Thermodynamics of Gases

18th March 2008

Last lecture

- Zeroth law: If system C is in thermal equilibrium (same temperature) with A and B, then A is in thermal equilibrium with B. Allows us to use thermometers.

- If two systems are not in thermal equilibrium, then heat will flow (conduction, convection, radiation)

- Heat is a form of energy ($\Delta Q = C \, \Delta T$)

- First Law: $dU = đQ + đW$

- For gas, $dW = -P \, dV$, so $dU = dQ - PdV$
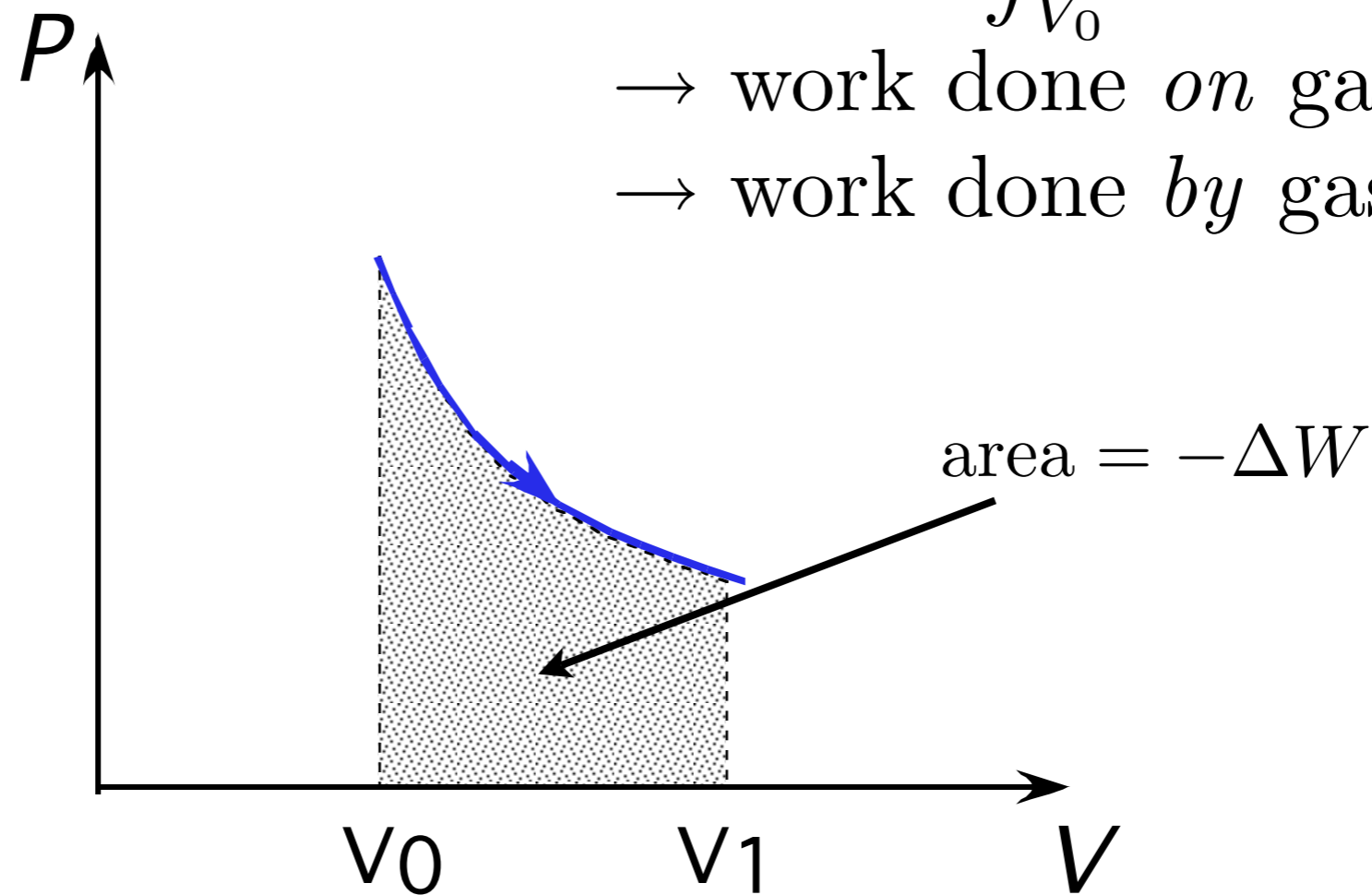
3.1 Quasistatic work on PV diagram

Quasistatic work on PV diagram

Expansion:

$$\Delta W = -\int_{V_0}^{V_1} P \, dV < 0$$

$\rightarrow$ work done *on* gas negative

$\rightarrow$ work done *by* gas

area $= -\Delta W$

Invented by James Watt and kept as a trade secret

Figure 1

Quasistatic work on PV diagram

Compression:

$$\text{area} = \Delta W = -\int_{V_0}^{V_1} P \, \mathrm{d}V > 0$$

$$= \text{work done } on \text{ gas}$$
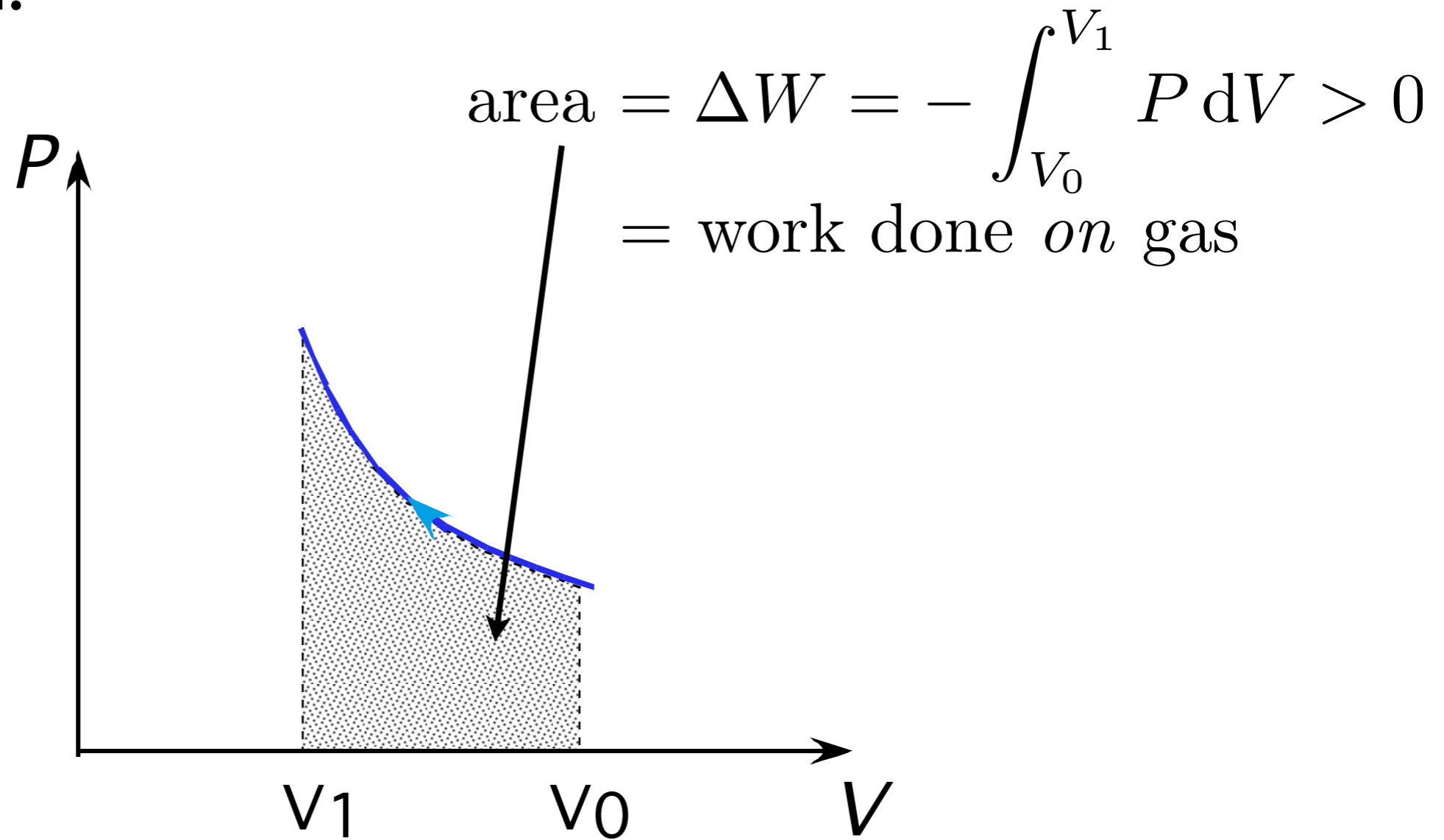
P

V_1 V_0 V

Figure 2

3.2 W & Q are process dependent

PV diagram jargon

- Isotherm ➜ line of constant temperature

- Isobar ➜ line of constant pressure

- Isochor ➜ line of constant volume

- adiabat ➜ line of zero heat flow

Path dependence of W

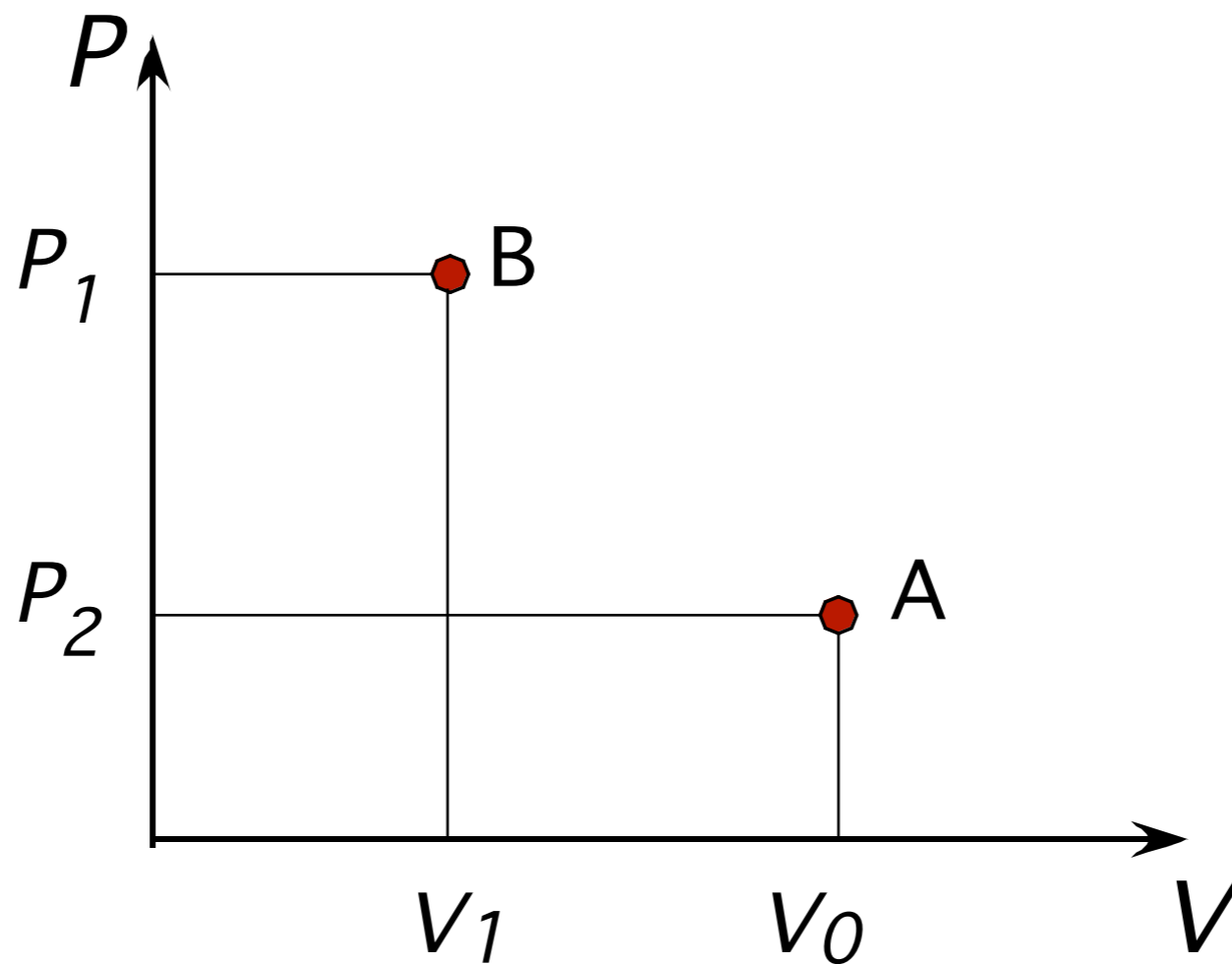Consider two paths from A to B on *PV* diagram at the same temperature:

Figure 3

Path dependence of W

Consider two paths from A to B on PV diagram at the same temperature:

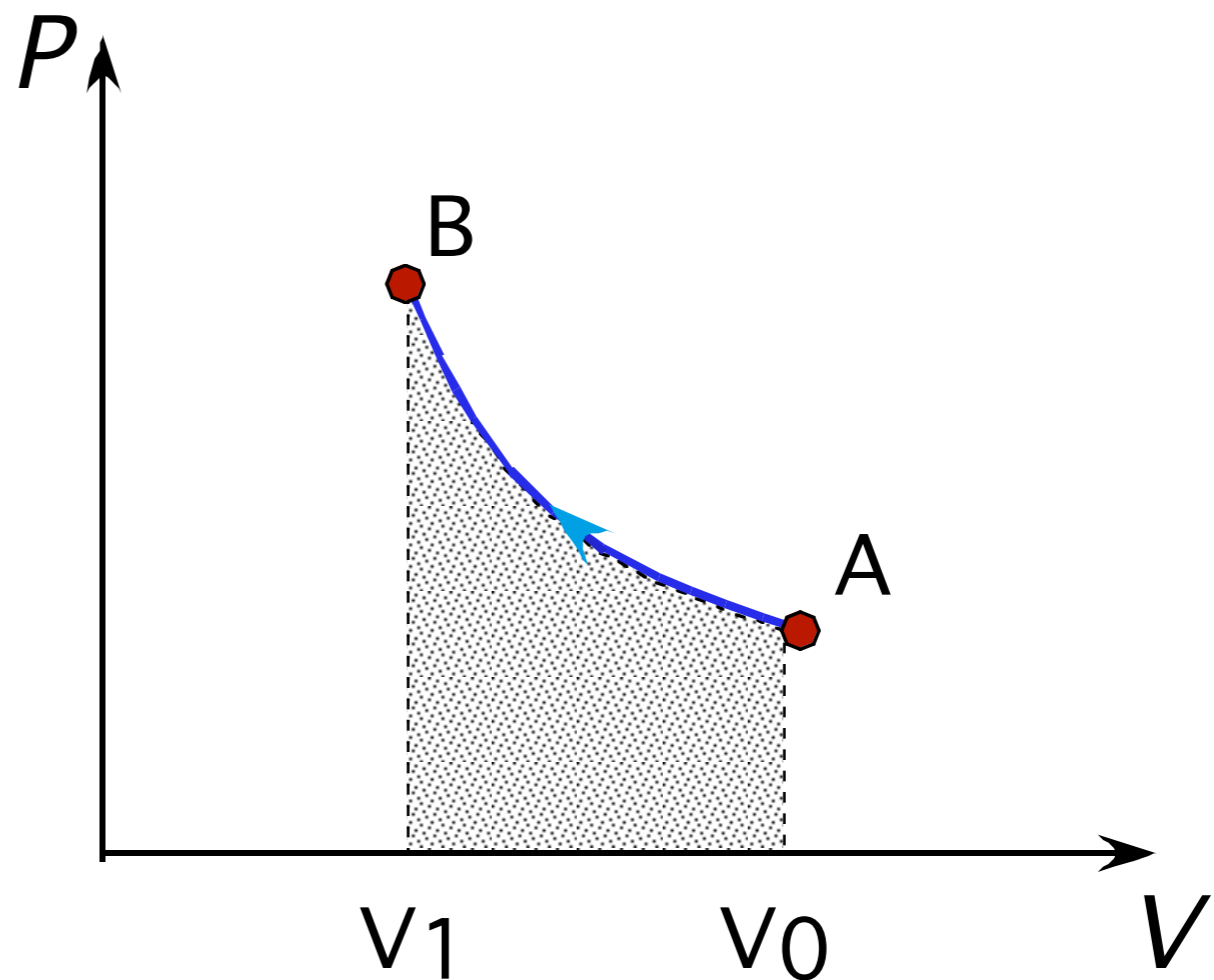Process 1 - Isothermal

$PV = Nk_BT \rightarrow P \propto (1/V)$

Figure 4

Isothermal process

$$PV = Nk_BT \rightarrow P = Nk_BT/V$$

$$
\begin{aligned}
W_1 &= -\int P \, \mathrm{d}V && (\text{A} \rightarrow \text{B}) \\
&= -\int (Nk_BT/V) \, \mathrm{d}V && (\text{A} \rightarrow \text{B}) \\
&= -(Nk_BT) \int \mathrm{d}V/V && (V \text{ goes from } V_0 \rightarrow V_1) \\
&= -(Nk_BT) \ln(V_1/V_0) && > 0 \text{ for } V_1 < V_0
\end{aligned}
$$

(work done ON system)

Path dependence of W

Consider two paths from A to B on PV diagram at the same temperature:

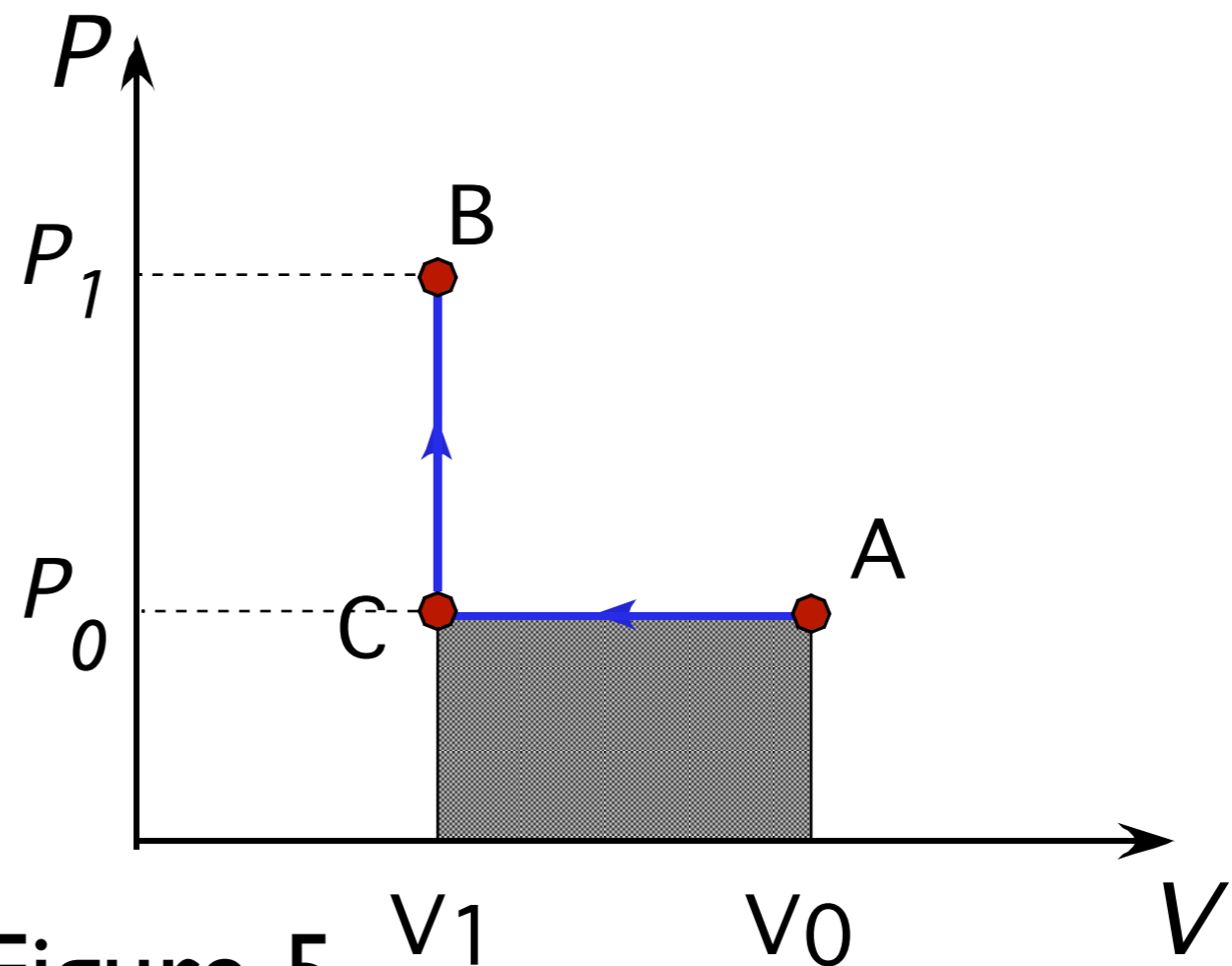Process 2 - Isobaric (constant pressure) followed by isochoric (constant volume)

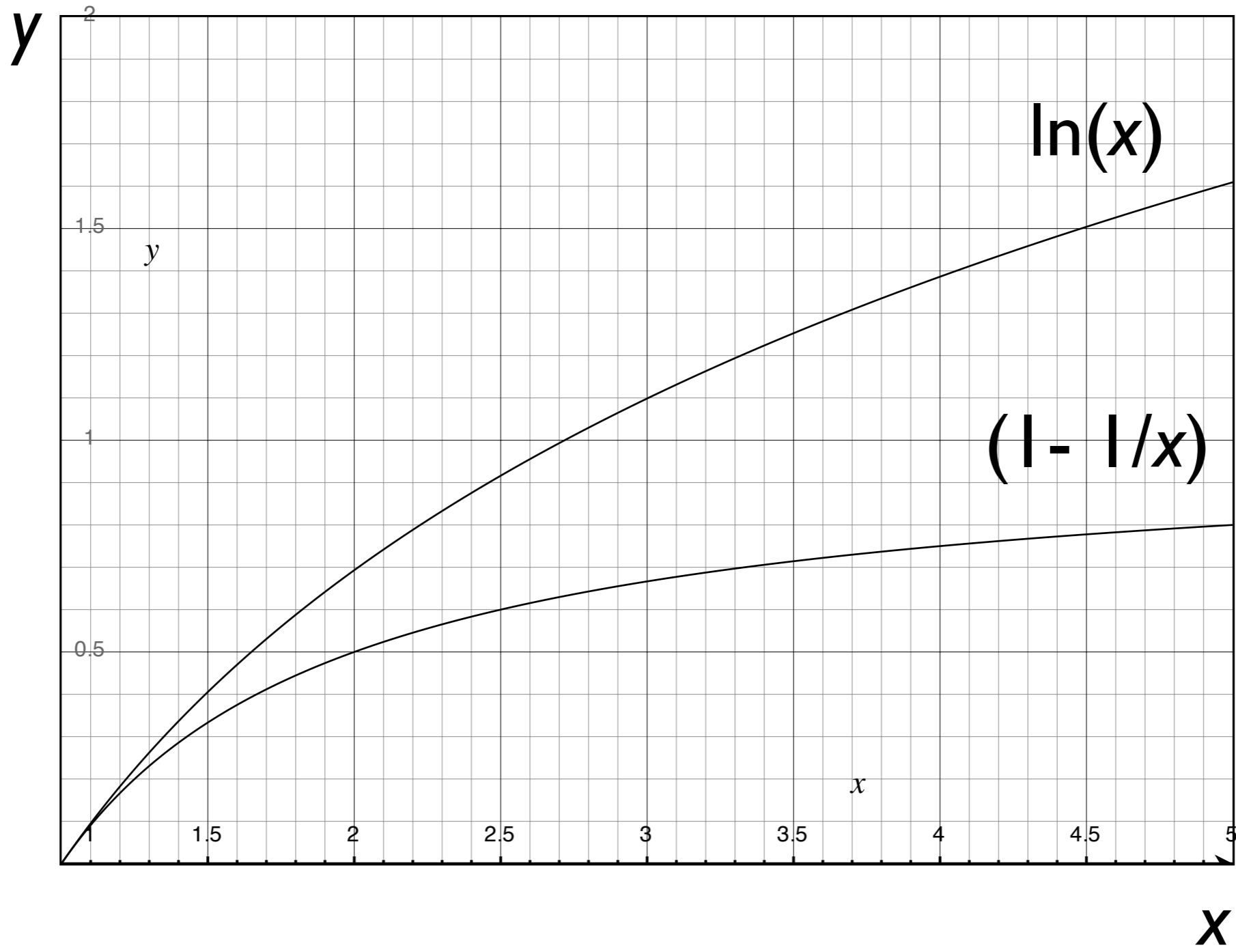Figure 5

Isobaric then isochoric

A $\rightarrow$ C : constant $P \rightarrow T$ falls

$$
\begin{aligned}
W_{A \rightarrow C} &= -\int P \, \mathrm{d}V && \text{(A} \rightarrow \text{C)} \\
&= -P_0 \int \mathrm{d}V && (V \text{ goes from } V_0 \rightarrow V_1) \\
&= -P_0(V_1 - V_0) && (\text{again} > 0 \text{ since } V_1 < V_0)
\end{aligned}
$$

C $\rightarrow$ B : constant V, T rises,

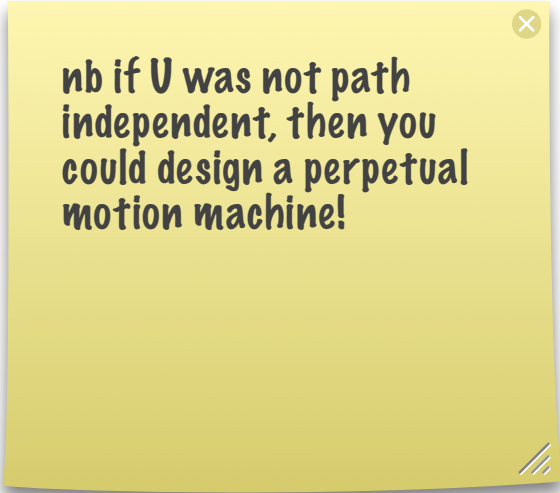$W_{C \rightarrow B} = 0$ since $\mathrm{d}V = 0$

$$
\begin{aligned}
W_2 = W_{A \rightarrow C \rightarrow B} &= P_0(V_0 - V_1) \\
&= (N k_B T)(1 - V_1/V_0) < W_1 \text{ (see graph!)}
\end{aligned}
$$

Path dependence of Q

Since $\Delta U = U_{fin} - U_{init} \quad \rightarrow$ depends only on initial and final states $\therefore$ NOT process dependent.

BUT W is process dependent and
$\quad \therefore$ so is $\Delta Q \, [= \Delta U - \Delta W]$

nb if U was not path independent, then you could design a perpetual motion machine!

3.3 Heat Capacity

Heat capacities

the change in temperature can be related to the heat change by,

$$dQ = N_{moles}\ C_m\ dT$$

C is the heat capacity, (C_m molar capacity), c (small c is the specific heat capacity i.e. per kilogram), so

$$dQ = m\ c\ dT$$

and $C_m = m_{molar}\ c$

As a result, things with small heat capacities (e.g. metals) cool faster than those with large heat capacities (e.g. water) (ditto pie fillings!)

NB since dQ is process dependent so is C

C_v for ideal gas

For ideal gas: $U = n_d \frac{1}{2} N k_B T$, n_d degs. freedom

differentiating $\mathrm{d}U = \frac{1}{2} n_d N k_B \, \mathrm{d}T$

1st Law: $\qquad \mathrm{d}Q = \mathrm{d}U - \mathrm{d}W = \frac{1}{2} n_d N k_B \, \mathrm{d}T + P \, \mathrm{d}V$

for constant V (*i.e.* $\mathrm{d}V = 0$) $\rightarrow \mathrm{d}Q = \frac{1}{2} n_d N k_B \, \mathrm{d}T$

$\therefore \quad C_V = \frac{1}{2} n_d N k_B$ – Heat capacity constant volume

$\therefore \quad$ can write $U = C_V T$ (for an ideal gas)

For 1 mole of gas $C_{V_m} = \frac{n_d}{2} R$.
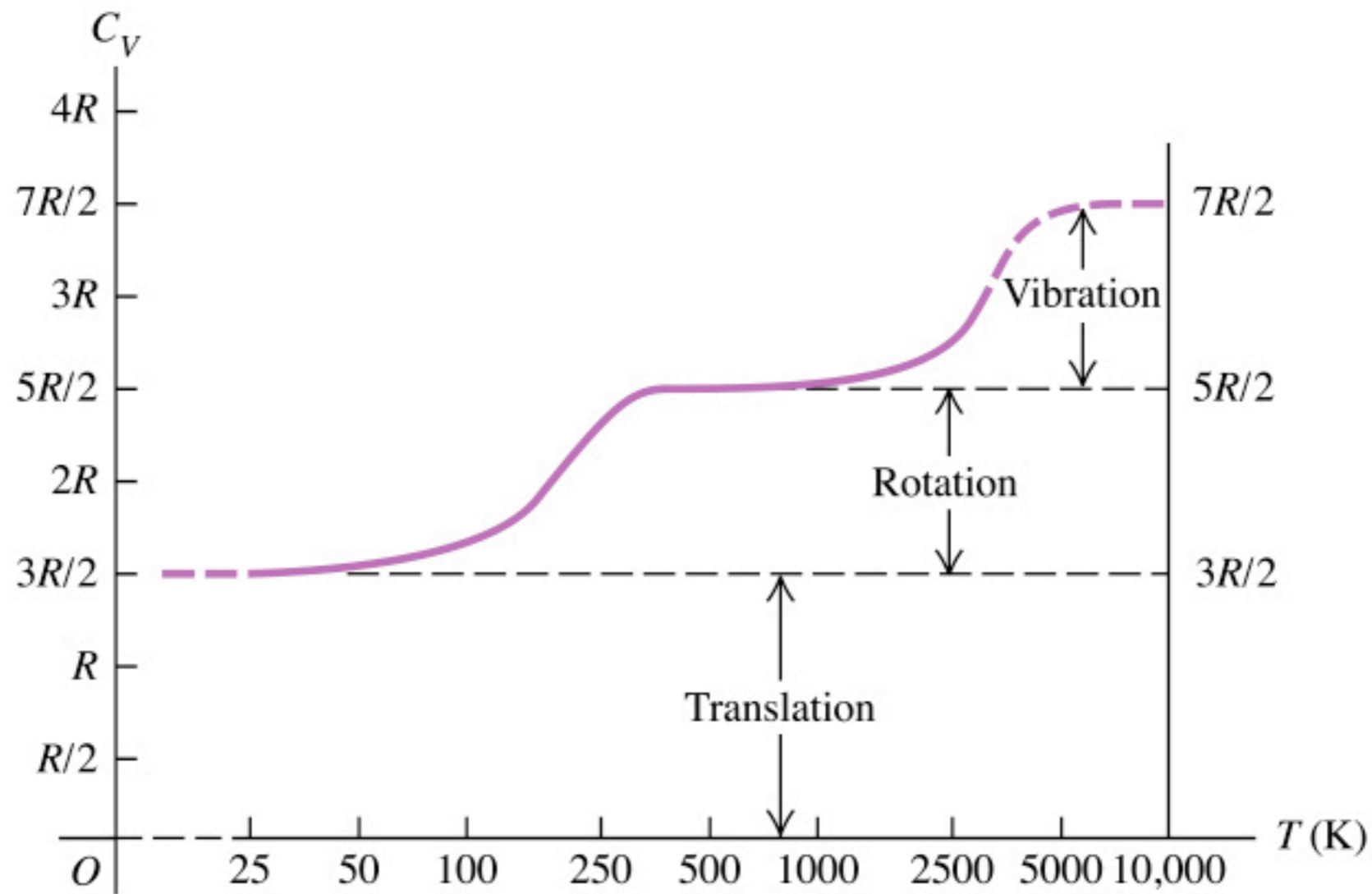
C_v for H_2
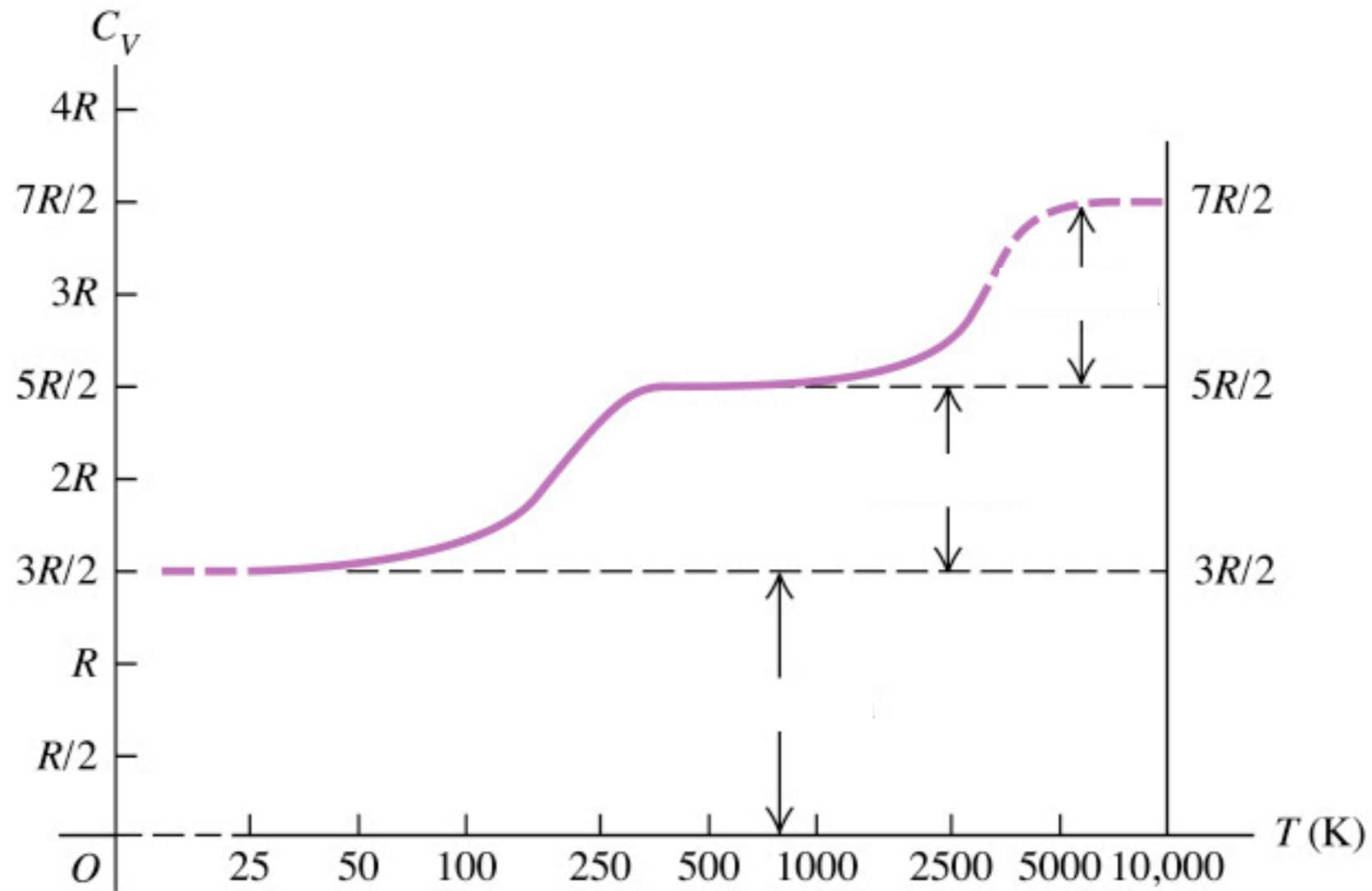
C_v for H_2

Figure 6

C_p for ideal gas

$$\mathrm{d}(PV) = V\,\mathrm{d}P + P\,\mathrm{d}V = Nk_B\mathrm{d}T$$
$$\rightarrow \quad P\,\mathrm{d}V = Nk_B\,\mathrm{d}T - V\,\mathrm{d}P$$

using 1st Law, $\mathrm{d}Q = \frac{1}{2}n_d Nk_B\,\mathrm{d}T + Nk_B\,\mathrm{d}T - V\,\mathrm{d}P$

for constant $P\,(i.e.\ \mathrm{d}P = 0) \rightarrow \mathrm{d}Q = (C_V + Nk_B)\,\mathrm{d}T$

$\rightarrow \quad C_P = C_V + Nk_B$ - Heat capacity at constant pressure

NB for 1 mole of ideal gas, $C_{P_m} = C_{V_m} + R$

C_p for ideal gas

As T rises for constant $P \rightarrow V$ must rise
$$\rightarrow \text{gas does work}$$
$$\rightarrow \text{need extra Q to compensate}$$
$$\rightarrow C_P > C_V$$

$$\rightarrow \gamma = C_P/C_V = (C_V + Nk_B)/C_V = (n_d + 2)/n_d$$

γ - ratio of heat capacities

3.4 Adiabatic process

Adiabatic processes

Adiabatic process $dQ = 0$, i.e. naturally reversible.

1st Law becomes: $dU = -P\,dV$

For ideal gas: $U = n_d \frac{1}{2} N k_B T = n_d \frac{1}{2} PV$

so $dU = (n_d/2)(P\,dV + V\,dP) = -P\,dV$

$\rightarrow (n_d + 2)\,P\,dV = -n_d V\,dP$

Adiabatic processes

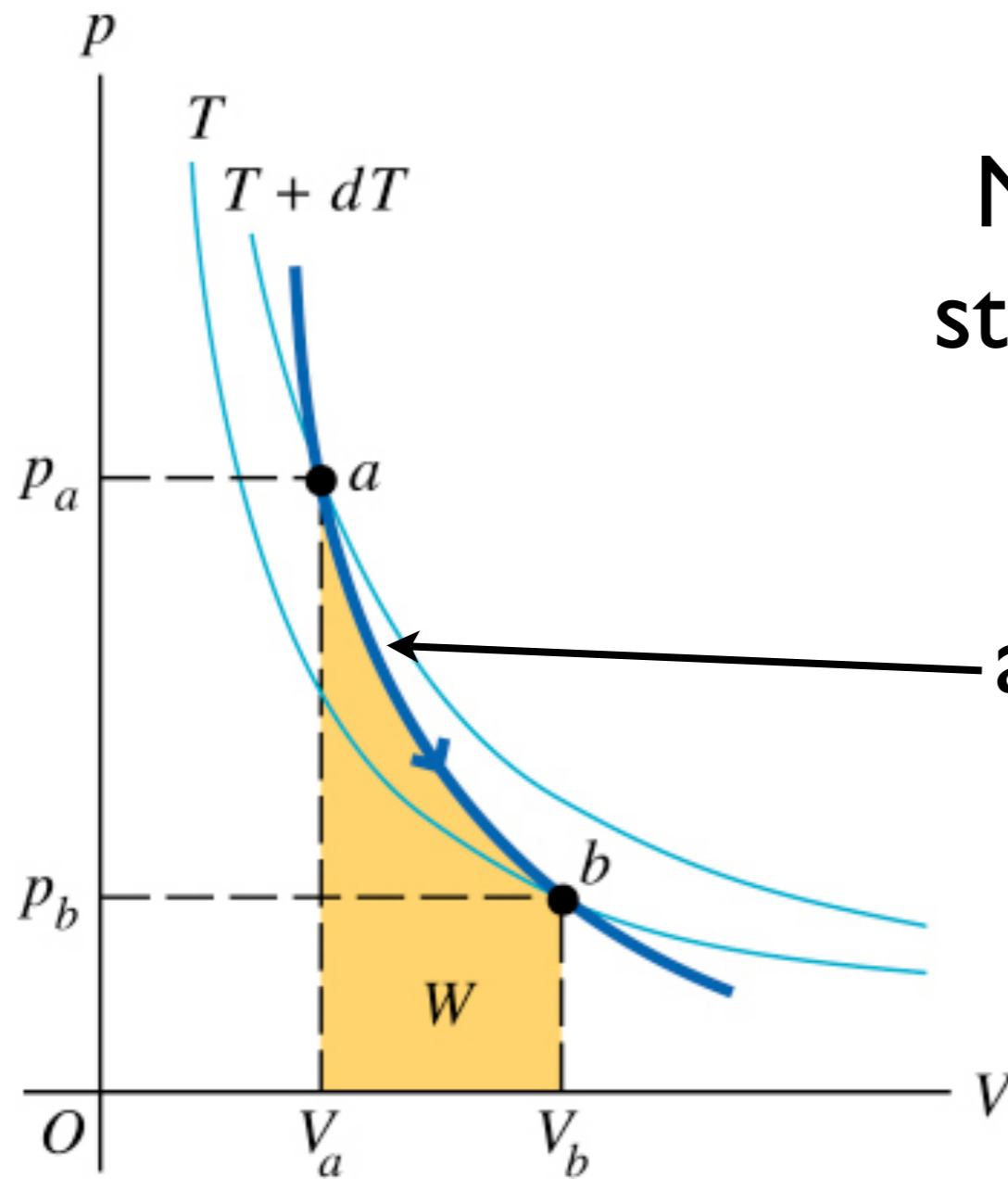$$\frac{(n_d+2)}{n_d} \int (1/V)dV = - \int (1/P)dP$$

$$\gamma \ln V = -\ln P + constant$$

$$\ln PV^\gamma = constant$$

$$\rightarrow PV^\gamma = constant \qquad \text{(adiabatic equation of state)}$$

For an adiabatic change, from state 1 to state 2,

$$P_1 V_1^\gamma = P_0 V_0^\gamma$$

Adiabat steeper than isotherm

Not that adiabats are steeper than isotherms

adiabat

NB light blues are isotherms, lines of equal (but different!) T

Figure 7