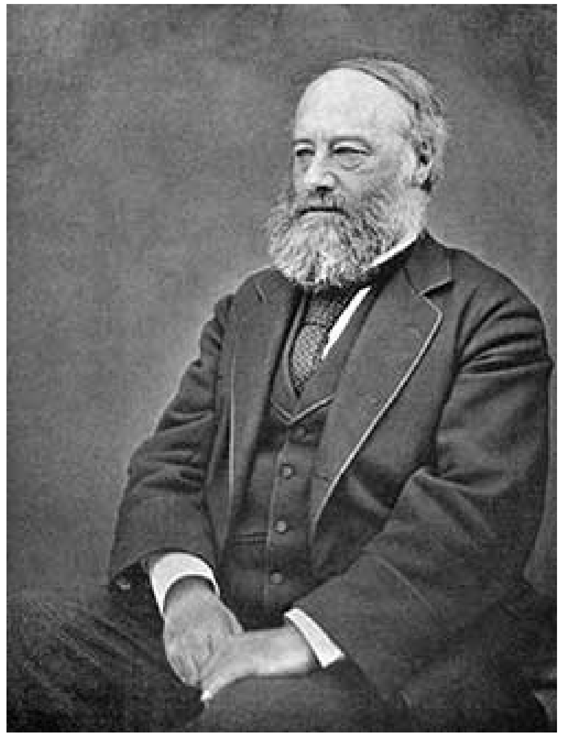
CH365 Chemical Engineering Thermodynamics

Lesson 4
Internal Energy, Energy Balances, and State Functions

Professor Andrew Biaglow

James P. Joule

24 December 1818 to 11 October 1889



Resistive Heating:
a.k.a. Joule's Law
$P=I^2R$

Joule-Thompson:
Joule's 2nd Law
Gas throttling

William Thomson
a.k.a. Baron Kelvin

Obscure home-schooled brewer's son. Tutored by John Dalton. Ran the brewery by day and conducted experiments at night as a hobby.

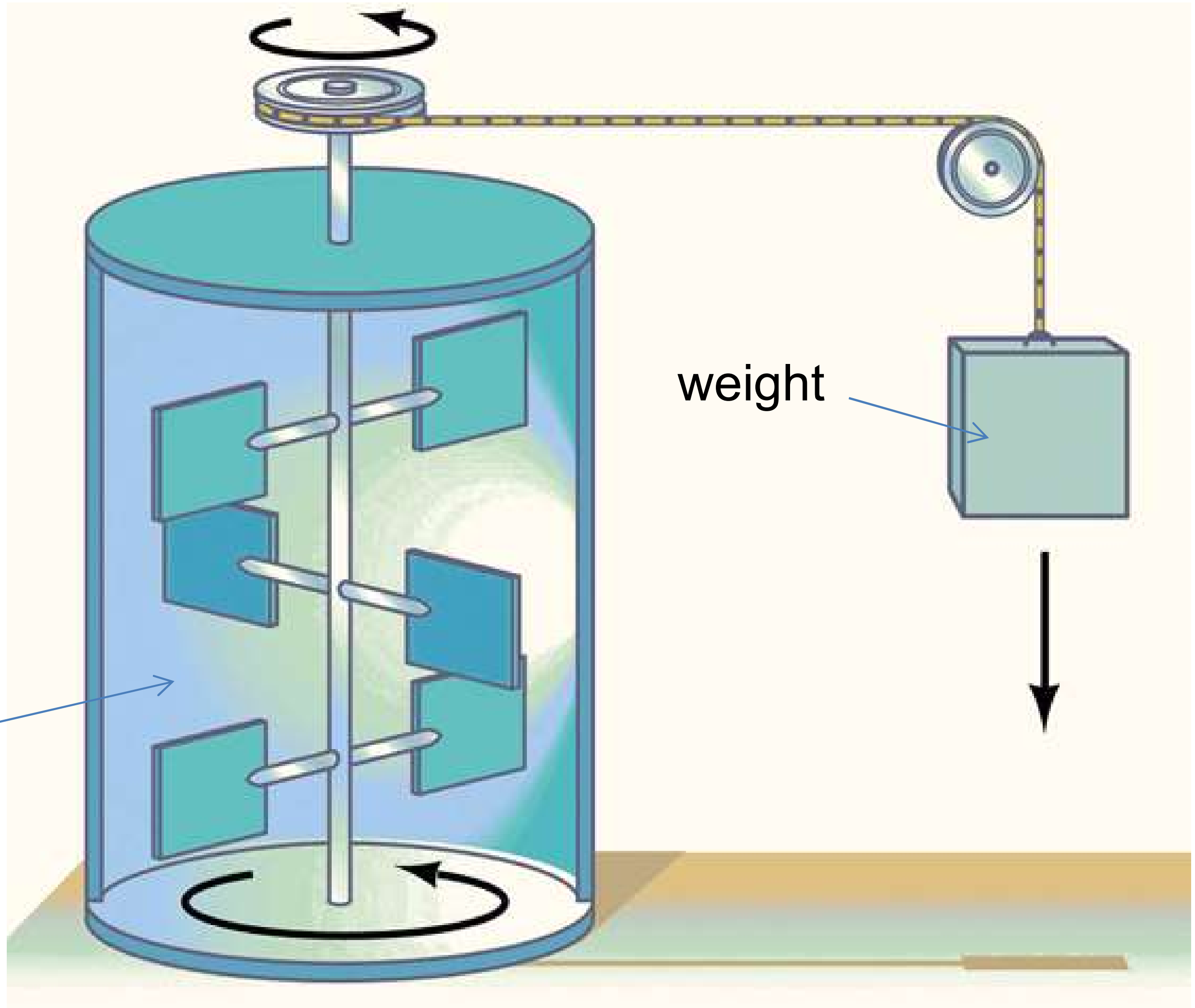
Impressed by the famous cannon-boring experiments of Count Rumford, in which heat is created continuously by the mechanical work of boring a cannon, and which violated the caloric theory of heat.

Joule's Experiment

relationship between work and heat

determined "the mechanical equivalent of heat with exactness"

J.P. Joule, On the Mechanical Equivalent of Heat, *Philosophical Transactions of the Royal Society of London* 140 (1850): 61-82



weight

Change in potential E of weight = $\rho g \Delta h$

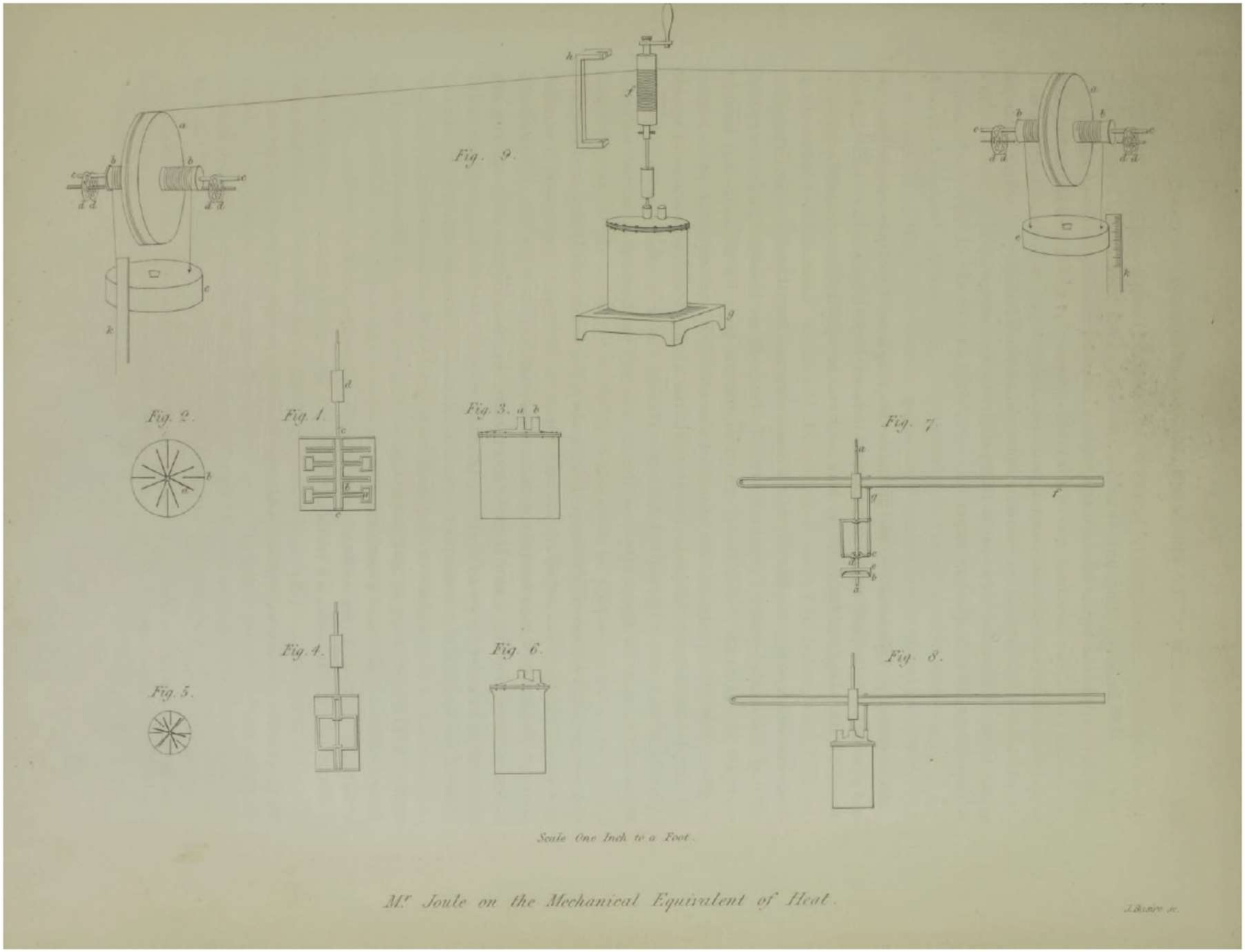
water, oil, mercury

Later contact with a colder object restores temperature

For each fluid, a fixed amount of work is required per unit mass for every degree of temperature rise.

Joule's Apparatus

J.P. Joule, On the Mechanical Equivalent of Heat, *Philosophical Transactions of the Royal Society of London* 140 (1850): 61-82



Joule's Data

J.P. Joule, On the Mechanical Equivalent of Heat, *Philosophical Transactions of the Royal Society of London* 140 (1850): 61-82

Table I.

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
1 Friction	1256·96	57°·698	2°·252—	55°·118	55°·774	0°·656 gain
1 Radiation ...	0	57·868	2·040—	55·774	55·882	0·108 gain
2 Friction	1255·16	58·085	1·875—	55·882	56·539	0·657 gain
2 Radiation ...	0	58·370	1·789—	56·539	56·624	0·085 gain
3 Friction	1253·66	60·788	1·596—	58·870	59·515	0·645 gain
3 Radiation ...	0	60·926	1·373—	59·515	59·592	0·077 gain
4 Friction	1252·74	61·001	1·110—	59·592	60·191	0·599 gain
4 Radiation ...	0	60·890	0·684—	60·191	60·222	0·031 gain
1	2	3	4	5	6	7

Internal Energy

Energy added as work can be removed later as heat. Where is this energy between its addition and transfer out?

Hidden Material – Take Notes!

First Law of Thermodynamics

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form, it appears simultaneously in other forms.

$$\Delta\left(\text{Energy of System}\right)+\Delta\left(\text{Energy of Surroundings}\right)=0$$

System: Region of space in which the process occurs

- a system can be any size
- boundaries may be real or imaginary
- can be a single substance or a component of a mixture

Surroundings: Everything with which the system interacts

Energy Balance for Closed Systems

Closed System vs. Open Systems (described later)

System boundary does not permit the transfer of matter between the system and surroundings

Q and W are positive for transfer into the system from surroundings, pages 26-27. Heat or work added to system increase internal energy.

$$\Delta(\text{Energy of System}) = Q + W$$

Internal energy changes only:

Intensive U vs extensive U^t (L1 Silde 16)

$$\Delta U^t = Q + W \qquad n\Delta U = Q + W \quad \text{eq 2.5}$$

$n\Delta U = \Delta U^t$ if n = 1 mol

Units: J, ft·lb_f, or Btu

Differential form:

$$dU^t = dQ + dW \qquad ndU = dQ + dW \quad \text{eq 2.6}$$

$ndU = dU^t$ if n=1 mol

Axiom to First Law:

There exists a form of energy, known as the internal energy U, which is an intrinsic property of a system, functionally related to the "measureable coordinates" which characterize the system. For a closed system not in motion, changes in this property are given by equations 2.5 and 2.6.

Example 2.3(a)

A gas is contained in a cylinder by a piston. The initial pressure of the gas is 7 bar, and the volume is 0.10 m^3. The piston is held in place by latches in the cylinder wall. The whole apparatus is placed in a total vacuum. What is the energy change of the apparatus if the restraining latches are removed so that the gas suddenly expands to double its initial volume, the piston striking other latches at the end of the process? (System: gas, piston, and cylinder)

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Thermodynamic State and State Functions

State Functions

Depend only on present conditions, however reached.
Calculated as a function of *intensive* variables, e.g.,

$$U = \underbrace{f(T,P)}_{\text{f is a function of "measurable coordinates" T and P}}$$

Postulate: fixing any two intensive properties fixes all others

Is pressure a state function?

$$PV = RT \Rightarrow P = \frac{RT}{V} = f(T,V)$$

Yes, pressure can be written as a state function.

(As long as we use intensive V and not extensive V^t)

$$\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P \qquad \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V$$

Q and W are not state functions and depend on path.

$$\int dQ = Q \qquad \int dW = W$$

(These are path integrals – mathematically different.)

Example 2.4

Refer to the figure below. When a system is taken from state *a* to state *b* along path *acb*, 100 J of heat flows into the system and the system does 40 J of work.

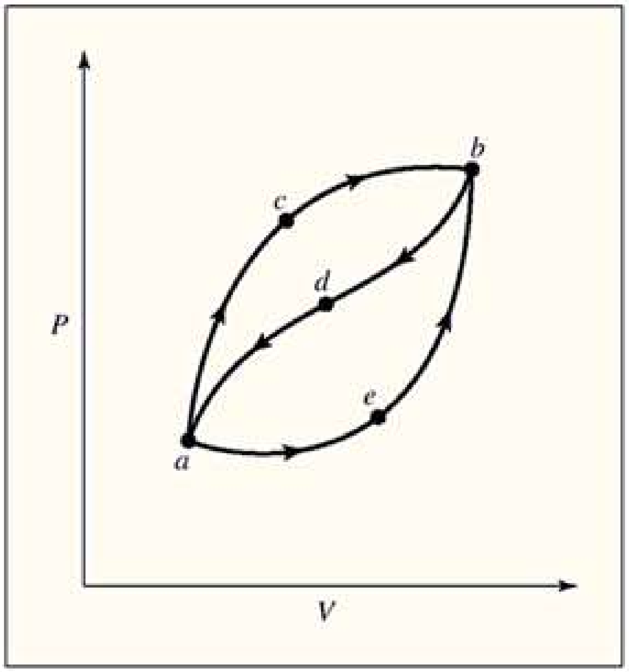

Diagram for Ex. 2.4.

Hidden Material – Take Notes!

Problem 2.6

One mole of a gas in a closed system undergoes a four-step thermodynamic cycle. Use the data given in the following table to determine the numerical values for the missing quantities, i.e., determine a-h.

Step	ΔU^t/J	Q/J	W/J
12	-200	a	-6000
23	b	-3800	c
34	d	-800	300
41	4700	e	f
12341	g	h	-1400

Questions?