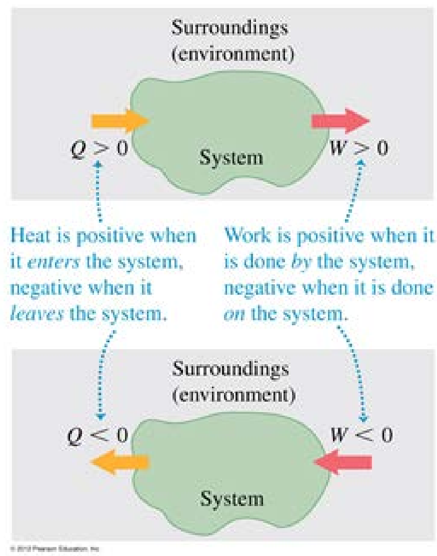
FIRST LAW OF THERMODYNAMICS I

Intended Learning Outcomes – after this lecture you will learn:
1. internal energy U of a thermodynamic system
2. first law of thermodynamics
3. work done W during volume change (pdV work)
4. path-dependence of heat Q

Textbook Reference: Ch 19.1 – 19.4

A **thermodynamic system** is one that has the potential to exchange energy with its surrounding



Such energy exchange can be in the form of heat Q and work done W

Sign convention:
$Q > 0$ if heat flows *into* the system, < 0 if flows *out of* the system
$W > 0$ if work done by the system, < 0 if work done on the system

An everyday life example:

work done by system $W > 0$ to lift the cover

system (popcorn)

stove provides heat $Q > 0$

An **isolated system** is one which does not exchange anything with its surrounding environment, in particular, $Q = W = 0$

A **thermodynamic process** is a process that changes the state (such as p, V, T) of a thermodynamic system
While going from initial to final state, need to go through intermediate states, called a **path**

A **cyclic** process is one whose initial and final states are the same

Internal energy U of a system is the sum of KE, and PE due to interaction among its constituent particles

⚠ U does *not* include PE due to external interaction (such as gravitational PE due to the earth on a gas)

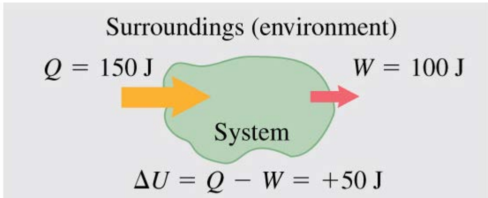
⚠ For an ideal gas, $U = \frac{f}{2}NkT \propto T$

⚠ U *usually* (but not always) increases with T

First Law of Thermodynamics

$$\boxed{Q = \Delta U + W}$$

generalization of conservation of energy to include heat



For an infinitesimal change of state, first law becomes

$$\boxed{dQ = dU + dW}$$

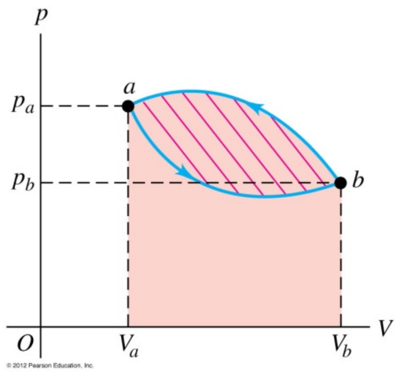
$\Delta U = Q - W$ can be used as an *operational definition* of U because both Q and W can be measured. No need to refer to KE or PE of microscopic particles

⚠ U is very much like a PE (of a conservative force) in that:

- U is defined up to a constant, i.e., need an arbitrary zero level, like gravitation PE
- U is experimentally found to be a **state function**, i.e., it depends on the thermodynamic state (such as p, V, T) only , but not on the path
  - Hence, for a **cyclic** process, $\Delta U = 0$
  - Equivalently, for fixed initial and final state, ΔU is **path independent**

But U is *not* just the PE of constituent particles

Example 19.3 P. 649 A cyclic process



The process *aba* is a cyclic process

Given: $W = -500$ J

$$Q = \Delta U + W = 0 + (-500\text{ J})$$
$$= -500\text{ J}$$

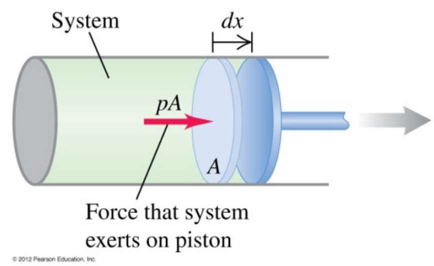
i.e., in this process external pressure does 500 J of work *on* the system, and the process *gives out* 500 J of heat

Work

Work is the form of energy exchange which can be accounted for macroscopically
For example, work done during volume changes of a gas

work done by system against external pressure in an infinitesimal volume change

$$dW = Fdx = pAdx = pdV$$



⚠ p always push outwards, i.e., $p > 0$

⚠ expansion, $dV > 0$, ∴ $dW > 0$ – work done *by* the gas *on* the surrounding

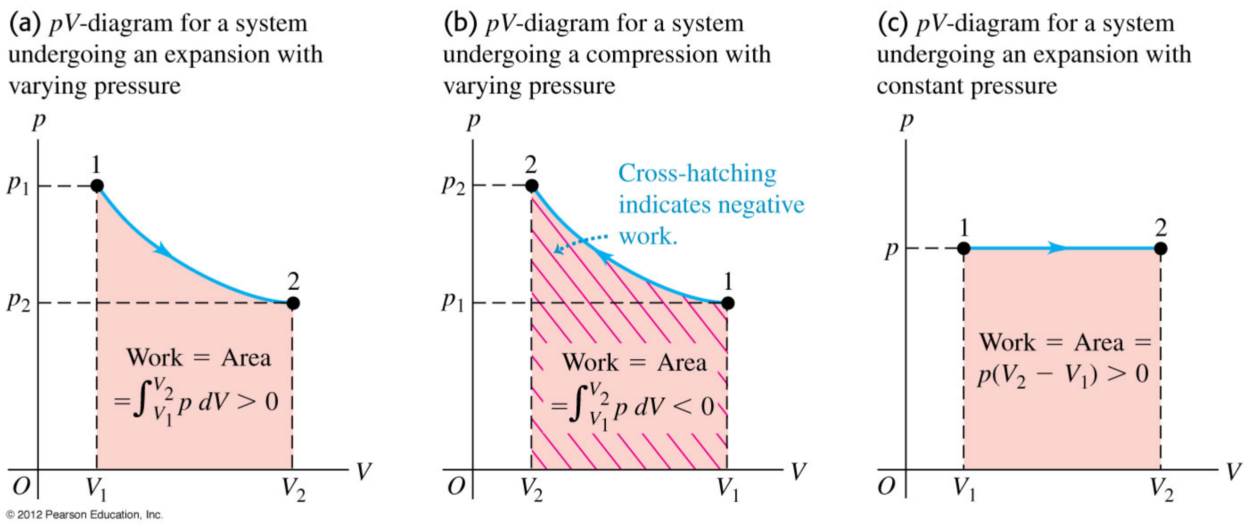
⚠ compression , $dV < 0$, ∴ $dW < 0$ – work done *on* the gas *by* the surrounding

work done in a finite volume change

$$\boxed{W = \int_{V_1}^{V_2} pdV} \leftarrow$$

area under the curve in a pV diagram, sometimes called $\boldsymbol{pdV}$ **work**

⚠ note the sign and the initial and final volume



Example 19.1 P. 644

Suppose an ideal gas changes volume at *constant pressure*

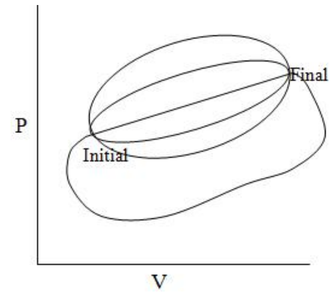
$$W = \int_{V_1}^{V_2} pdV = p(V_2 - V_1)$$

at *constant temperature*

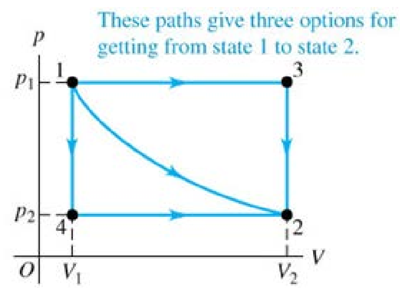
$$W = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{p_1}{p_2}$$

Question: is W a state function?

From same initial state to same final state along different paths
Areas under the paths are different
⚠ work done is **path-dependent**
⚠ W is not a state function



Example
An ideal gas. Suppose the initial state 1 and the final state 2 have the same temperature, find W_{142}, W_{132}, and W_{12} along isotherm.



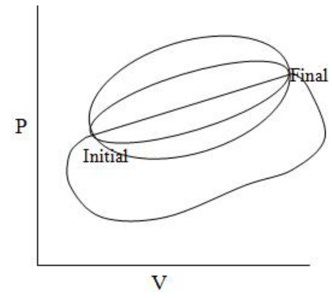
$W_{14} = 0$ since no volume change
$W_{42} = p_2(V_2 - V_1)$
So $W_{142} = W_{14} + W_{42} = p_2(V_2 - V_1)$

$W_{13} = p_1(V_2 - V_1)$
$W_{32} = 0$ since no volume change
So $W_{132} = W_{13} + W_{32} = p_1(V_2 - V_1)$

$$W_{12} \text{ along isotherm} = nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{p_1}{p_2}$$

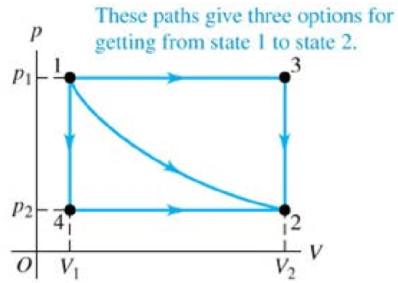
Heat
Heat is the form of energy exchange which *cannot* be accounted for macroscopically (as contrary to work)
For example, boiling water by fire

Since ΔU is path-independent
W is path-dependent
By first law, $Q = \Delta U + W$
⚠ heat is **path-dependent**
⚠ Q is not a state function



Example

Suppose the initial state 1 and the final state 2 have the same temperature, find Q_{142}, Q_{132}, and Q_{12} along isotherm.



Ideal gas internal energy depends on temperature only

Same temperature → $\Delta U = 0$

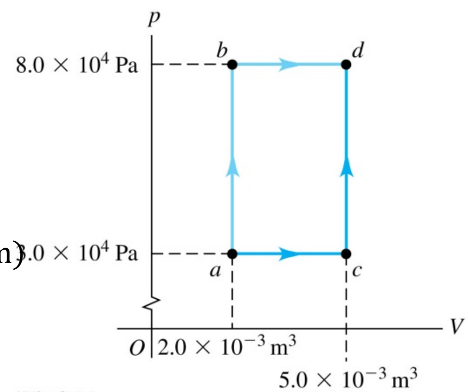
By first law, $Q = \Delta U + W = W$

$Q_{142} = W_{142} = p_2(V_2 - V_1)$

$Q_{132} = W_{132} = p_1(V_2 - V_1)$

$$Q_{12} \text{ along isotherm} = W_{12} \text{ along isotherm} = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{p_1}{p_2}$$

Example 19.4 P. 650



Given: $\Delta U_{ad} = 510\text{ J}$

In process *ab*:

$W_{ab} = 0$ since no volume change

In process *bd*:

$W_{bd} = p(V_2 - V_1) = (8.0 \times 10^4\text{ Pa})(3.0 \times 10^{-3}\text{ m})$
$= 240\text{ J}$

So $W_{abd} = W_{ab} + W_{bd} = 240\text{ J}$

Hence in process *abd*:

$Q_{abd} = \Delta U_{ad} + W_{abd} = 750\text{ J}$

In process *ac*:

$W_{ac} = (3.0 \times 10^4\text{ Pa})(3.0 \times 10^{-3}\text{ m}) = 90\text{ J}$

In process *cd*:

$W_{cd} = 0$ since no volume change

So $W_{acd} = W_{ac} + W_{cd} = 90\text{ J}$

Hence in process *acd*:

$Q_{acd} = \Delta U_{ad} + W_{acd} = 600\text{ J}$

Example 19.5 P. 651

1 g of water (1 cm^3) becomes 1671 cm^3 of steam when boiled at a constant pressure of 1 atm (1.013×10^5 Pa). The heat of vaporization at this pressure is $L_v = 2.256 \times 10^6\text{J/kg}$.

$$W = (1.013 \times 10^5\text{ Pa})(1670 \times 10^{-6}\text{ m}^3) = 169\text{ J}$$

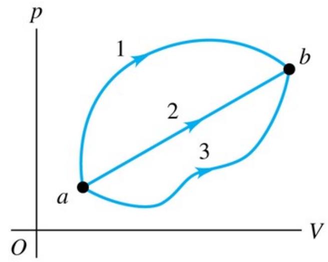
$$Q = mL_v = (10^{-3}\text{ kg})(2.256 \times 10^6\text{ J/kg}) = 2256\text{ J}$$

$\Delta U = Q - W = 2087\text{ J}$

Clicker Questions

Q19.1

A system can be taken from state a to state b along any of the three paths shown in the p-V diagram. If state b has greater internal energy than state a, along which path is the absolute value $|Q|$ of the heat transfer the greatest?



A. path 1

B. path 2

C. path 3

D. $|Q|$ is the same for all three paths.

E. Not enough information is given to decide.

Q19.4

In an isothermal expansion of an ideal gas, the amount of heat that flows into the gas

A. is greater than the amount of work done by the gas.

B. equals the amount of work done by the gas.

C. is less than the amount of work done by the gas, but greater than zero.

D. is zero.

E. is negative (heat flows *out of* the gas).

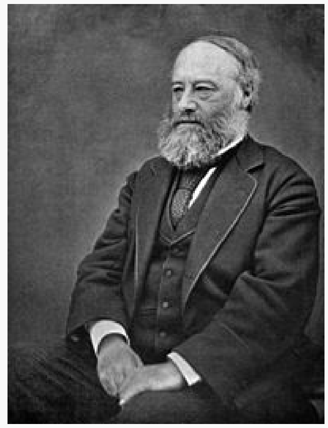
Ans: Q19.1) A, Q19.4) B

James Prescott Joule

From Wikipedia, the free encyclopedia

James Prescott Joule FRS (/dʒuːl/;[1] (24 December 1818 – 11 October 1889) was an English physicist and brewer, born in Salford, Lancashire. Joule studied the nature of heat, and discovered its relationship to mechanical work (see energy). This led to the law of conservation of energy, which led to the development of the first law of thermodynamics. The SI derived unit of energy, the joule, is named for James Joule. He worked with Lord Kelvin to develop the absolute scale of temperature. Joule also made observations of magnetostriction, and he found the relationship between the current through a resistor and the heat dissipated, which is now called Joule's first law.

James Prescott Joule



James Joule – physicist

Born	24 December 1818 Salford, Lancashire, England, UK
Died	11 October 1889 (aged 70) Sale, Cheshire, England, UK
Citizenship	British
Fields	Physics
Known for	First law of thermodynamics Disproving Caloric Theory
Influences	John Dalton John Davies
Notable awards	Royal Medal (1852) Copley Medal (1870) Albert Medal (1880)

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Early years [edit]

The son of a wealthy brewer, Joule was tutored as a young man by the famous scientist John Dalton and was strongly influenced by chemist William Henry and Manchester engineers Peter Ewart and Eaton Hodgkinson. He was fascinated by electricity, and he and his brother experimented by giving electric shocks to each other and to the family's servants.

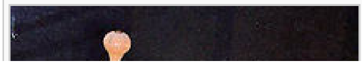
As an adult, Joule managed the brewery. Science was merely a serious hobby. Sometime around 1840, he started to investigate the feasibility of replacing the brewery's steam engines with the newly invented electric motor. His first scientific papers on the subject were contributed to William Sturgeon's *Annals of Electricity*.

Motivated in part by a businessman's desire to quantify the economics of the choice, and in part by his scientific inquisitiveness, he set out to determine which prime mover was the more efficient. He discovered Joule's first law in 1841, that *the heat which is evolved by the proper action of any voltaic current is proportional to the square of the intensity of that current, multiplied by the resistance to conduction which it experiences*.[2] He went on to realise that burning a pound of coal in a steam engine was more economical than a costly pound of zinc consumed in an electric battery. Joule captured the output of the alternative methods in terms of a common standard, the ability to raise one pound, a height of one foot, the *foot-pound*.

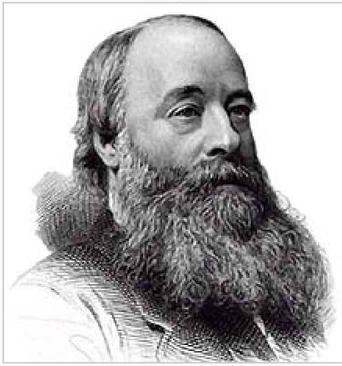
However, Joule's interest diverted from the narrow financial question to that of how much work could be extracted from a given source, leading him to speculate about the convertibility of energy. In 1843 he published results of experiments showing that the heating effect he had quantified in 1841 was due to generation of heat in the conductor and not its transfer from another part of the equipment. This was a direct challenge to the caloric theory which held that heat could neither be created or destroyed. Caloric theory had dominated thinking in the science of heat since introduced by Antoine Lavoisier in 1783. Lavoisier's prestige and the practical success of Sadi Carnot's caloric theory of the heat engine since 1824 ensured that the young Joule, working outside either academia or the engineering profession, had a difficult road ahead. Supporters of the caloric theory readily pointed to the symmetry of the Peltier-Seebeck effect to claim that heat and current were convertible in an, at least approximately, reversible process.

In June 1845, Joule read his paper *On the Mechanical Equivalent of Heat* to the British Association meeting in Cambridge.[7] In this work, he reported his best-known experiment, involving the use of a falling weight, in which gravity does the mechanical work, to spin a paddle-wheel in an insulated barrel of water which increased the temperature. He now estimated a mechanical equivalent of 819 ft·lbf/Btu (4.41 J/cal). He wrote a letter to the Philosophical Magazine, published in September 1845 describing his experiment.[8]

In 1850, Joule published a refined measurement of 772.692 ft·lbf/Btu (4.159 J/cal), closer to twentieth century estimates.[9]



Kinetic theory [edit]



James Prescott Joule

Kinetics is the science of motion. Joule was a pupil of Dalton and it is no surprise that he had learned a firm belief in the atomic theory, even though there were many scientists of his time who were still skeptical. He had also been one of the few people receptive to the neglected work of John Herapath on the kinetic theory of gases. He was further profoundly influenced by Peter Ewart's 1813 paper *On the measure of moving force*.

Joule perceived the relationship between his discoveries and the kinetic theory of heat. His laboratory notebooks reveal that he believed heat to be a form of rotational, rather than translational motion.

Joule could not resist finding antecedents of his views in Francis Bacon, Sir Isaac Newton, John Locke, Benjamin Thompson (Count Rumford) and Sir Humphry Davy. Though such views are justified, Joule went on to estimate a value for the mechanical equivalent of heat of 1034 foot-pound from Rumford's publications. Some modern writers have criticised this approach on the grounds that Rumford's experiments in no way represented systematic quantitative measurements. In one of his personal notes, Joule contends that Mayer's measurement was no more accurate than Rumford's, perhaps in the hope that Mayer had not anticipated his own work.

Joule has been attributed with explaining the Green Flash phenomenon in a letter to the Manchester Literary and Philosophical Society in 1869: actually, he just noted (with a sketch) the last glimpse as bluish green.[12]

For more detail see http://en.wikipedia.org/wiki/James_Prescott_Joule