

Thermodynamics lecture 3.

W.A.L.T.

Energy and the First Law

- Relationship between First Law and mechanics (hence definition of heat)
- Work on a pV system
- Heat capacities
- Energy equation
- Example calculations

Principle of adiabatic work: The amount of work required to change the state of a thermally isolated system depends solely on the initial and final states.

Logic:

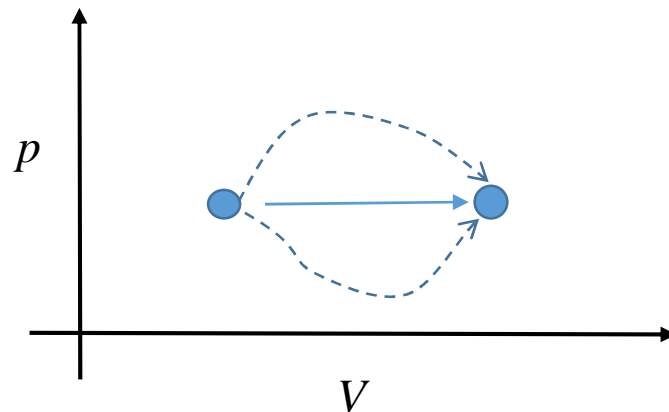
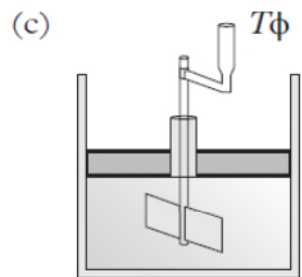
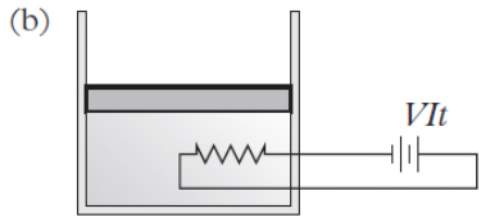
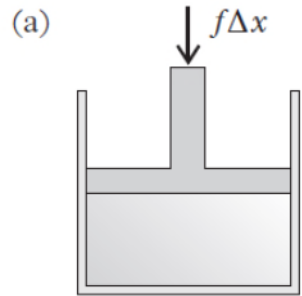
1. First we have motivating evidence
2. Then we generalise from the evidence, making the conjecture as written above
3. Then we use it to discover lots of other predictions ...
4. If the other predictions match experimental observations then we are reassured that the conjecture is insightful and we call it a 'law of nature'

The word 'law' in 'law of nature' means 'what is observed to hold in practice'

Principle of adiathermal work: The amount of work required to change the state of a thermally isolated system depends solely on the initial and final states.

Experiments by J. P. Joule in 1843-47

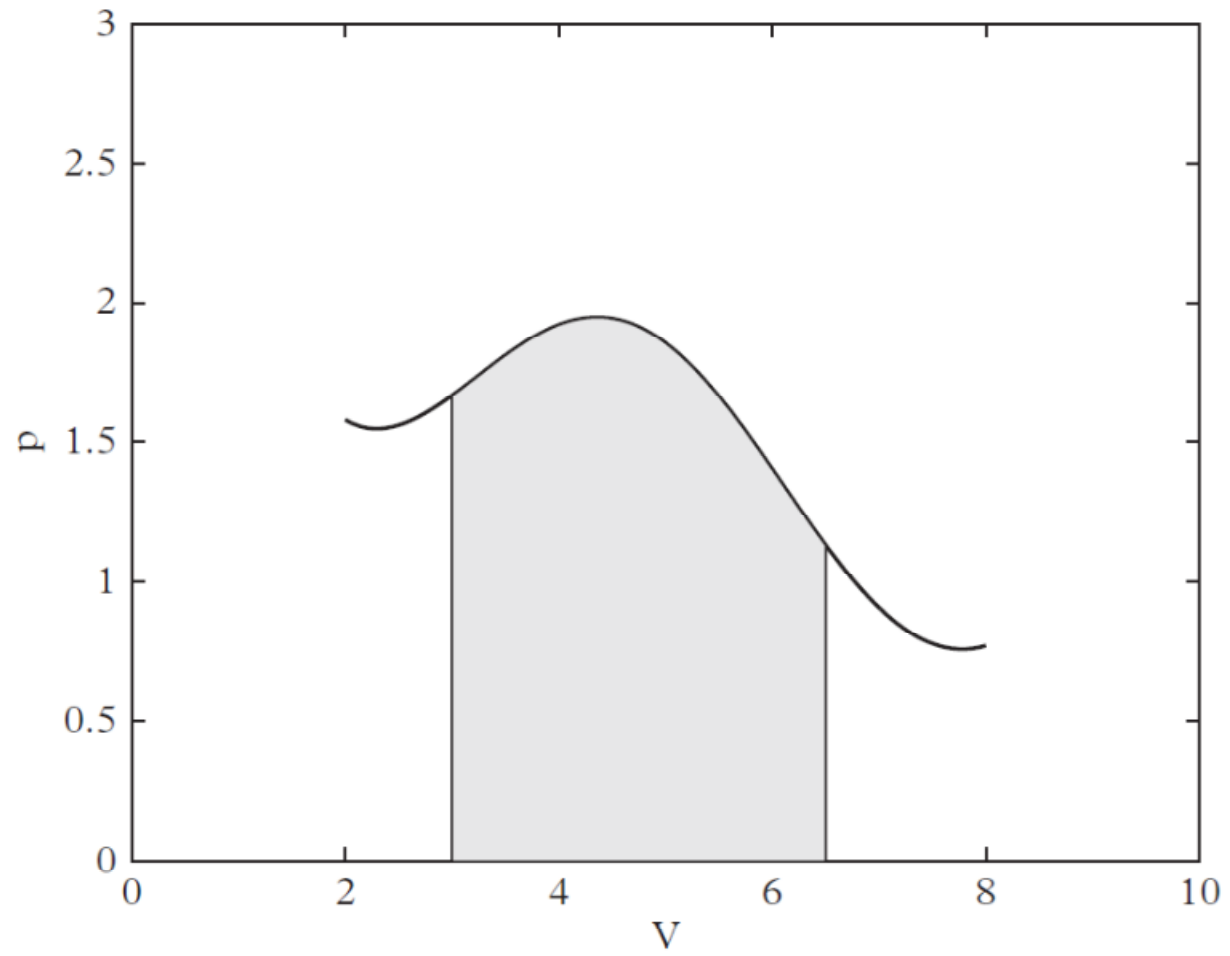
Method	Quantity of work
1. Turbulent motion produced by paddle wheel	773 ft lb
2. Electric current through resistance	838 ft lb
3. Compression of gas in thermal contact with water	795 ft lb
4. Friction of metal blocks in thermal contact with water	775 ft lb



$$W_{\text{adiathermal}} = \Delta U$$

Work done on a pV system during a reversible process

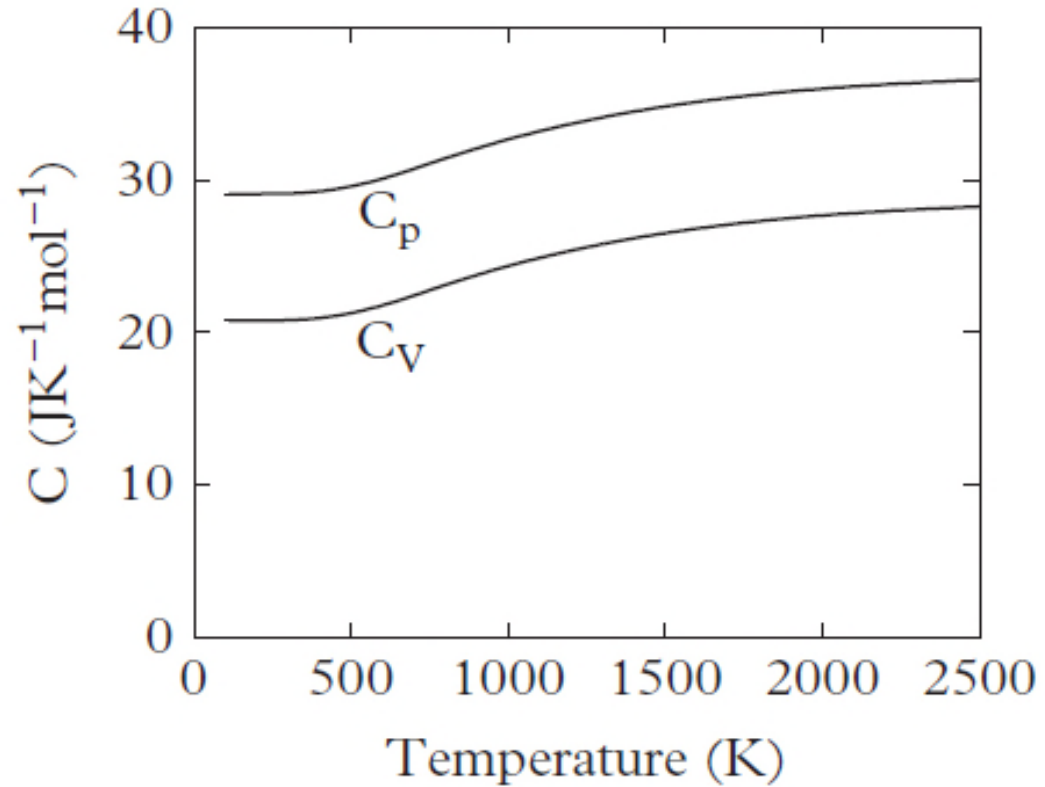
$$W_{\text{rev}} = \int -pdV$$



$$\begin{array}{l}
 dU = \bar{d}Q + \bar{d}W \quad [\text{always}] \\
 dU = \bar{d}Q - p dV + |\epsilon dx| \quad [\text{for quasistatic process,}] \\
 \quad \quad \quad \quad \quad \quad [|\epsilon dx| \text{ is energy from friction etc.}] \\
 dU = \bar{d}Q_{\text{rev}} - p dV \quad [\text{for reversible process}]
 \end{array}
 \left. \vphantom{\begin{array}{l} \\ \\ \\ \end{array}} \right\} \text{First Law}$$

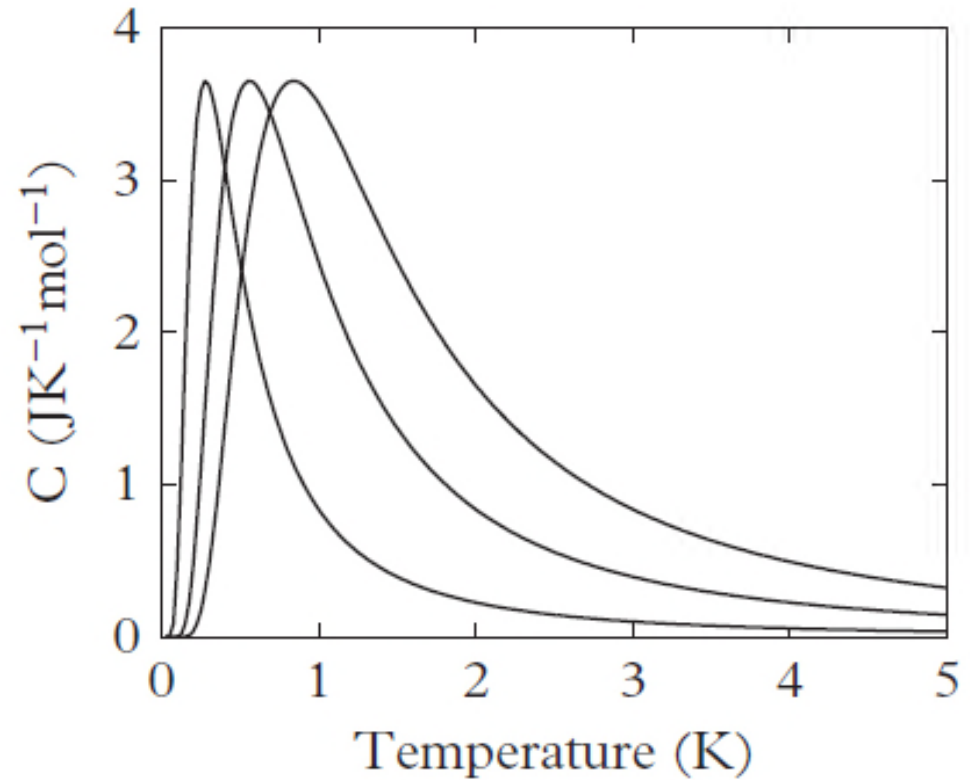
$$dU = T dS - p dV \quad [\text{always}] \qquad \text{First and Second Law together}$$

Example heat capacities



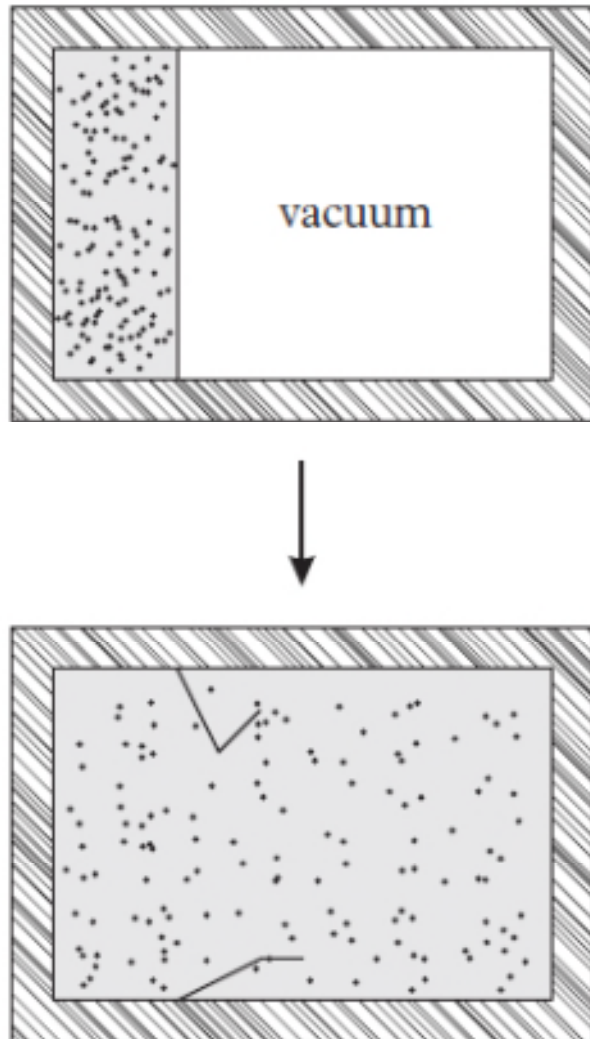
Nitrogen (N_2) gas

$$(pV = Nk_B T)$$



Simple (spin-1/2) paramagnet

Free expansion (also called Joule expansion)



For any fluid: $U = \text{constant}$ in this process
For **ideal gas**: **it is observed that** $T = \text{constant}$

Hence, **for ideal gas**: $\left. \frac{\partial T}{\partial V} \right|_U = 0.$

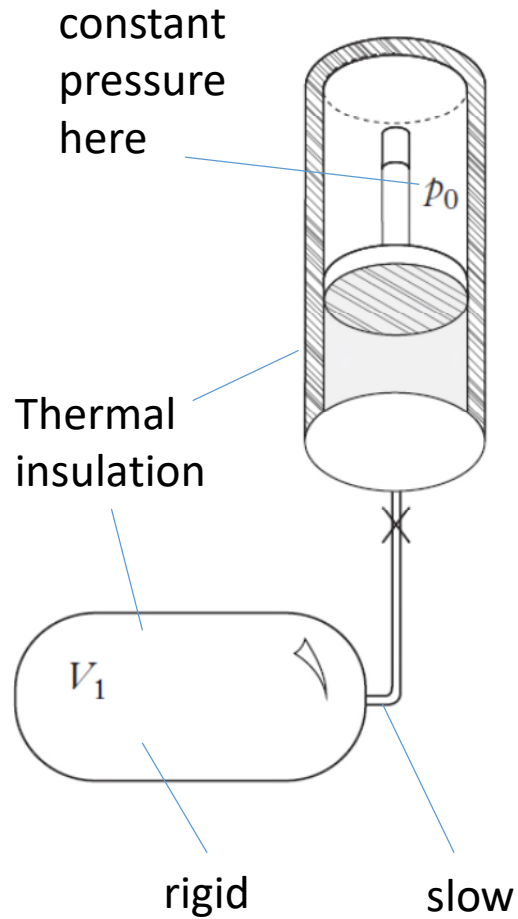
$\Rightarrow \left. \frac{\partial T}{\partial U} \right|_V \left. \frac{\partial U}{\partial V} \right|_T = 0$ (reciprocity)

$\Rightarrow \left. \frac{\partial U}{\partial V} \right|_T = 0$

$\Rightarrow U(V, T)$ depends on T alone, i.e. $U = U(T).$

This is Joule's law.

How to calculate in thermodynamics



- (1) Identify clearly the thermodynamic system to be treated.
- (2) Identify the nature of the interaction with the surroundings, and hence the type of *process*.
- (3) Use the equation of state to gain information about initial and final conditions.
- (4) At this stage you may well be able to calculate the heat and work inputs to the system, in terms of the state variables, although there may be some unknowns remaining in your expressions.
- (5) If there remain some unknowns, use information about the heat capacity or the energy equation or both.

Adiabatic (i.e. reversible adiathermal) expansion of ideal gas

For:

- ideal gas
- with constant heat capacities

find: $pV^\gamma = \text{constant}$ during an adiabatic change

where $\gamma \equiv \frac{C_p}{C_V}$ (“adiabatic index”)

Example

- (i) Explain carefully why, when gas leaks slowly out of a chamber, the expansion of the gas remaining in the chamber may be expected to be adiabatic (that is, quasistatic and without heat exchange). [Hint: choose carefully the physical system you wish to consider.]
- (ii) A gas with $\gamma = 5/3$ leaks out of a chamber. If the initial pressure is $32p_0$ and the final pressure is p_0 , show that the temperature falls by a factor 4, and that $1/8$ of the particles remain in the chamber.