show that the mean energy is $\bar{E} = -\Delta \tanh \beta\Delta$, where $\beta = 1/k_B T$.

$$Z = \sum_i e^{-E_i/kT} = e^{-\Delta/kT} + e^{+\Delta/kT} = e^{-\beta\Delta} + e^{\beta\Delta}$$

$$= 2\cosh\beta\Delta$$

$$\bar{E} = \frac{\partial \ln Z}{\partial \beta} = \frac{-2\Delta\sinh\beta\Delta}{2\cosh\beta\Delta} = -\Delta\tanh\beta\Delta$$

$$\left(\bar{E} = \frac{-\Delta e^{\beta\Delta} + \Delta e^{-\beta\Delta}}{e^{\beta\Delta} + e^{-\beta\Delta}} \right.$$

$$\left. = \sum_i P_i E_i \right)$$

Name Solutions

4. [10] A balloon contains 2.4 liters of CO_2 gas at 300 K and 1 bar. A CO_2 molecule can be taken to be a rigid rod approximately $0.1\ \text{nm}^2 = 10^{-19}\ \text{m}^2$ in cross-section and of mass $m = 7 \times 10^{-26}$ kg. First, *estimate* the typical spacing of CO_2 molecules in the balloon.

$$\text{Spacing} \sim \left(\frac{V}{N}\right)^{1/3} = \left(\frac{0.024\,m^3}{6\times10^{23}}\right)^{1/3} = \left(40\,nm^3\right)^{1/3} \simeq 3\,nm$$

5. [10] Estimate the mean free path of a CO_2 molecule.

$$L \simeq \frac{1}{(\sqrt{2})\,n\sigma} = \frac{V}{N\sigma} \simeq \frac{40\,nm^3}{\underset{\substack{\nearrow \\ 10^{-19}m^2}}{0.1\,nm^2}} \simeq 400\,nm$$

6. [10] Estimate the rms speed of a CO_2 molecule.

$$\left\langle \tfrac{1}{2} m v_{rms}^2 \right\rangle = \frac{3}{2}kT \quad \text{so} \quad v_{rms} = \sqrt{\frac{3kT}{m}} = \left(\frac{3\times1.4\times10^{-23}\times300}{7\times10^{-26}}\right)^{1/2}$$

$$= \left(\frac{9\times1.4}{7}\times10^{-23+2+26}\right)^{1/2}$$

$$= \left(1.8\times10^{5}\right)^{1/2} = \sqrt{18}\times10^{2} \simeq 400\,ms^{-1}$$

7. [10] Estimate the internal energy of the CO_2 gas.

$$U = \frac{Nf}{2}kT = \frac{nf}{2}RT \qquad n = \text{no. of moles} = \frac{2.4\,L}{24\,L} = 0.1$$

$$f = 3\ \text{trans} + 2\ \text{rot} = 5$$

$$U \simeq \frac{0.1\times5}{2}\times 8.3\,JK^{-1}\times 300\,K \simeq 2\times300\,J = 600\,J$$

8. [10] Estimate the amplitude of the fluctuations of the internal energy with time.

$$\delta U \simeq \frac{U}{\sqrt{N}} = \frac{600\,J}{\left(0.1\times6\times10^{23}\right)^{1/2}} \simeq \frac{600\,J}{\sqrt{6}\times10^{11}}$$

$$= \sqrt{6}\times10^{-9}\,J \simeq 2.5\times10^{-9}\,J$$

9. [10] Assume that the pressure inside the balloon is 1% greater than that outside and assume that CO_2 is an ideal gas. How much heat, if any, is generated if the balloon bursts? (Consider enthalpy. Ignore the energetics of the rubber.) don't.

This is a lousy question. Anyway, you could say that $\Delta U = 0$ because initial & final T are the same, but gas expands doing work $-W \doteq p\Delta V = p \times 2.4L \times 1\%$ $\Delta U = Q + W$
$\therefore$ Some heat flows <u>in</u>, $Q = -W \doteq 10^5\,Pa \times 2.4 \times 10^{-5}\,m^3 = 2.4\,J$

10. [5] Does the total entropy increase or remain the same during this process, and why?

It increases, because the process is irreversible –
it's fast so not quasistatic
& the CO_2 mixes with the air, creating entropy

11. [8] State the fundamental statistical mechanical definitions of temperature and pressure.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad p = T\left(\frac{\partial S}{\partial V}\right)_{U,N}$$

12. [6] Is temperature ever negative in a real system? What would happen if something at negative temperature were brought in contact with something at positive temperature?

Yes, eg in a paramagnet, or any system with a maximum possible energy. Heat flows from -ve to positive temperature.

13. [8] Define the Gibbs free energy G in terms of U and other macroscopic variables, and give or deduce the thermodynamic identity relating small changes in G to those in T, p and N.

$$G = U + pV - TS \qquad dG = dU + d(pV) - d(TS)$$
$$= -SdT + Vdp + \mu dN$$

14. [8] From this you can deduce that $\left(\frac{\partial G}{\partial p}\right)_{T,N} = V$. Write down the other two relationships for derivatives of G that can be deduced immediately from the thermodynamic identity.

Hold p, N fixed: $\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S$

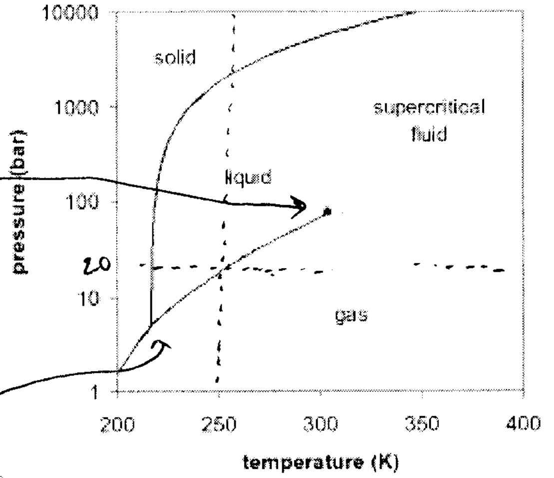
Hold p, T fixed: $\left(\frac{\partial G}{\partial N}\right)_{p,T} = \mu$

15. [8] What thermodynamic condition determines the positions of phase boundaries on a phase diagram, and why?

At a phase boundary two phases have equal Gibbs free energy G (per mole), $G_A = G_B$. In equilibrium G is minimized so two phases can only coexist if there's no decrease in total free energy on converting one to the other.

Name Solutions

[8] Here is part of the phase diagram of CO_2 (from Wikipedia.) Identify the triple point and the critical point and say what happens at each of them.



Critical point

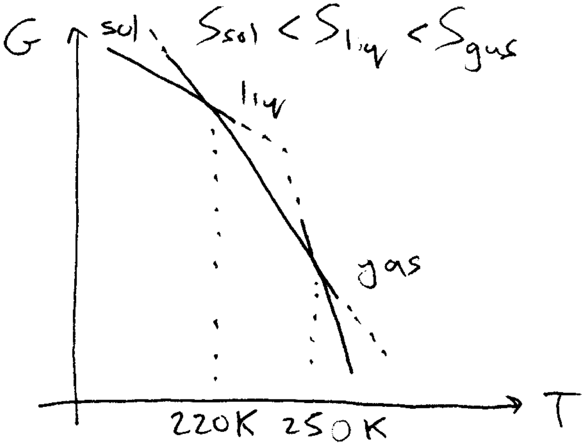
above it there's no distinction between liquid and gas

Triple point

at this unique p and T the three phases can coexist in equilibrium.

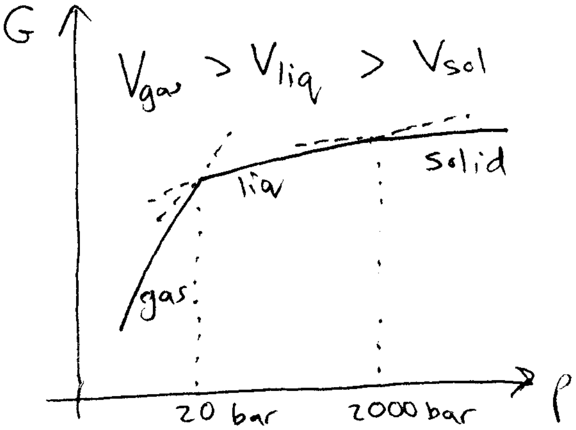
16. [10] Sketch the variation with T of the Gibbs free energy of an amount of CO_2 at a pressure p = 20 bar, taking into account the answer to Question 14, and add comments.

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S < 0$$



17. [10] Sketch the variation with p of the Gibbs free energy at T = 250 K, and add comments.

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = V > 0$$



18. [8] Describe what would happen if a cup of liquid CO_2 kept at 250 K and 20 bar were suddenly brought into a room at normal pressure (1 bar).

Liquid is not stable for $p < 10$ bar.

It will spontaneously convert to solid + gas.

– probably fast and violent. Speed will depend on nucleation of these other phases.

Name Solutions

19. [5] Consider a fuel cell that uses methane as fuel. The reaction is $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$, for which $\Delta H = -890$ kJ/mole and $\Delta G = -818$ kJ/mole at $T = 300$ K, $p = 1$ bar. What is the maximum amount of electrical work that can be extracted, per mole of methane fuel?

$$W_{electrical} = W_{useful} \leqslant -\Delta G = 818 \text{ kJ/mole}$$

20. [8] In this best possible case, how much waste heat is produced per mole of methane?

Total energy released $= -\Delta H$ (allowing for $\Delta(pV)$ work)

$$\therefore \text{Waste heat} = -\Delta H - W_{electrical} = 890 - 818 = 72 \text{ kJ/mole.}$$

21. [5] Why can this amount of waste heat not be avoided under any circumstances?

The reactants have higher entropy than the products, Since S_{total} must increase, this entropy has to be transferred to the environment: $Q \geqslant \frac{-\Delta S}{T}$

22. [8] The reaction at the cathode is $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$. What is the voltage of the cell? (Without a calculator an approximate calculation will do.)

$p = 8$

$$W_{electrical} = QV = \underset{\text{no. molecules reacted}}{N}\,\underset{\text{electrons per molecule}}{p}\,e.V = -\Delta G \qquad \therefore V = \frac{-\Delta G}{npe} = \frac{818 \text{ kJ}}{6\times10^{23} \times 8 \times 1.6\times10^{-19} \text{ C}}$$

$$\boxed{\simeq \frac{100\times10^{3}}{6\times1.6\times10^{23-19}} = 10^{5-23+19-1} = 1.0 \text{ V}}$$

23. [10] If the methane were instead simply burnt, and the hot products at $T = 1000$ K (limited by the enclosure material) were used to run a heat engine with a river as the cold reservoir, what would be the maximum possible efficiency of that heat engine?

$$e \leqslant 1 - \frac{T_c}{T_h}$$

Say $T_c \simeq 300$ K for river

$$\therefore e \leqslant 1 - \frac{300\text{K}}{1000\text{K}} = 0.7$$