Lecture 7

The first law of thermodynamics continued

Pre-reading: §19.5

Where we are

The pressure p, volume V, and temperature T are related by an equation of state. For an ideal gas,

$$pV = nRT = NkT$$

For an ideal gas, the temperature T is is a direct measure of the average kinetic energy of its molecules:

$$KE_{\mathrm{tr}} = \frac{3}{2}nRT = \frac{3}{2}NkT$$

and

$$v_{\mathrm{rms}} = \sqrt{(v^2)_{\mathrm{av}}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Where we are

We define the *internal energy* of a system:

$$U = \sum \underbrace{KE}_{\text{Random chaotic motion}} + \sum \underbrace{PE}_{\text{interaction between atoms \& molecules}}$$

For an ideal gas,

$$U = \frac{f}{2} N k T$$

i.e. the internal energy depends only on its temperature

Where we are

By considering adding heat to a fixed volume of an ideal gas, we showed

$$Q = \frac{f}{2} Nk\Delta T = \frac{f}{2} nR\Delta T$$

and so, from the definition of heat capacity

$$Q = nC\Delta T$$

we have that $C_V = \dfrac{f}{2}R$ for *any* ideal gas.

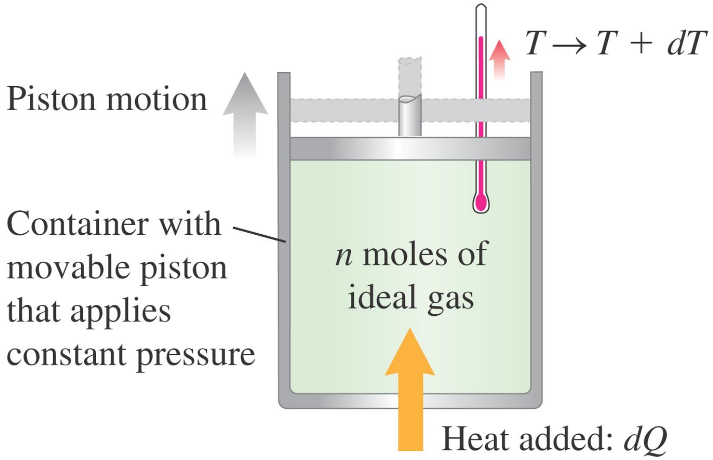
Change in internal energy: $\Delta U = nC_V\Delta T$

Table 19.1 Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	C_V (J/mol · K)
Monatomic	He	12.47
	Ar	12.47
Diatomic	H_2	20.42
	N_2	20.76
	O_2	20.85
	CO	20.85
Polyatomic	CO_2	28.46
	SO_2	31.39
	H_2S	25.95

Heat capacity of an ideal gas

Now consider adding heat to an ideal gas at *constant pressure*.



By definition, $Q = nC_p\Delta T$

and $W = p\Delta V = nR\Delta T$

So from $\Delta U = Q - W$

we get $nC_V\Delta T = nC_p\Delta T - nR\Delta T$

or

$$C_p = C_V + R$$

It takes *greater heat input* to raise the temperature of a gas a given amount at constant pressure than constant volume

YF §19.4

Ratio of heat capacities

Look at the ratio of these heat capacities: we have

$$C_V = \frac{f}{2}R$$

and

$$C_p = C_V + R = \frac{f+2}{2}R$$

so

$$\gamma = \frac{C_p}{C_V} > 1$$

For a monatomic gas, $C_V = \frac{3}{2}R$

so $C_p = \frac{3}{2}R + R = \frac{5}{2}R$

and

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

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Problem

An ideal gas is enclosed in a cylinder which has a movable piston. The gas is heated, resulting in an increase in temperature of the gas, and work is done by the gas on the piston so that the pressure remains constant.

a) Is the work done by the gas positive, negative or zero? Explain

b) From a microscopic view, how is the internal energy of the gas molecules affected?

c) Is the heat less than, greater than or equal to the work? Explain.

The first law of thermodynamics

The total change in internal energy of a system is the sum of the heat added to it and the work done on it.

$$\Delta U = Q - W$$

(conservation of energy).

ΔU depends *only* on the initial and final states, i.e. does not depend on the path, and does not depend on the kind of process that occurs.

Two special cases of the first law are worth mentioning.

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Isolated processes

An *isolated* process is one where the system does no work, and there is no heat flow:

$$W = Q = 0$$

and hence

$$U_2 = U_1 = \Delta U = 0$$

so *the internal energy of an isolated system is constant*.

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Cyclic processes

A *cyclic process* is one where the system returns to its original state.

Since the final state is the same as the initial state, the total energy change must be zero; so

$$U_2 = U_1 \qquad \text{and} \qquad Q = W$$

If work is done by the system, then an equal quantity of heat must have flowed into the system as Q; but in general Q and W do *not* have to be zero.

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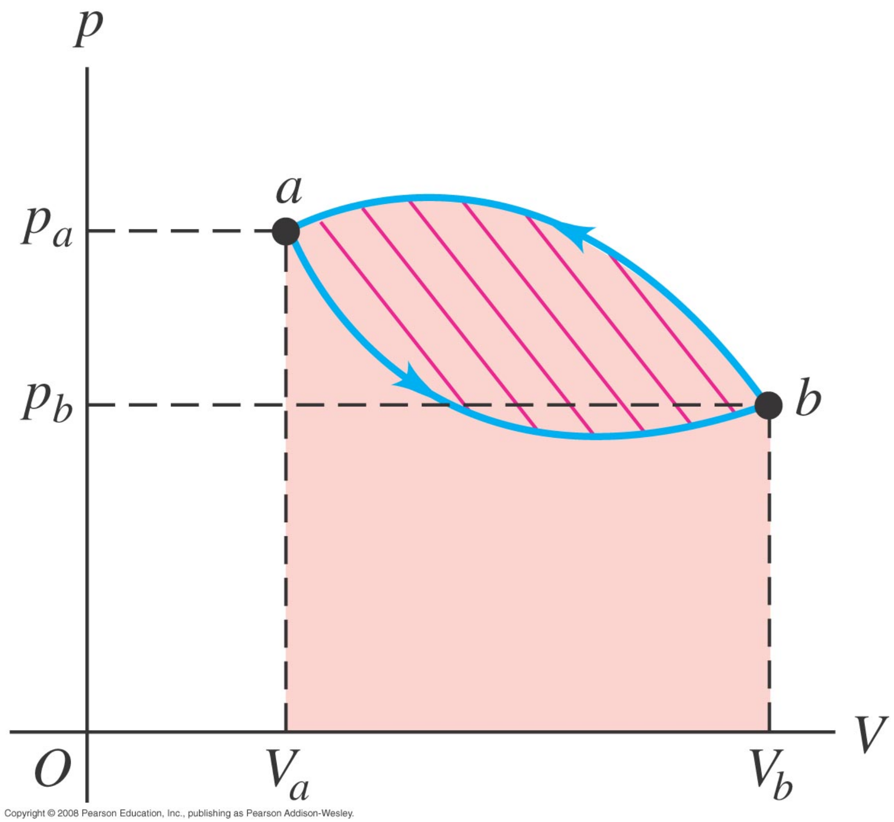
Thermodynamic processes

Now we want to think in detail about different thermodynamic processes.

For an ideal gas, we can represent these processes using pV-diagrams.

In each case, we want to relate the change in internal energy, the heat added, and the work done.



Thermodynamic processes

We can identify four specific kinds of thermodynamic processes that often occur:

- *Adiabatic* – no heat transfer into or out of the system
- *Isochoric* – occurs at constant volume
- *Isobaric* – occurs at constant pressure
- *Isothermal* – occurs at constant temperature

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Adiabatic processes

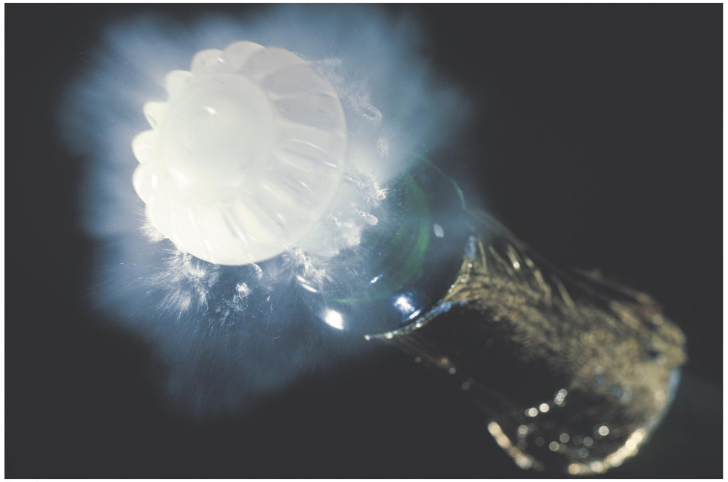
An *adiabatic* process is one there is no heat flow:

$$Q = 0$$

A process can be adiabatic if the system is thermally insulated, or if it is so rapid that there is not enough time for heat to flow.

For an adiabatic process,

$$U_2 - U_1 = \Delta U = -W$$

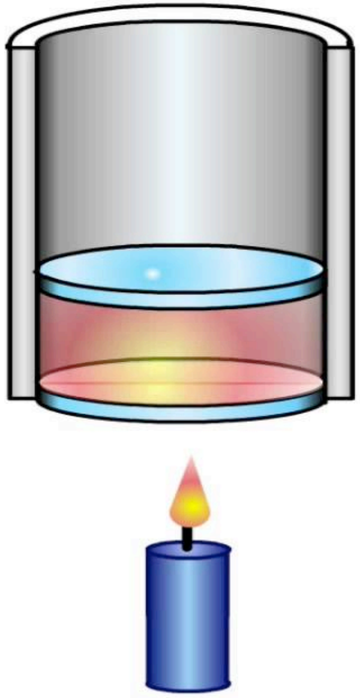


Isochoric processes

An *isochoric* process is a constant volume process. With no volume change, there is no work:

$$W = 0$$

All the energy added as heat remains in the system as an increase in internal energy.



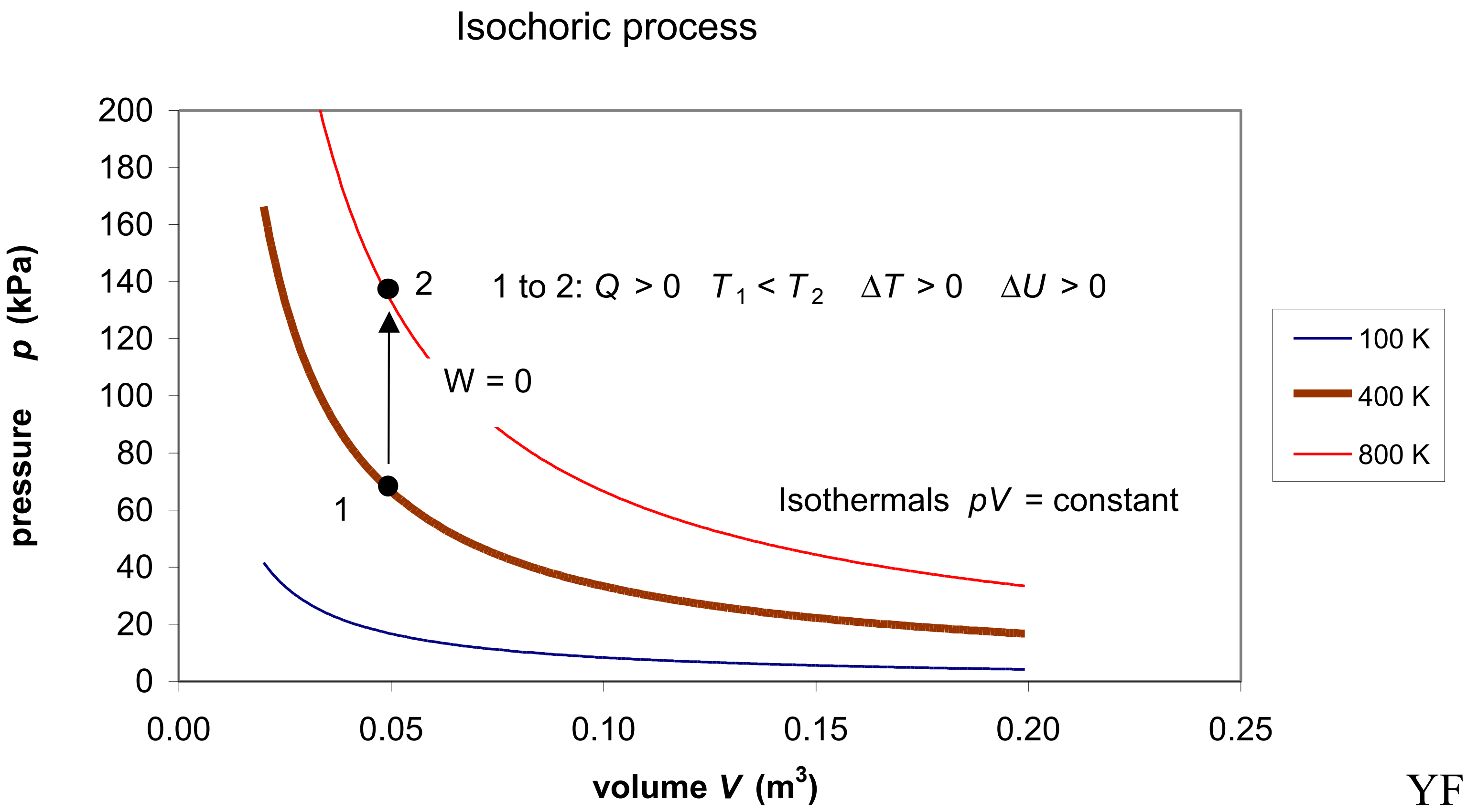
For an isochoric process,

$$U_2 - U_1 = \Delta U = Q$$

Isochoric processes

Isochoric process for an ideal gas: $\Delta V = 0$

$W = 0; \Delta U = Q = n\, C_V\, \Delta T$



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Isobaric processes

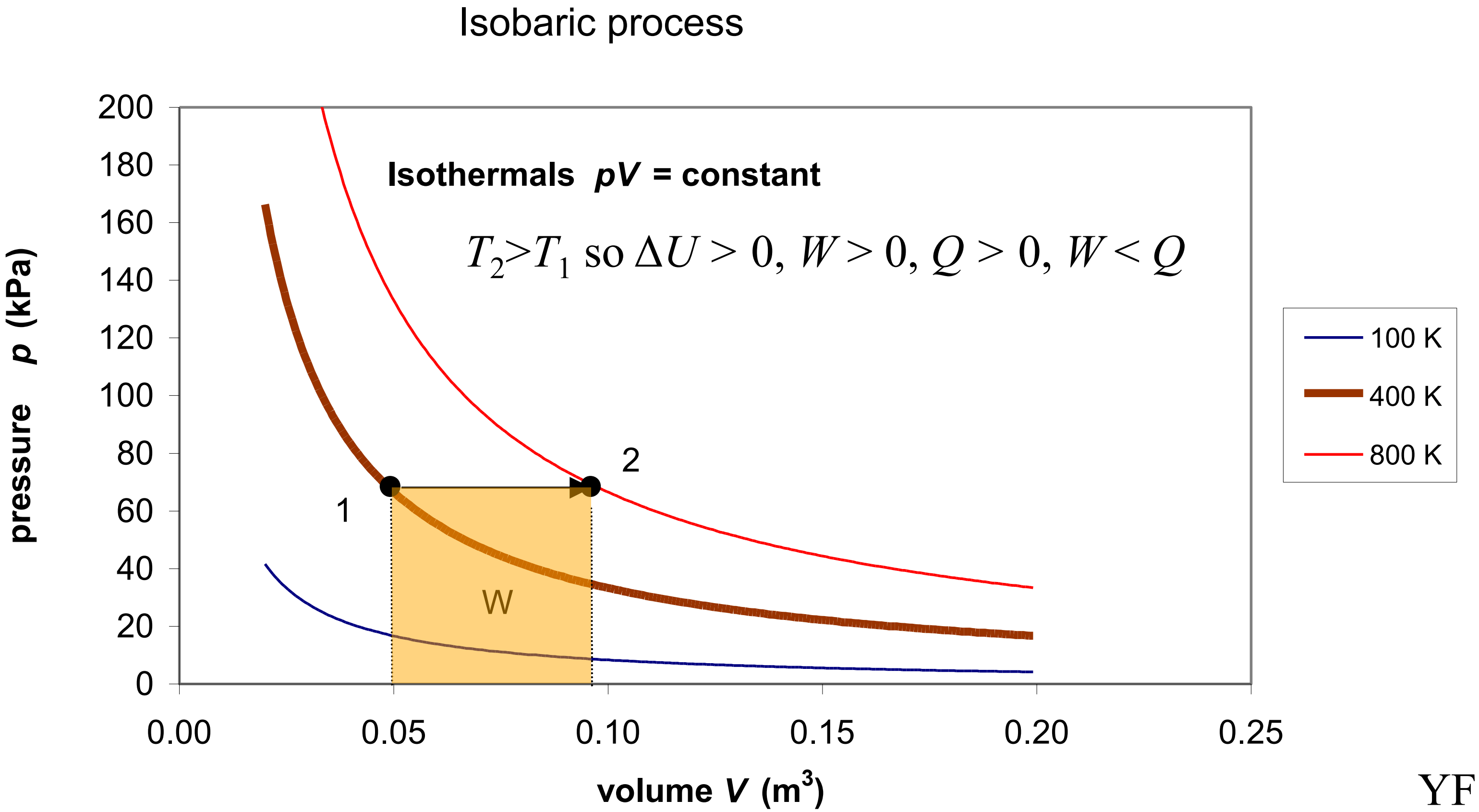
An *isobaric* process is a constant pressure process. In general, none of ΔU, Q or W is zero, but:

$$W = p(V_2 - V_1)$$

Isobaric processes

Isobaric process for an ideal gas: $\Delta p = 0$

$W = p\,\Delta V, \quad Q = n\,C_P\,\Delta T,\ \Delta U = Q - W = n\,C_V\,\Delta T$



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Isothermal processes

An *isothermal* process is a constant temperature process. For a process to be isothermal, any heat flow must occur slowly enough that thermal equilibrium is maintained. In general, none of ΔU, Q or W is zero.

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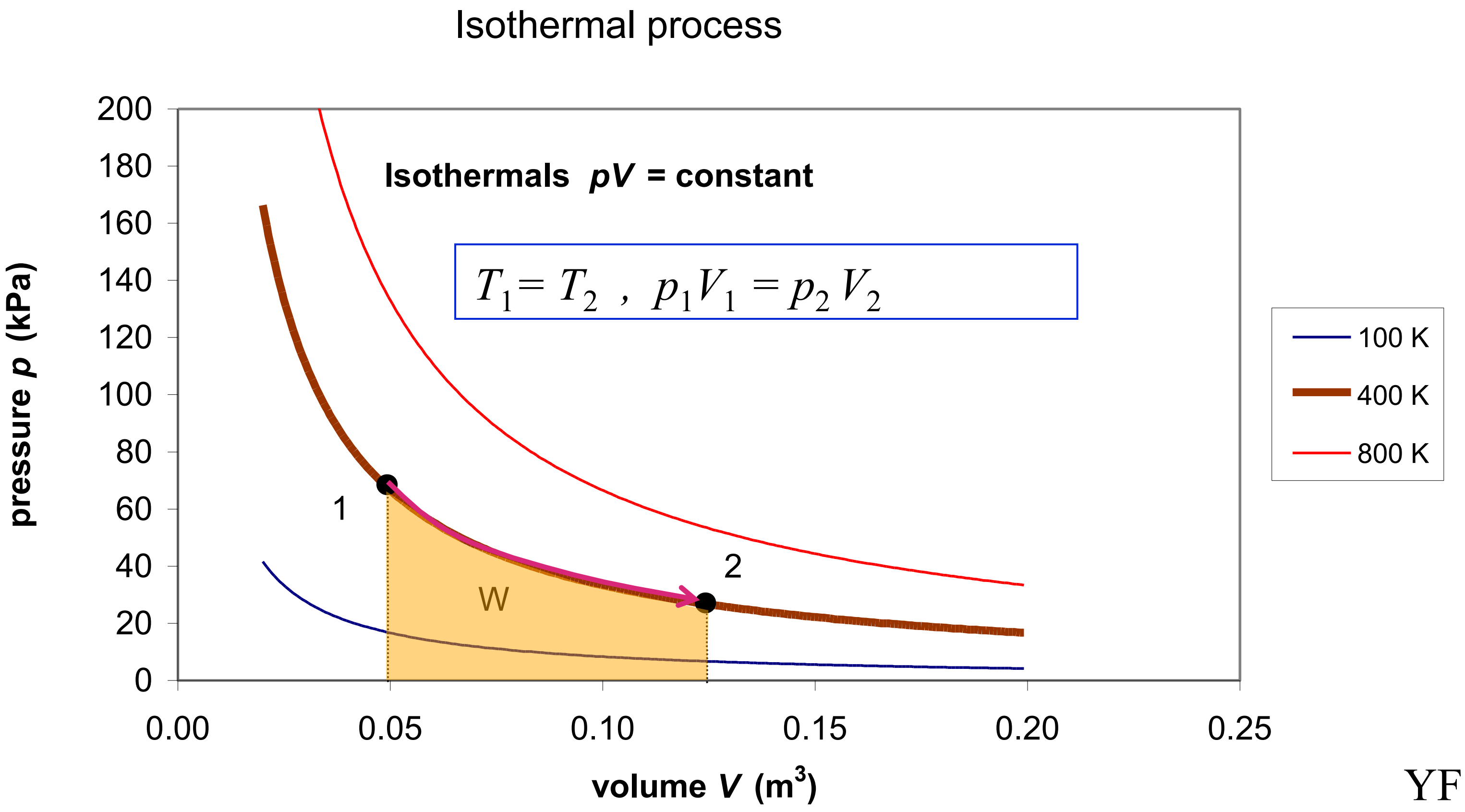
Isothermal processes

Isothermal process for an ideal gas: $\Delta T = 0$

$T_1 = T_2, \quad p_1V_1 = p_2V_2$; W is the area under the isothermal curve.



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Adiabatic process

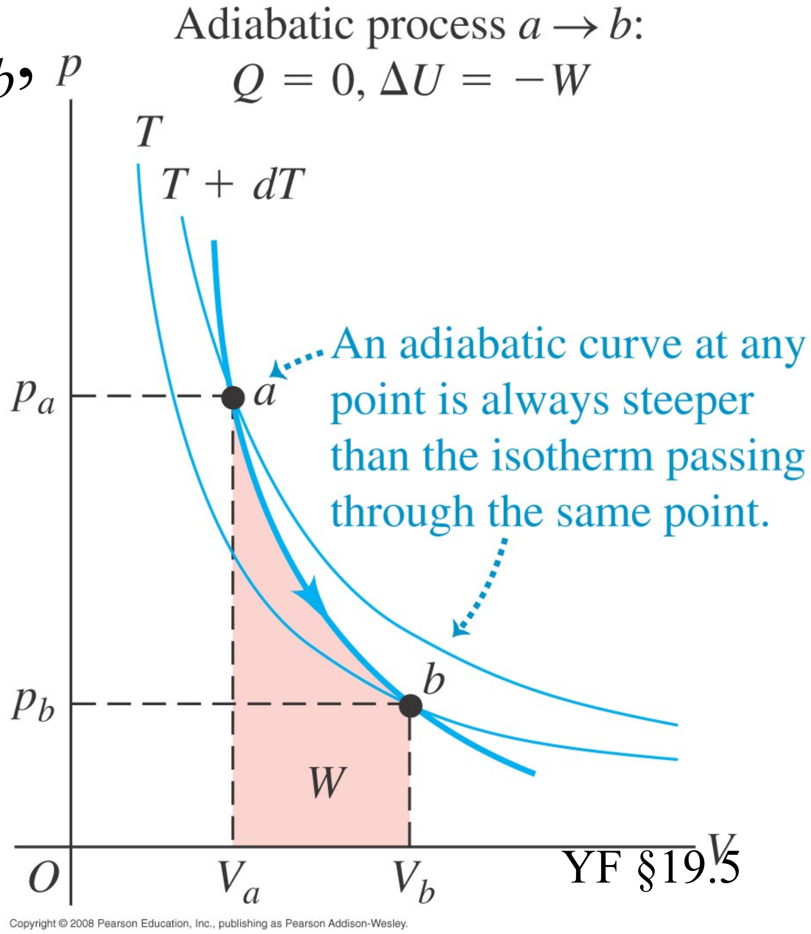
Adiabatic process for an ideal gas: $Q = 0$

so $\Delta U = -W$

As gas expands from V_a to V_b, it does positive work so U drops and T drops.

So if a is on an isotherm with temperature $T + dT$, point b is on an isotherm with lower temperature T

➔ adiabat is *steeper*.



An adiabatic curve at any point is always steeper than the isotherm passing through the same point.

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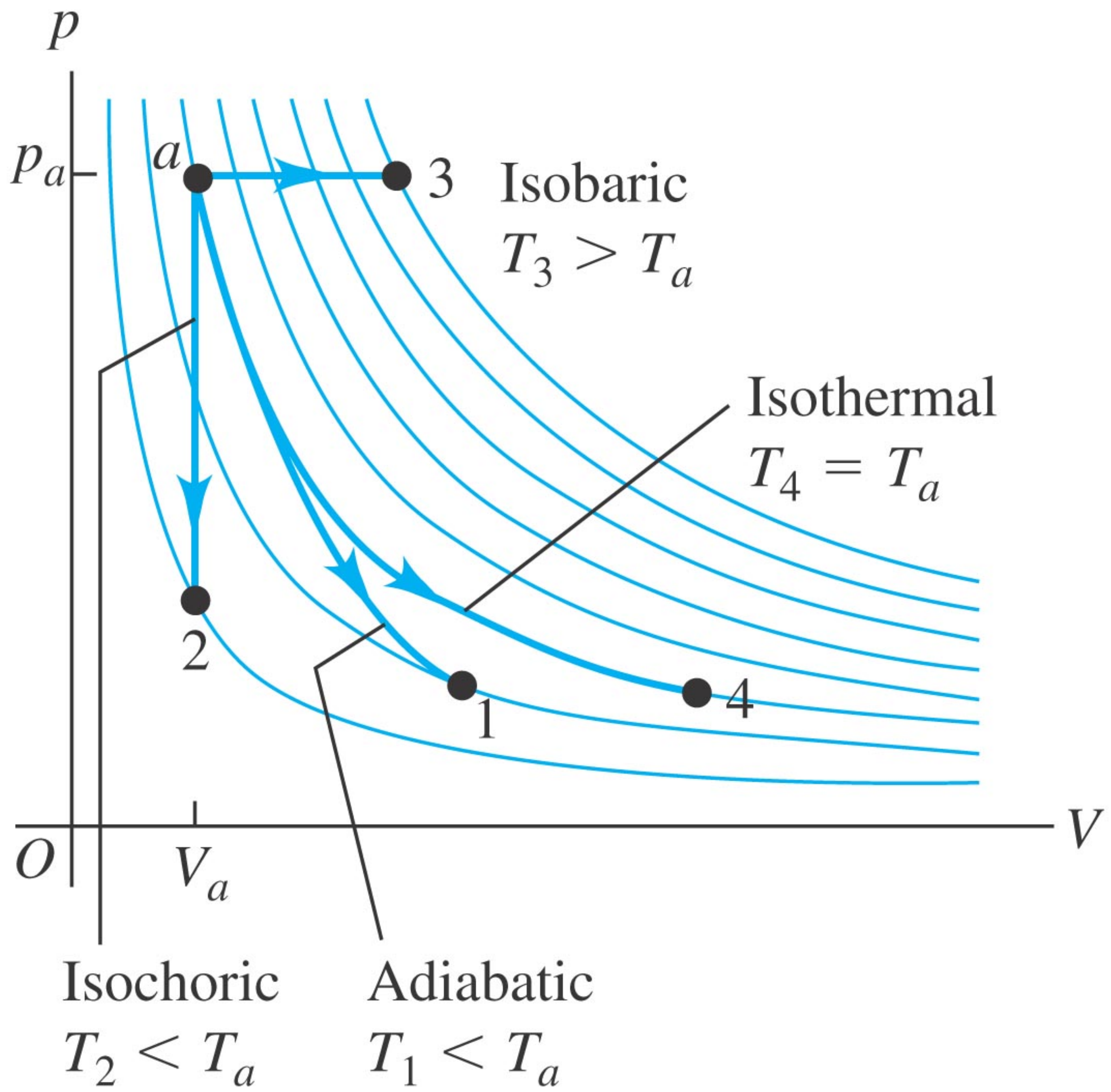

p
p_a
a
3
Isobaric
$T_3 > T_a$
Isothermal
$T_4 = T_a$
2
1
4
O
V_a
V
Isochoric
$T_2 < T_a$
Adiabatic
$T_1 < T_a$

Adiabatic process

Recall that for an ideal gas, $\Delta U = nC_V\Delta T$, and $W = p\,\Delta V$. Then since $\Delta U = -W$, we have

$$nC_V\Delta T = -p\,\Delta V$$

Using the ideal gas equation, we can show that

$$pV^\gamma = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

where $\gamma = \dfrac{C_P}{C_V}$

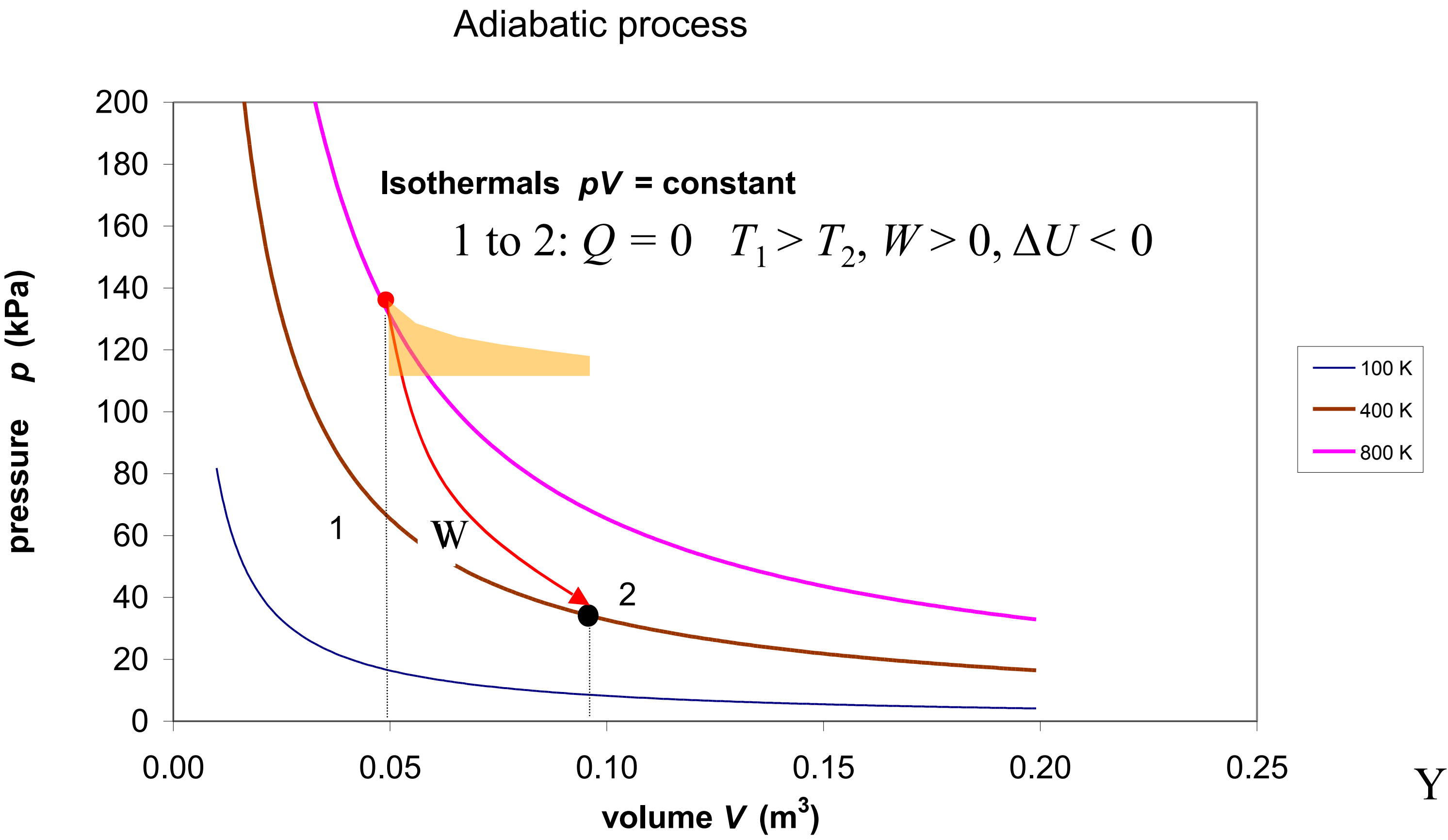
$$W = \frac{C_V}{R}(p_1V_1 - p_2V_2) = \frac{1}{\gamma - 1}(p_1V_1 - p_2V_2)$$

YF §19.5

Adiabatic processes

Adiabatic process for an ideal gas: $\Delta T = 0$

$T_1 = T_2, \quad p_1V_1 = p_2V_2$; W is the area under the isothermal curve.



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Problem

A cylinder with a movable piston contains 0.25 mole of monatomic idea gas at 2.40×10^5 Pa and 355 K. The ideal gas first expands isobarically to twice its original volume. It is then compressed adiabatically back to its original volume, and finally it is cooled isochorically to its original pressure.

a) Compute the temperature after the adiabatic compression.

b) Compute the total work done by gas on the piston during the whole process.

Take $C_V = 12.47\ J.mol^{-1}.K^{-1}$ $\gamma = 1.67$

Next lecture

The second law of thermodynamics

Read: YF §20.1