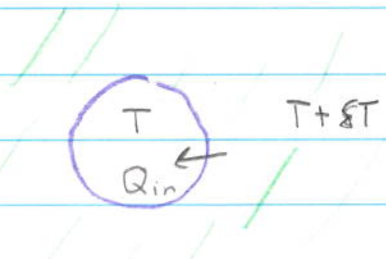
Entropy Changes in Reversible Processes

(1) Consider an object at constant pressure in contact with a heat reservoir whose temperature slowly changes, from T_i to T_f. The object and reservoir are in equilibrim at the same temperature.



$$dS = \frac{dQ_{rev}}{T} \quad \text{and} \quad dQ = C_p \, dT$$

approx constant

So

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} C_p(T) \frac{dT}{T} \simeq C_p \int \frac{dT}{T}$$

For constant specific heat $C_p(T) = C_p$ we have

$$\boxed{\Delta S = C_p \ln\left(\frac{T_f}{T_i}\right)}$$

we had similar results previously

(2) Now consider the change in entropy during a phase transition, e.g. melting ice to have liquid water. Assme that the heat is transferred reversibly. The temperature is fixed at the transition temperature. This process is at fixed pressure $Q_{in} = \Delta H$ ← enthalpy

$$\Delta S = \frac{Q_{melt}}{T_{tr}} = \frac{\Delta H}{T}$$

we had similar results previously

③ For an ideal gas with constant specific heat $U = c_V T$. Then for Volume changes we have

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV$$

$pV = NkT$

$$dS = c_V \frac{dU}{U} + Nk\frac{dV}{V}$$

integrate

$$S_f - S_i = c_V \ln\left(\frac{U_f}{U_i}\right) + Nk \ln\left(\frac{V_f}{V_i}\right)$$

For a MAIG the specific heat is $3/2\, Nk$ and this result is the same as we got by counting states, $\Omega = C\, U^{3N/2} V^N$, with $S = k \ln \Omega$. But now c_V is general.

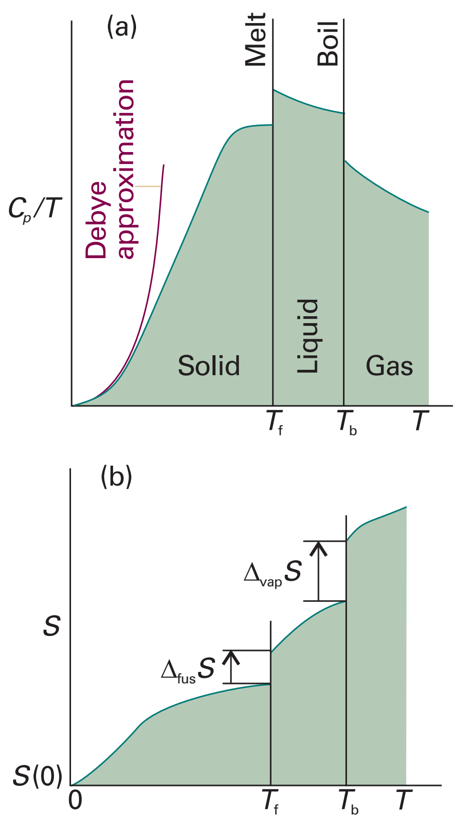
④ The figure shows how we can use thermodynamic results to find the absolute entropy of boiling liquid nitrogen by integrating C_p up from close to zero temperature:

$$S(T) = S(0) + \int_0^{T_f} C_p(s)\frac{dT}{T} + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} C_p(\ell)\frac{dT}{T}$$

solid — melting — liquid

we stop at T_b. But one could integrate to higher T

Entropy of Boiling Liquid Nitrogen



	$S_m^\ominus/(\mathrm{J\ K^{-1}\ mol^{-1}})$
Debye extrapolation	1.92
Integration, from 10 K to 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration, from 35.61 K to 63.14 K	23.38
Fusion at 63.14 K	11.42
Integration, from 63.14 K to 77.32 K	11.41

Total 79.8 J/mol K

Nitrogen has an extra solid-to-solid phase transition at 35.61 K, which make the example of Nitrogen somewhat unusual. This extra phase transition is not shown in (b), which was mean to illustrate the typical case.

- Liquid nitrogen boils at $T_b = 77\,°K$. It freezes to a Solid at $T_f = 35.6\,°K$

- At zero temperature the entropy is assumed to be small (the system is almost in its ground state). and $S(0)$ can be ignored (This is by something called the third law of thermodynamics.)

A model for the specific heat of solids, known as the Debye model, is used to estimate C_p at very low temperatures where there is no experimental data

- Putting the ingrediants together, there are tables which record the entropies at various Substances at various temperatures