CHAPTER 7

We need to broaden our tools for the study of thermodynamics.

Why don't 1st and 2nd laws suffice?

The problem is that it is difficult to measure *U* and *S*.

What we can measure is *T, p, w, q,* C_v, $[c_i]$, etc.

Need to get *S, U* in terms of quantities that we can measure

How does a gas convert heat to work?

$$p_1, V_1, T_1 \xrightarrow{\quad q \quad} p_2, V_2, T_2$$

Assume ideal gas: $pV = NkT$

first law $dU = \delta q + \delta w$ | δ for path-dependent variables

↑ state function

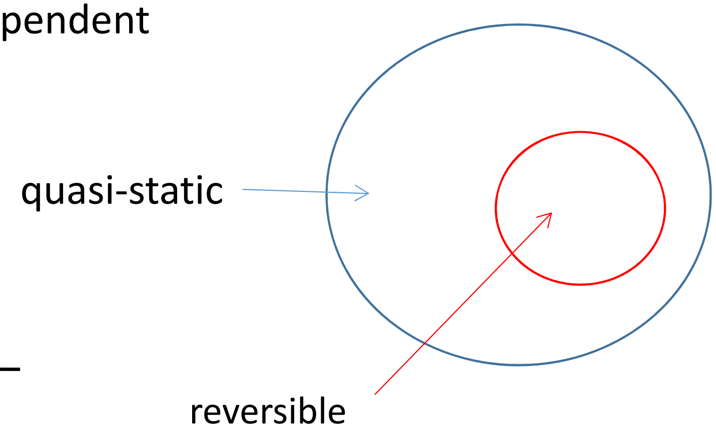
U > when heat flows into system
or work is done on system

quasi-static process – carried out slowly so that properties are independent of time + speed of process

gas in piston $\delta w = -p_{ex} dV$

work is + when vol <

quasi-static



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work: mechanical energy transfer
heat: thermal energy transfer

heat capacity = heat uptake per unit temperature change

Measured using a calorimeter which maintains constant *V*

at const vol: $\delta w = -p_{ext} dV = 0$

heat quasi-statically $dU = \delta q$

$$C_v = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

again assuming quasi-static

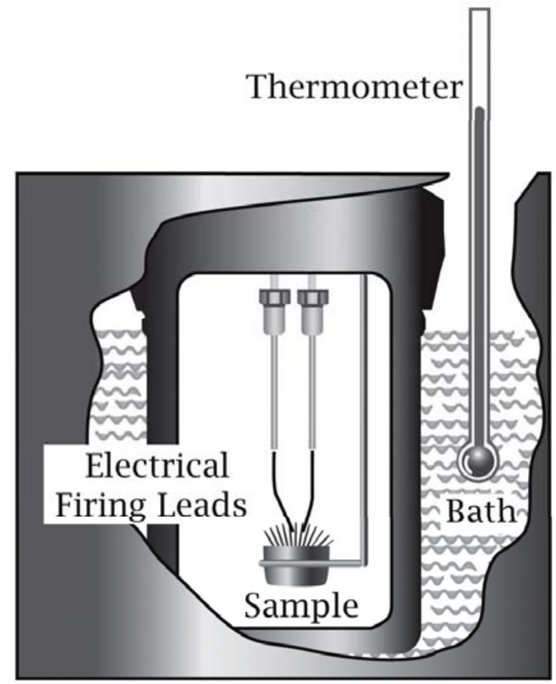


Figure 7.1 Molecular Driving Forces 2/e (© Garland Science 2011)

Later, we will consider C_p *the* heat capacity at const. pressure

In general, C_V and C_p depend on T, generally (but not always) increasing as T increases

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \rightarrow \quad dU = C_V\, dT$$

$$\Delta U = \int_{T_A}^{T_B} C_V\, dT = C_V\left(T_B - T_A\right)$$ if C_V independent of T

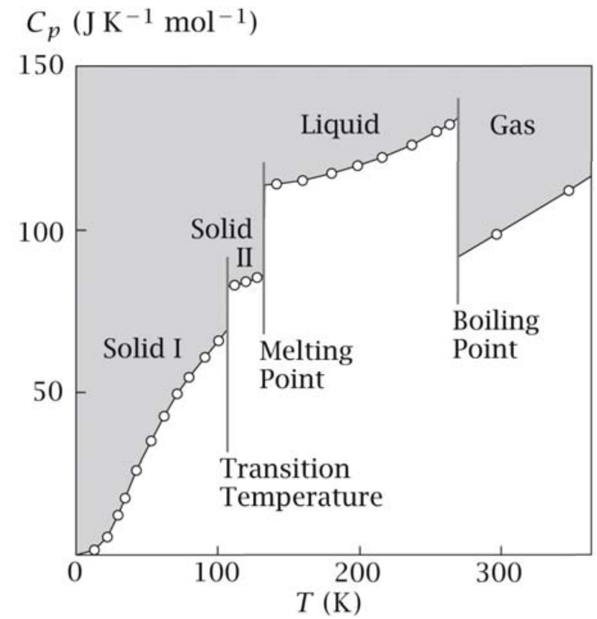


Figure 7.2 Molecular Driving Forces 2/e (© Garland Science 2011)

Heat capacity of gases: Internal energy depends on *V, T*

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

for an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$ | if molecules don't interact, density changes are unimportant

$$dU = C_V\, dT$$

| for ideal gas $C_V = 3/2R$

$$\Delta U = C_V\left(T_2 - T_1\right)$$ (ideal gas)

no matter if vol. changes or if process is fast or slow (but gas must be ideal)

Industrial revolution: Major contributor – steam engines
first generation < 1% efficient; Watt engine ~7% efficient
modern internal combustion engine: 25% efficient

Much of the early work in thermodynamics was carried out to improve the operation of steam engines

work $\rightarrow$ work – can be 100% efficient if no friction
heat $\rightarrow$ work – efficiencies at best 30-50%
work $\rightarrow$ heat – can accomplish with 100% efficiency

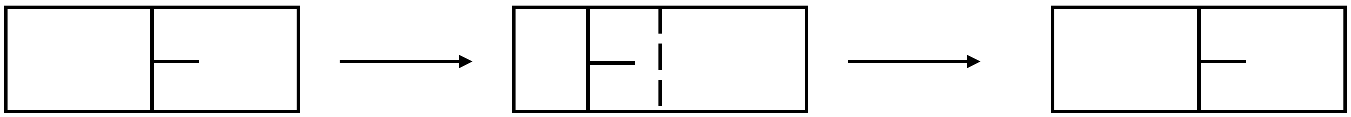
work is somehow "better" than heat

We need to develop strategies to determine efficiencies of engines and other devices.

work $\rightarrow$ work – for high efficiency, process needs to be slow
heat $\rightarrow$ work – to get max work, needs to be slow and **reversible**

Reversible: if system and surroundings are both restored to initial values

reversible $\Rightarrow$ no dissipation



A $\rightarrow$ B if there is friction, some work $\rightarrow$ heat as well as for B $\rightarrow$ C: so not reversible

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For a reversible process

$$q = q_{rev}$$

$$dS = \frac{\delta q_{rev}}{T}$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV \quad \text{but} \quad dU = \delta q - p_{ext}dV$$

Assuming ideal gas

The text uses $dU = \delta q = C_V dT$

But the first equality holds only if V is fixed. One does not have to assume dU = δq to show this.

$$dS = \frac{C_V dT}{T}$$

Assumes fixed V

If C_V is constant

$$\Delta S = \int_{T_A}^{T_B} \frac{C_V}{T} dT = C_V \ell n \frac{T_A}{T_B}$$

Processes that can occur for an ideal gas

ideal gas $pV = NkT$ (equation of state)

a real gas has a more complicated equation

① fix V: $p_1, V_0, T_1 \rightarrow p_2, V_0, T_2$

add q reversibly

fixed volume (isochoric): No work is done

$$q = \Delta U = C_V (T_2 - T_1) = C_V \frac{V_0}{Nk}(p_2 - p_1)$$

$$\Delta S = C_V \ell n\left(\frac{T_2}{T_1}\right)$$

$$S = \frac{dq_{rev}}{T} = \frac{C_V dT}{T}$$

So can calculate $\Delta U, \Delta S,$ etc.

In general, q depends on the path

But here we carried out the process with const. V and reversibly (which specifies the path)

Now, fix p $\quad p_0, V_1, T_1 \rightarrow p_0, V_2, T_2$ | constant p = isobaric

apply $p_{ext} = p_0$ to reversibly moving piston
and transfer in heat q

$$w = -\int p_{ext}\,dV = -\int_{V_1}^{V_2} p_o\,dV$$
$$= -p_0\left(V_2 - V_1\right)$$

quasi-static so slow,
p_{int} always = p_{ext}

$$\Delta U = C_V \Delta T = \frac{C_V\, p_0}{Nk}\left(V_2 - V_1\right)$$

Makes use of the
ideal gas law

$$\Delta U = q + w$$
$$q = \Delta U - w = \left(\frac{C_V}{nK} + 1\right) p_0 \left(V_2 - V_1\right)$$

The text has the wrong sign in front of the "1"

so if you know q, you can calculate V_2
Then can calculate ΔU and $\quad \Delta S = C_p \ell n\left(\frac{T_2}{T_1}\right)$

The text mistakenly gives the equation with C_V.
$C_p = C_V + Nk$.