

**Thermal Physics 224
Autumn 2008****Final exam 8.25 am, Wednesday 10 December, 2008**
Instructor: David Cobden

Do not turn this page until 8.25. 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 sheet 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 are allowed.*



1. [8] From the definition of entropy in terms of multiplicity, show that it is an extensive quantity.

$$S = k \ln \Omega \quad \text{If we combine two systems, A and B,}$$

$$\Omega_{\text{total}} = \Omega_A \Omega_B \quad \therefore S_{\text{total}} = k \ln \Omega_{\text{total}} = k (\ln \Omega_A + \ln \Omega_B) = S_A + S_B$$

2. [12] The entropy of an ideal gas is $S = Nk \left[\ln \left\{ \frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right\} + \frac{5}{2} \right]$. An isolated portion of gas containing N molecules undergoes free expansion from volume V_1 to volume V_2 . Use the First Law to show that its internal energy U does not change, and hence find the change in entropy ΔS .

$$\Delta U = Q + W \quad Q = 0 \text{ (isolated)}, \quad W = 0 \text{ (free expansion)}$$

$$\therefore \Delta U = 0$$

\therefore Only quantity that changes in the expression is V .

$$S = Nk \ln V + \text{function of } N, U$$

$$\therefore \Delta S = \Delta(Nk \ln V) = Nk \ln \frac{V_2}{V_1}$$

3. [4] Why is ΔS positive for this process, in a microscopic picture?

larger $V \rightarrow$ more ways to place/arrange particles
(more quantum states)

4. [6] Apply the Second Law to show that the free expansion is irreversible.

2nd Law S always increases.

Reverse of free expansion would have $\Delta S = -Nk \ln \frac{V_2}{V_1} < 0$
So it's impossible.

5. [10] A balloon filled with krypton gas has a volume of 10 liters. It bursts in a 10 m^3 bathroom with the door closed. Estimate the increase in entropy as the krypton spreads throughout the room, mixing with the air. [A mole of gas at 1 atm and room temperature occupies about 20 liters; the gas constant is $R = N_A k \approx 10 \text{ J/K/mole}$; $\ln 10 = 2.3$].

Assume ideal \rightarrow can neglect interactions.

$\therefore \Delta S$ is as for free expansion

$$= Nk \ln \frac{V_2}{V_1} = \frac{20 \text{ liters}}{10 \text{ liters}} \times N_A k \times \ln \frac{10 \text{ m}^3}{10^{-2} \text{ m}^3} \quad (1 \text{ L} = 10^{-3} \text{ m}^3)$$

$\underbrace{\hspace{2cm}}$
fraction of a mole

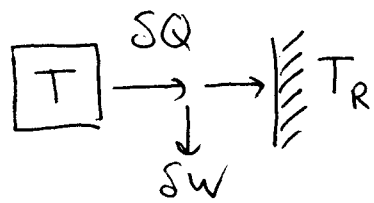
$$\approx 0.5 \times 10 \text{ J/K}^{-1} \times \ln 1000$$

$$= 5 \times 3 \ln 10 \text{ J/K}^{-1} \approx 35 \text{ J/K}^{-1}$$

6. [6] A copper block with constant heat capacity C is initially warmed to a temperature T_0 . A small heat engine is then operated between this block and a large reservoir at constant temperature T_R , cooling it as a result. State the definition of the efficiency e relating the small amount of work δW done by the engine in one cycle to the heat δQ extracted from the block, and state the maximum value of e allowed by thermodynamics in terms of the temperature T of the block.

$$e = \frac{\delta W}{\delta Q} \leq 1 - \frac{T_L}{T_h} = 1 - \frac{T_R}{T}$$

7. [10] Hence show that the theoretical maximum total amount of work that could be done by the heat engine is $C[T_0 - T_R - T_R \ln(T_0/T_R)]$.



$$\delta W = e \delta Q \leq \left(1 - \frac{T_R}{T}\right) (C \delta T)$$

$$\begin{aligned} \therefore W &= \int dW \leq \int_{T_0}^{T_R} (C) \left(1 - \frac{T_R}{T}\right) dT \\ &= C \left[T - T_R \ln T \right]_{T_R}^{T_0} = C \left[T_0 - T_R - T_R \ln \frac{T_0}{T_R} \right] \end{aligned}$$

8. [10] If the temperature inside a kitchen fridge is 0°C and in the room outside it is 27.3°C , what is the maximum possible coefficient of performance (COP) it could have according to thermodynamics?

$$\begin{aligned} T_h \left| \begin{array}{c} \leftarrow Q_h \\ \leftarrow Q_c \\ \uparrow W \end{array} \right| T_L \quad \text{COP} = \frac{Q_L}{W} &\leq \frac{1}{\frac{T_h}{T_L} - 1} \left(\begin{array}{l} \Delta S > 0 \text{ so } \frac{Q_h}{T_h} > \frac{Q_c}{T_L} \\ \text{COP} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{\frac{Q_h}{Q_c} - 1} \leq \frac{1}{\frac{T_h}{T_L} - 1} \end{array} \right) \\ &= \frac{273\text{K}}{300.3\text{K} - 273\text{K}} \\ &= \frac{273}{27.3} = 10 \quad \therefore \text{COP} \leq 10 \end{aligned}$$

9. [10] State the equipartition theorem, and find the rms speed of a dust particle weighing $1.2 \mu\text{g}$ in still air ($kT \approx 4 \times 10^{-21} \text{J}$ at room temperature.)

$\bar{E} = \frac{kT}{2}$ for a single (unfrozen) quadratic degree of freedom

$$\therefore \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} m \langle v_x^2 \rangle = 3 \left\langle \frac{1}{2} m v_{x_i}^2 \right\rangle = 3 \cdot \frac{kT}{2}$$

$$\begin{aligned} \therefore v_{\text{rms}} &= \langle v^2 \rangle^{1/2} = \left(\frac{3kT}{m} \right)^{1/2} = \left(\frac{3 \times 4 \times 10^{-21} \text{J}}{1.2 \times 10^{-9} \text{kg}} \right)^{1/2} \\ &= (10^{-11} \text{m}^2 \text{s}^{-2})^{1/2} \approx 3 \mu\text{ms}^{-1} \end{aligned}$$

10. [5] The i 'th quantum state of a system in contact with a reservoir at temperature T has energy E_i . Write down the probability P_i of finding a system in the i 'th state in terms of the Boltzmann factor and the partition function Z .

$$P_i = \frac{1}{Z} e^{-E_i/kT}$$

11. [6] Deduce Z by requiring that the probabilities add to unity (be normalized).

$$\sum_i P_i = 1 \quad \therefore \frac{1}{Z} \sum_i e^{-E_i/kT} = 1 \quad \therefore Z = \sum_i e^{-E_i/kT}$$

12. [8] Show that P_i is independent of the choice of energy zero (by considering adding a constant offset to all energies.)

If $E_i' = E_i + \delta E$ for all i , then

$$P_i' = \frac{e^{-E_i'/kT}}{\sum_i e^{-E_i'/kT}} = \frac{e^{-(E_i + \delta E)/kT}}{\sum_i e^{-(E_i + \delta E)/kT}} = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} = P_i$$

13. [6] A system has three states equally spaced by Δ in energy. Show that the partition function can be written as $Z = 1 + 2\cosh(\Delta/kT)$ with a suitable choice of the energy zero.

$$\begin{aligned} - E_3 &= +\Delta & Z &= \sum_{i=1}^3 e^{-E_i/kT} = e^{+\Delta/kT} + e^{0/kT} + e^{-\Delta/kT} \\ - E_2 &= 0 & &= 1 + 2 \left(\frac{e^{\Delta/kT} + e^{-\Delta/kT}}{2} \right) \\ - E_1 &= -\Delta & &= 1 + 2 \cosh \frac{\Delta}{kT} \end{aligned}$$

14. [6] Find an expression for the average energy \bar{E} in the system.

$$\begin{aligned} \bar{E} &= \sum_i E_i P_i = \frac{1}{Z} \sum_{i=1}^3 E_i e^{-E_i/kT} = \frac{-\Delta e^{\Delta/kT} + 0 e^{0/kT} + \Delta e^{-\Delta/kT}}{Z} \\ &= \frac{-2\Delta \sinh \Delta/kT}{1 + 2 \cosh \Delta/kT} \quad \left(\text{or use } \bar{E} = -\frac{\partial}{\partial \beta} \ln Z \right) \end{aligned}$$

15. [3] Can this system be meaningfully held at a negative temperature?

Yes, (because \bar{E} has an upper bound)

16. [10] State the generalized thermodynamic identity for the internal energy $U(S, V, N)$ and deduce the corresponding differential identity for the Gibbs free energy $G(T, P, N)$.

$$\begin{aligned} dU &= TdS - PdV + \mu dN & G &= U - TS + PV \\ \therefore dG &= TdS - d(TS) - PdV + d(PV) + \mu dN \\ &= -SdT + VdP + \mu dN \end{aligned}$$

17. [9] Hence express S , V and μ as derivatives of G .

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P, N} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T, N} \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T, P}$$

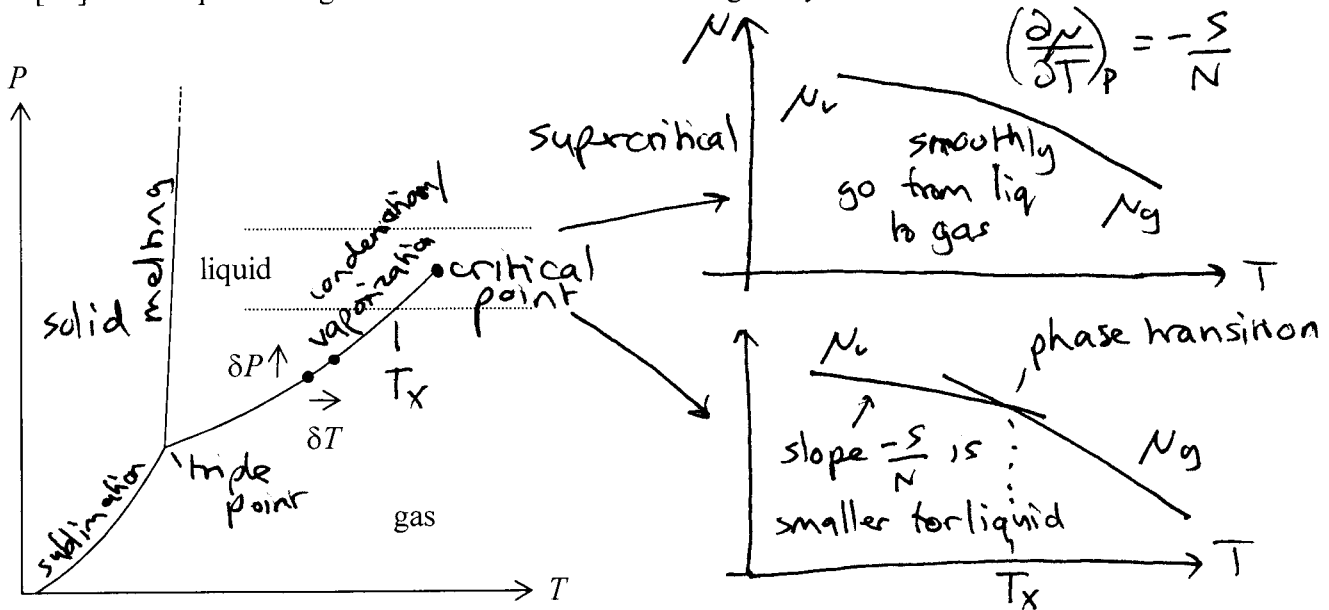
18. [10] Using one of these, argue that the chemical potential μ is equal to the Gibbs free energy per particle G/N , and hence using the result of Q16 write the thermodynamic identity for $\mu(T,P)$ given fixed N (relate $d\mu$ to dT and dP).

$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$ must be function of T, P only because N is extensive

\therefore Integrate $\rightarrow G = N\mu + f(T, P)$ but $G=0$ at $N=0$ so $f(T, P)=0$

\therefore from Q16 $\mu = \frac{G}{N}$ $d\mu = \frac{1}{N}dG$ at fixed N $\therefore d\mu = \frac{-S}{N}dT + \frac{V}{N}dP$

19. [10] On this phase diagram label all the feature and regions you can.



20. [8] Sketch on the right the variation of μ with T along the two horizontal dotted lines, making use of the results of Q17 and Q18, labeling appropriately.

21. [10] (Clausius-Clapeyron relation). The liquid-gas phase boundary is determined by $\mu_l = \mu_g$. Thus the difference in μ_l between the two points marked must be the same as the difference in μ_g , ie, $\delta\mu_l = \delta\mu_g$. Use this and the result of Q18 to show that the slope of the phase boundary is given by

$$\left(\frac{\partial P}{\partial T}\right)_{\text{boundary}} = \frac{\delta P}{\delta T} = \frac{\Delta S}{\Delta V}$$

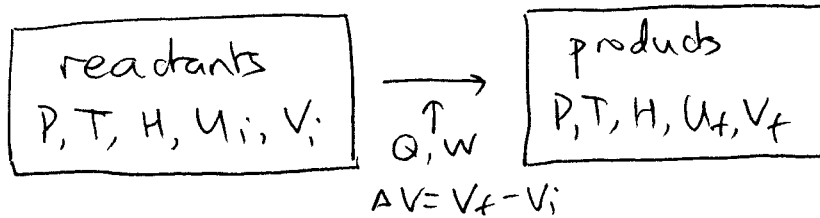
where ΔS and ΔV are respectively the difference in entropy and volume between the liquid and gas phases.

$$\delta\mu_l = \delta\mu_g$$

$$\therefore -\frac{S_l}{N}\delta T + \frac{V_l}{N}\delta P = -\frac{S_g}{N}\delta T + \frac{V_g}{N}\delta P$$

$$\therefore (V_g - V_l)\delta P = (S_g - S_l)\delta T \quad \therefore \frac{\delta P}{\delta T} = +\frac{\Delta S}{\Delta V}$$

22. [10] A chemical reaction occurs in which the products end up at the same T and P as the reactants, no non-mechanical work is extracted, and the enthalpy of the products exactly equals that of the reactants ($\Delta H = 0$). Show that the net heat exchange with the environment is zero.



$$\begin{aligned}\Delta U &= Q + W & W &= -P\Delta V \text{ only} \\ \therefore Q &= U_f - U_i + P\Delta V \\ &= U_f + PV_f - U_i - PV_i \\ &= H_f - H_i \\ &= 0\end{aligned}$$

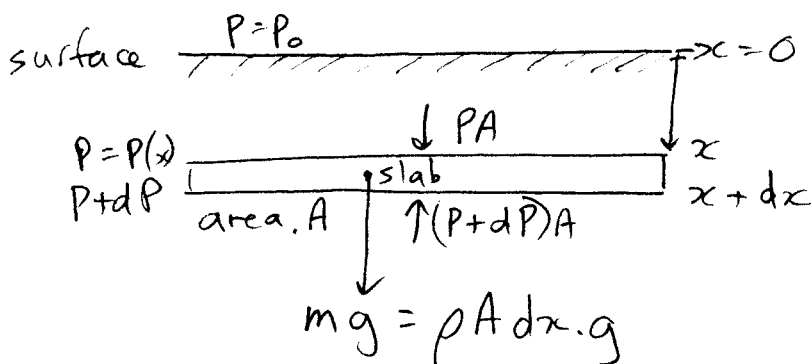
23. [10] Show that when an ideal gas is throttled ($\Delta H = 0$), its temperature does not change.

$$\begin{aligned}\Delta H &= 0 \\ \therefore \Delta(U + PV) &= 0 \\ \therefore \Delta\left(\frac{f}{2}NkT + NkT\right) &= 0 \\ \therefore \left(\frac{f}{2} + 1\right)Nk\Delta T &= 0 & \therefore \Delta T &= 0\end{aligned}$$

24. [4] Which is harder – to do something quasistatically, or to do it reversibly? Indicate why.

Reversibly – then you also have to ensure that any heat that flows is through a negligible T difference.

25. [10] By considering forces on a thin horizontal layer to get a simple differential equation, show that the pressure p at a depth x under water is given by $p = p_0 + \rho gx$, where p_0 is the pressure at the surface, ρ is the density of water and g is the acceleration due to gravity. (Take it to be incompressible.)



$$\begin{aligned}\text{Balance forces on slab:} \\ P.A + \rho g.A dx - (P+dP).A &= 0 \\ \therefore dP &= \rho g dx \\ \therefore P &= \rho g x + \text{const} \\ P = P_0 \text{ at } x=0 &\therefore P = P_0 + \rho g x\end{aligned}$$