Basic Thermodynamics

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Goals

- Learn how to calculate work and heat for quasi-static state changes.
- Analyze the efficiency of typical thermodynamic cycles used to model heat engines.
- Investigate entropy changes in thermodynamics processes.

The ideal gas

The equations of state of an ideal gas are $pV = nRT$ and $U = nC_VT$. Here $p$ is the pressure, $V$ the volume, $n$ the amount of substance (in mols), $T$ the temperature, $R \approx 8.314 \text{J/(mol K)}$ the ideal gas constant, $U$ the internal energy, and $C_V$ the specific heat capacity at constant volume. The value of $C_V$ depends on the internal structure of the gas particles and is e.g. $C_V = 3R/2$ for a monoatomic gas and $C_V = 5R/2$ for a diatomic gas. Note that $nR = Nk_B$ where $N$ is the number of particles in the gas and $k_B \approx 1.381 \times 10^{-23} \text{J/K}$ is the Boltzmann constant. We will in this problem sheet consider $n = 1$ mol and hence leave out $n$. Furthermore we define the specific heat at constant pressure $C_p = C_V + R$ and the ratio $\gamma = C_p/C_V$.

Entropy, Heat and Work

In general we have $dU = TdS - pdV$ where $S$ is entropy. Since $U$, $S$, $V$ are functions of state $dU$, $dS$, $dV$ are exact differentials. Changes in heat $dQ \leq TdS$ and work $dW \geq -pdV$ are not described by exact differentials which is indicated by the $d$. Heat and work are not functions of state but depend on how a state change occurs.

Quasi-static processes

We consider quasi-static processes where the system always remains in a thermal state. These processes must in principle happen infinitely slowly but are nevertheless a good approximation in many situations. If a quasi-static process is reversible, i.e. preserves the entropy of system + environment then $dQ = TdS$ and work $dW = -pdV$ and we can thus write the (path dependent) work done to the system and heat transferred to the system in a state change from $(p_1, V_1, T_1)$ to $(p_2, V_2, T_2)$ as

$$W = -\int_{V_1}^{V_2} pdV \quad \text{and} \quad Q = \int_{S_1}^{S_2} TdS.$$ 

The heat transferred to the system then follows from the 1st law of thermodynamics as $Q = \Delta U - W$ where $\Delta U = C_V(T_2 - T_1)$ is the (path independent) change in internal energy during the state change.

Along an isobar we have constant $p$ and thus $W = p(V_1 - V_2) = RT_1 - T_2)$, $Q = C_V(T_2 - T_1)$. An isochore has constant $V$ and thus $W = 0$, $Q = C_V(T_2 - T_1)$. Along an adiabat no heat is transferred and thus $W = C_V(T_2 - T_1)$, $Q = 0$. Along an isotherm we have constant $pV = RT$, no change in internal energy, and thus $W = RT \ln(V_1/V_2)$, $Q = RT \ln(V_2/V_1)$.

Note that there are quasi-static processes which are irreversible. For instance, a piston might be moving sufficiently slowly for the quasi-static approximation to hold but sufficiently fast for friction to be non-negligible.

Adiabatic process

For an adiabatic process we need to have $\Delta U = W$, i.e. for infinitesimal processes $C_V \delta T = -p \delta V$. From the ideal gas law $R \delta T = \delta (pV)$ and thus $(C_V/R)(\delta p + p \delta V) = -p \delta V$. This gives $p(C_V/R + 1) \delta V = -C_V/R \delta p$ and thus

$$\frac{\delta p}{p} = -\frac{C_V + R \delta V}{C_V V} = -\gamma \frac{\delta V}{V} \quad \rightarrow \quad \ln(p_1V_1^\gamma) = \ln(p_2V_2^\gamma).$$

\textsuperscript{1}Several of these problems are based on problem sets by Profs A. Boothroyd, A.A. Schekochihin, S.J. Blundell, and previous Oxford exam questions.
Therefore \( pV^\gamma \) is constant in an adiabatic process. Using the ideal gas equation we find that also \( TV^{\gamma-1} \) is constant and \( T^\gamma p^{1-\gamma} \) is constant in an adiabatic process.

**Entropy changes**

In an isochore state change we have \( dQ = C_V dT \) and in an isobar process \( dQ = C_p dT \). If the heat capacity is constant we can thus work out the change of entropy in a state change from \( T_1 \) to \( T_2 \) as \( \Delta S = C \ln(T_2/T_1) \). If heat \( Q \) is transferred to a large system without changing it temperature \( T \) the change in entropy is given by \( \Delta S = Q/T \).

**Problems**

1. A possible ideal-gas cycle operates as follows:
   
   (i) From an initial state \((p_1, V_1)\) the gas is cooled at constant pressure to \((p_1, V_2)\);  
   (ii) The gas is heated at constant volume to \((p_2, V_2)\);  
   (iii) The gas expands adiabatically back to \((p_1, V_1)\).

   Assuming constant heat capacities, show that the thermal efficiency \( \eta \) is
   
   \[ \eta = 1 - \gamma \frac{(V_2/V_1) - 1}{(p_2/p_1) - 1}. \]

   (You may quote the fact that in an adiabatic change of an ideal gas, \( pV^\gamma \) stays constant)

2. Show that the efficiency of the standard Otto cycle (shown in Fig. 1a) is \( 1 - r^{1-\gamma} \), where \( r = V_1/V_2 \) is the compression ratio.

3. An ideal gas is changed from an initial state \((p_1, V_1, T_1)\) to a final state \((p_2, V_2, T_2)\) by the following quasi-static processes shown in Fig. 1b): (i) 1A2 (ii) 1B2 and (iii) 1C2. For each process, obtain the work that must be done on the system and the heat that must be added in terms of the initial and final state variables, and hence show that \( \Delta U = C_V (T_2 - T_1) \) independent of path. (Assume that the heat capacity \( C_V \) is constant.)

4. A building is maintained at a temperature \( T \) by means of an ideal heat pump which uses a river at temperature \( T_0 \) as a source of heat. The heat pump consumes power \( W \), and the building loses heat to its surroundings at a rate \( \alpha(T - T_0) \). Show that \( T \) is given by

   \[ T = T_0 + \frac{W}{2\alpha} \left( 1 + \sqrt{1 + 4\alpha T_0/W} \right). \]
5. A block of lead of heat capacity 1kJ/K is cooled from 200K to 100K in two ways:
   (a) It is plunged into a large liquid bath at 100 K;
   (b) The block is first cooled to 150K in one bath and then to 100K in another bath.

Calculate the entropy changes in the system consisting of block plus baths in cooling from 200K to 100K in these two cases. Prove that in the limit of an infinite number of intermediate baths the total entropy change is zero.

6. Two identical bodies of constant heat capacity $C_p$ at temperatures $T_1$ and $T_2$ respectively are used as reservoirs for a heat engine. If the bodies remain at constant pressure, show that the amount of work obtainable is

$$ W = C_p(T_1 + T_2 - 2T_f), $$

where $T_f$ is the final temperature attained by both bodies. Show that if the most efficient engine is used, then $T_f^2 = T_1T_2$. Calculate $W$ for reservoirs containing 1kg of water initially at 100°C and 0°C, respectively. The specific heat capacity of water is $C_p = 4200$ J/(K kg). Solution: $W = 32.7$ kJ.

7. Three identical bodies are at temperatures 300K, 300K and 100K. If no work or heat is supplied from outside, what is the highest temperature $T_h$ to which any one of these bodies can be raised by the operation of heat engines? Solution: $T_h = 400$ K.

Class Problems

8. Two thermally insulated cylinders, $A$ and $B$, of equal volume, both equipped with pistons, are connected by a valve. When open, the valve allows unrestricted flow. Initially $A$ has its piston fully withdrawn and contains a perfect monatomic gas at temperature $T_i$, and $B$ has its piston fully inserted, and the valve is closed. The thermal capacity of the cylinders is to be ignored. The valve is fully opened and the gas slowly drawn into $B$ by pulling out the piston $B$; piston $A$ remains stationary. Show that the final temperature of the gas is $T_f = T_i/2^{2/3}$.

9. In a free expansion of a perfect gas (also called a Joule expansion), we know $U$ does not change, and no work is done. However, the entropy must increase because the process is irreversible. How are these statements compatible with $dU = TdS - pdV$?

10. A mug of tea has been left to cool from 90°C to 18°C. If there is 0.2kg of tea in the mug, and the tea has specific heat capacity 4200J/(K kg), show that the entropy of the tea has decreased by 185.7J/K. How is this result compatible with an increase in entropy of the Universe?

11. Calculate the changes in entropy of the Universe as a result of the following processes:
   (a) A copper block of mass 400g and heat capacity 150J/K at 100°C is placed in a lake at 10°C;
   (b) The same block, now at 10°C, is dropped from a height of 100m into the lake;
   (c) Two similar blocks at 100°C and 10°C are joined together (hint: save time by first realising what the final temperature must be, given that all the heat lost by one block is received by the other, and then re-use previous calculations);
   (d) A capacitor of capacitance 1µF is connected to a battery of e.m.f. 100V at 0°C. (NB think carefully about what happens when a capacitor is charged from a battery.);
   (e) The capacitor, after being charged to 100V, is discharged through a resistor at 0°C;
   (f) One mole of gas at 0°C is expanded reversibly and isothermally to twice its initial volume;
   (g) One mole of gas at 0°C is expanded adiabatically to twice its initial volume;
   (h) The same expansion as in (f) is carried out by opening a valve to an evacuated container of equal volume.