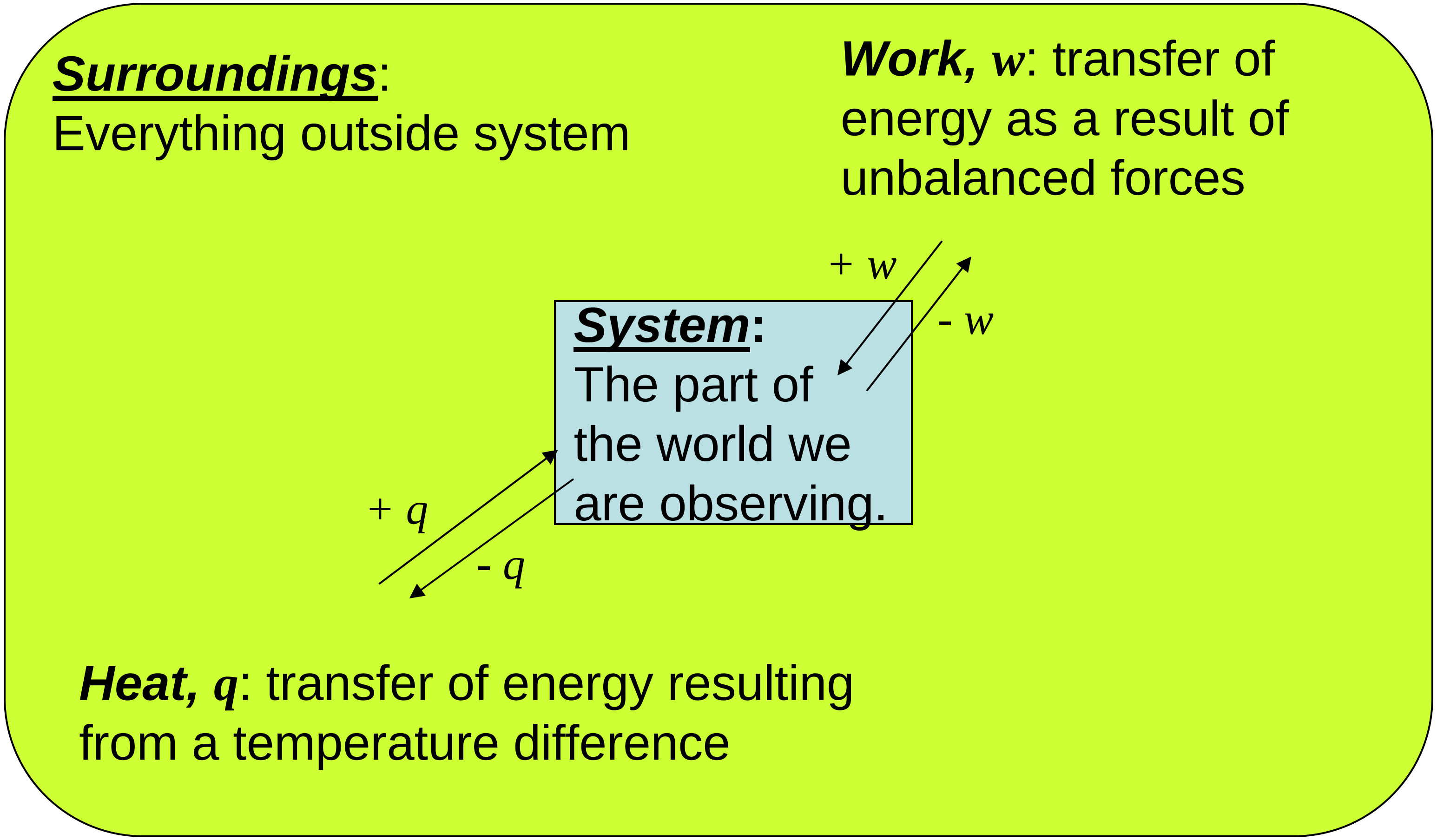
Work and Heat Definitions



Surroundings:
Everything outside system

Work, *w*: transfer of energy as a result of unbalanced forces

System:
The part of the world we are observing.

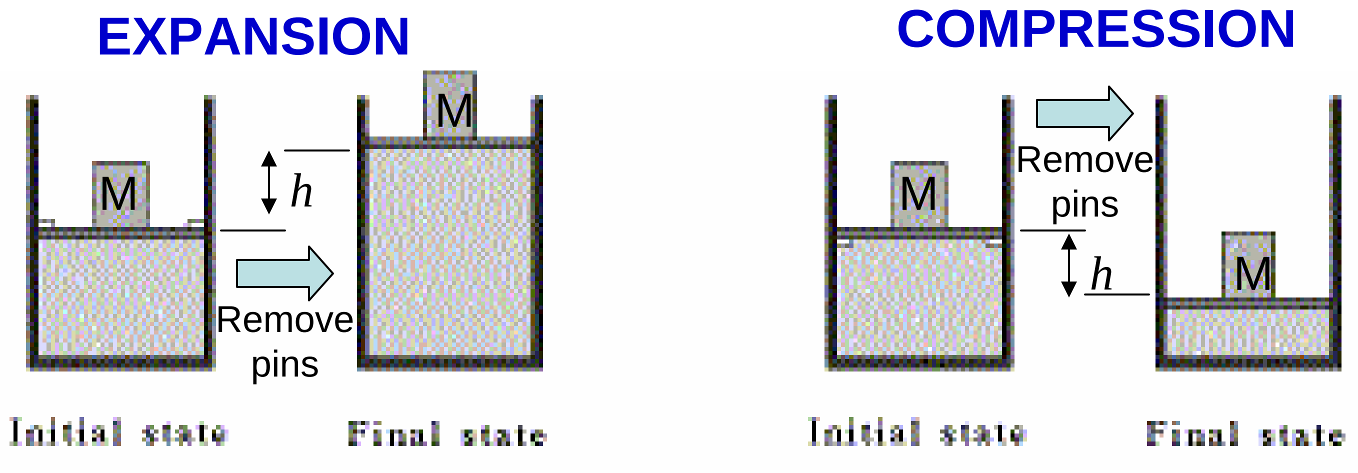
Heat, *q*: transfer of energy resulting from a temperature difference

Heat Sign convention:
Positive – heat is input to the system
Negative – heat is output from system

Work Sign convention:
Positive – work done on the system
Negative – work done by the system

Expansion and compression

Figure 19.1



Questions

1. What is system? Surroundings?
2. How does initial and final pressure correspond to P_{ext}?
3. What is sign of work for both cases?
4. Exactly how much work has been done?

What if P_{ext} is **not** constant?

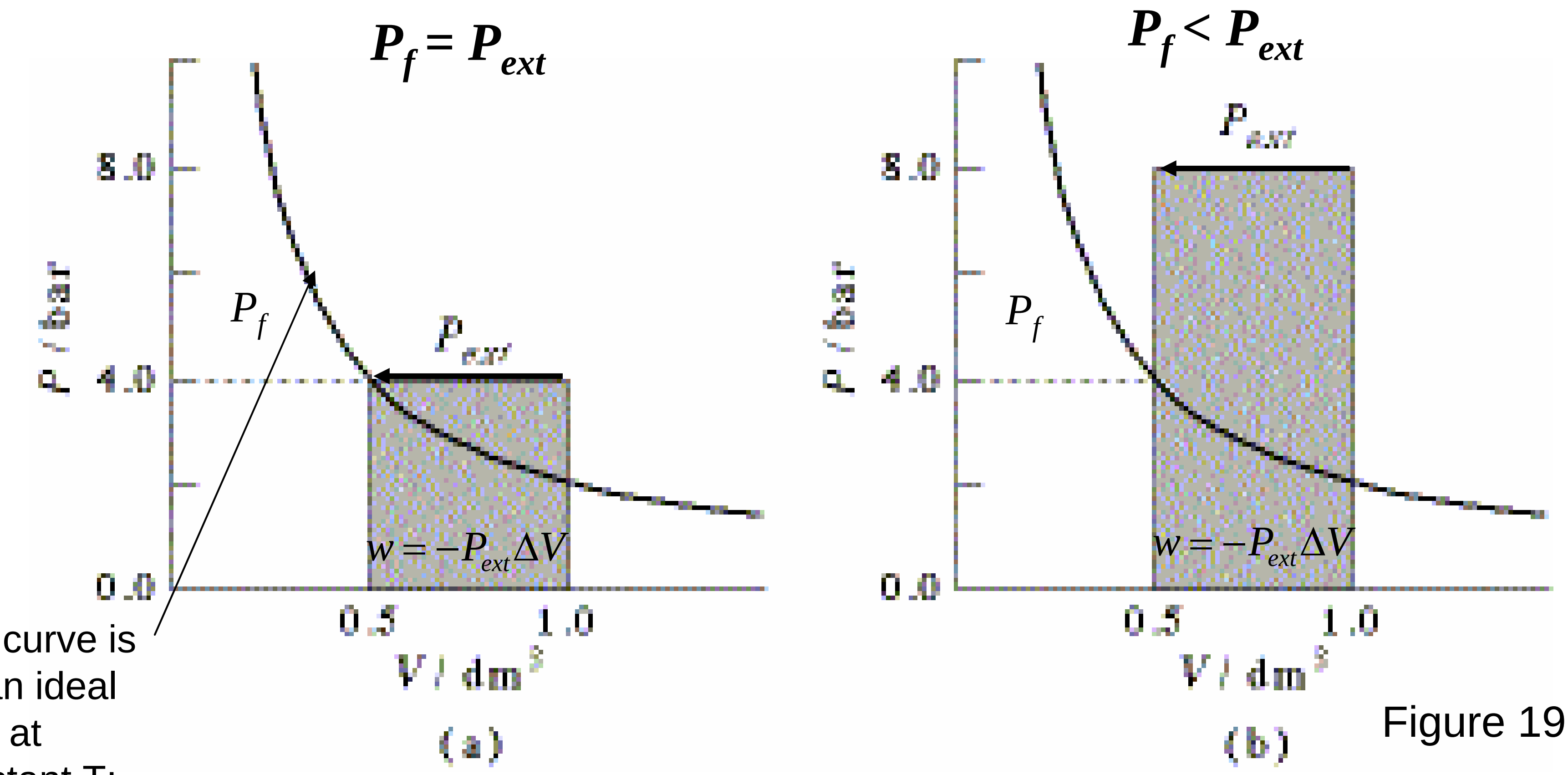
If P_{ext} is not constant during the expansion (or compression), the work is the integral over the path from V_i to V_f and we need to know how P_{ext} varies with V:

$$w = -\int_{V_i}^{V_f} P_{ext} dV$$

General expression. P_{ext} is a function of V.

Work is the area under P_{ext} vs V. . .

Consider an *isothermal compression at constant pressure*, P_{ext}



The curve is for an ideal gas, at constant T:

$$P = \frac{nRT}{V}$$

Figure 19.2

The work is equal to the shaded area: note how it depends on P_{ext}.

Reversible isothermal compression

Work depends on the path taken from V_1 to V_2. For compression, ***the absolute minimum work is done along the <u>reversible</u> path***.

Reversible path: At every infinitesimal step P_{ext} is made infinitesimally larger than P. At every step, P_{ext} is equal to the equilibrium gas pressure,. $P_{gas} = \frac{nRT}{V}$

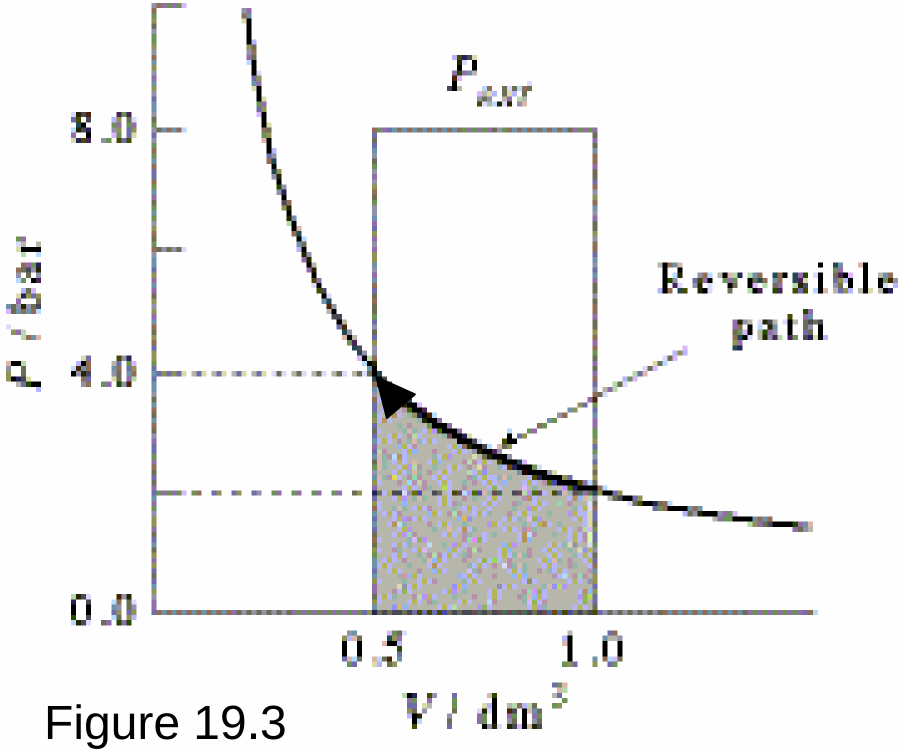


Figure 19.3

Is work positive or negative?

Reversible isothermal expression

Work depends on the path taken from V_1 to V_2. For expansion, ***the absolute maximum work is done on surroundings along the <u>reversible</u> path***.

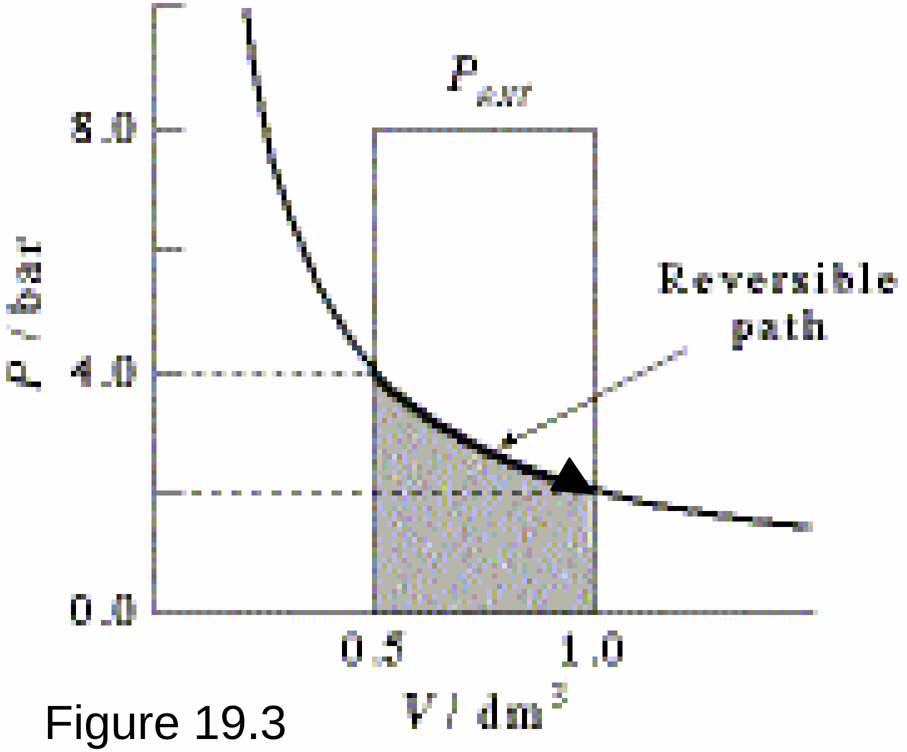


Figure 19.3

$$\boxed{w_{rev} = -nRT \ln \frac{V_2}{V_1}}$$

(Ideal gas)

Is work positive or negative?

State Functions vs Path Functions

As we've seen, the work depends on the *path* taken between initial and final state. Work and heat are ***path functions***.

State functions don't depend on the path taken but only upon the state of the system. Energy, U or H, are state functions.

Why is this important???

The differentials of *path* functions are inexact and *can't* be integrated normally!
The differentials of *state* functions are exact and *can* be integrated normally!

State functions	*Path functions*

The First Law

The First Law of Thermodynamics:

Energy is Conserved.

$$dU = \delta q + \delta w$$ Differential Form

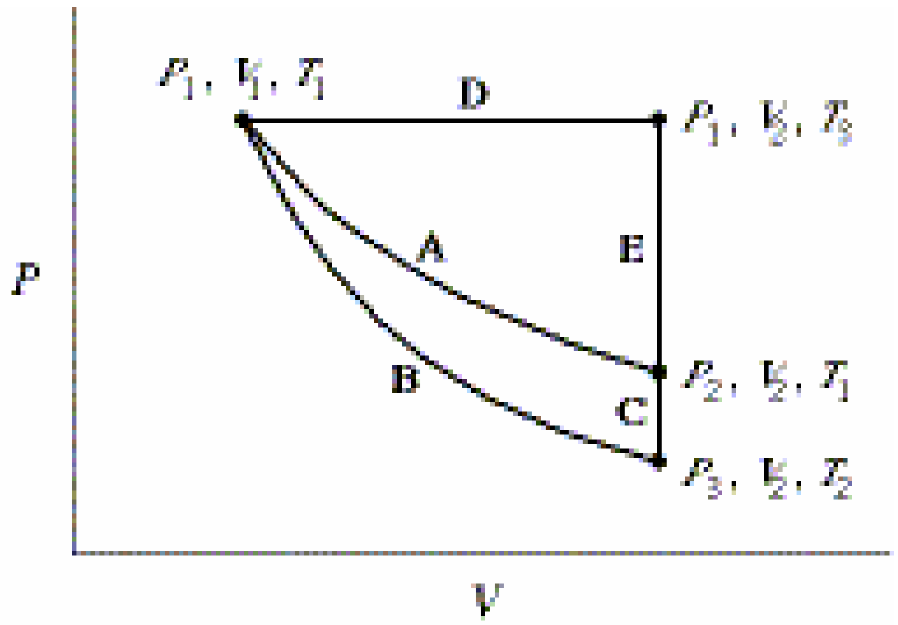
$$\Delta U = q + w$$ Integral Form

Even though δq and δw are *path* functions (inexact differentials), their sum is a *state* function (exact differential).

Let's explore state vs. path more deeply!

3 reversible paths to the same place…

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$



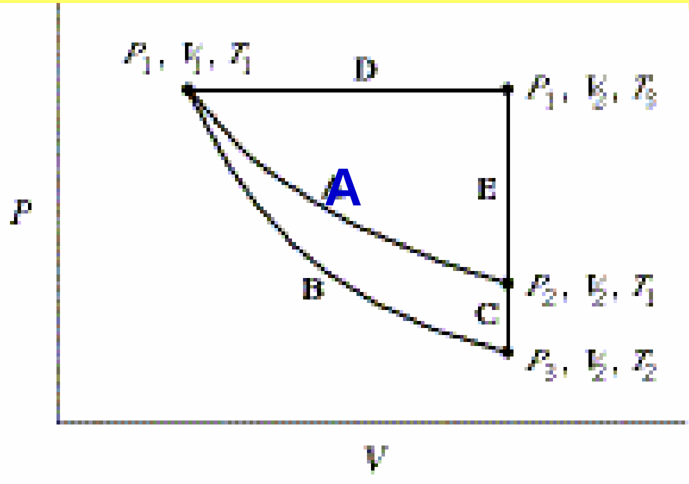
Path A: Reversible isothermal expansion

Path B+C: Reversible adiabatic expansion followed by heating at constant volume

Path D+E: Reversible constant-pressure expansion followed by cooling at constant volume

All three paths are reversible, but will they all involve the same work? ΔU?

Path A: Reversible Isothermal Expansion



$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$

The energy of an ideal gas depends only on the temperature… Recall U = (3/2)RT

$$dU_A =$$

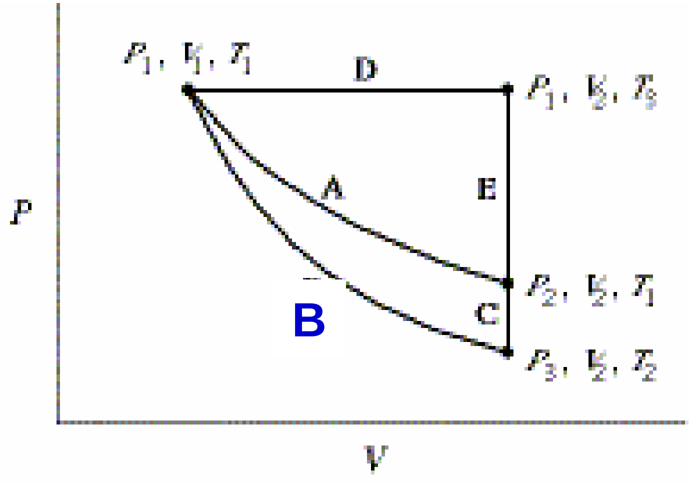
$$\xrightarrow{dU = \delta q + \delta w}$$

Since the process is reversible…

$$\delta w_{rev,A} = -P_{gas} dV = -\frac{nRT_1}{V} dV$$

Path B: Reversible Adiabatic Expansion

$$P_1, V_1, T_1 \rightarrow P_3, V_2, T_2$$



Adiabatic: No energy transferred as heat.
So … $q = 0$.

$$\boxed{dU = \delta w}$$

We can get w from dU…

Recall from BZ/PFIG slides:

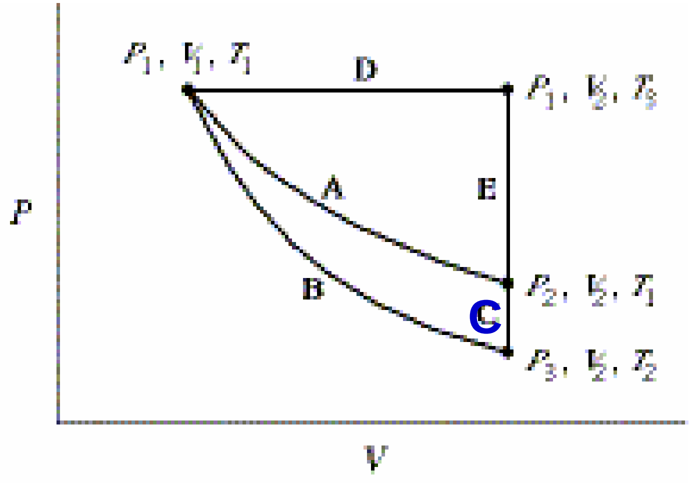
Since ideal gas U depends only on T:

or

Put it all together…

Path C: Heat at Constant V

$$P_3, V_2, T_2 \rightarrow P_2, V_2, T_1$$



Constant volume = NO PV Work!!

$$\Delta U_C = q_{rev,C} + w_{rev,C} = q_{rev,C}$$

We need to find $q_{rev,C}$ and ΔU_C…

$$q_{rev,C} = \Delta U_C = \int_{T_2}^{T_1} C_V(T)dT$$

From T_2 to T_1

Path B + Path C…

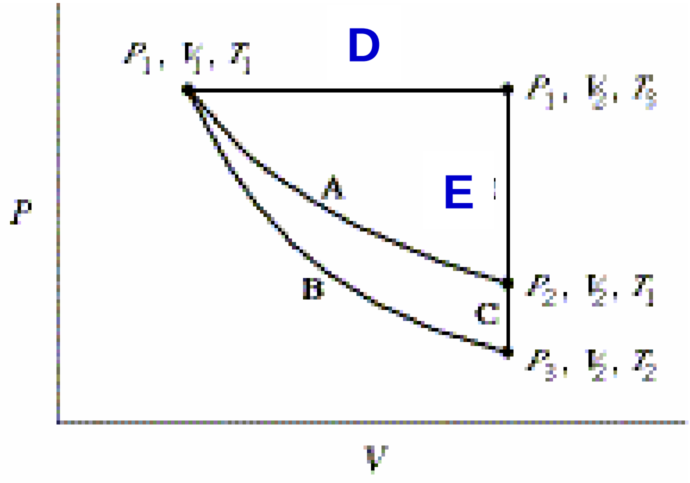
$$\Delta U_B + \Delta U_C = \int_{T_1}^{T_2} C_V(T)dT - \int_{T_1}^{T_2} C_V(T)dT = 0$$

$$w_{rev,B} + w_{rev,C} = \int_{T_1}^{T_2} C_V(T)dT$$

Paths D and E

Path D: Constant pressure expansion

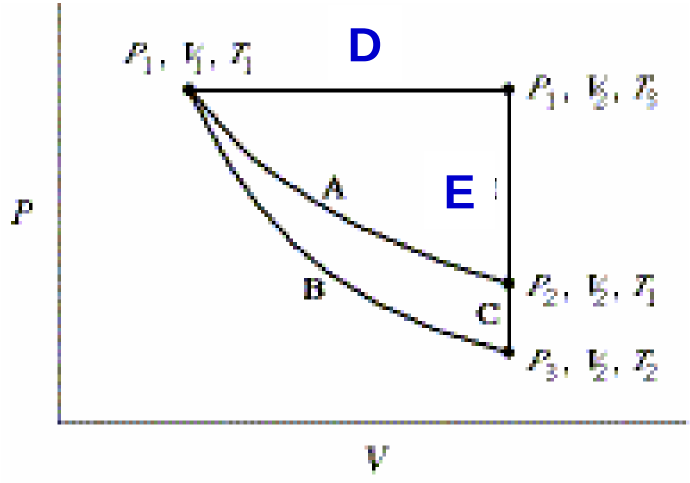
$$P_1, V_1, T_1 \rightarrow P_1, V_2, T_3$$



Path E: Cooling at constant V

$$P_1, V_{2,} T_3 \rightarrow P_2, V_2, T_1$$

Path D + E



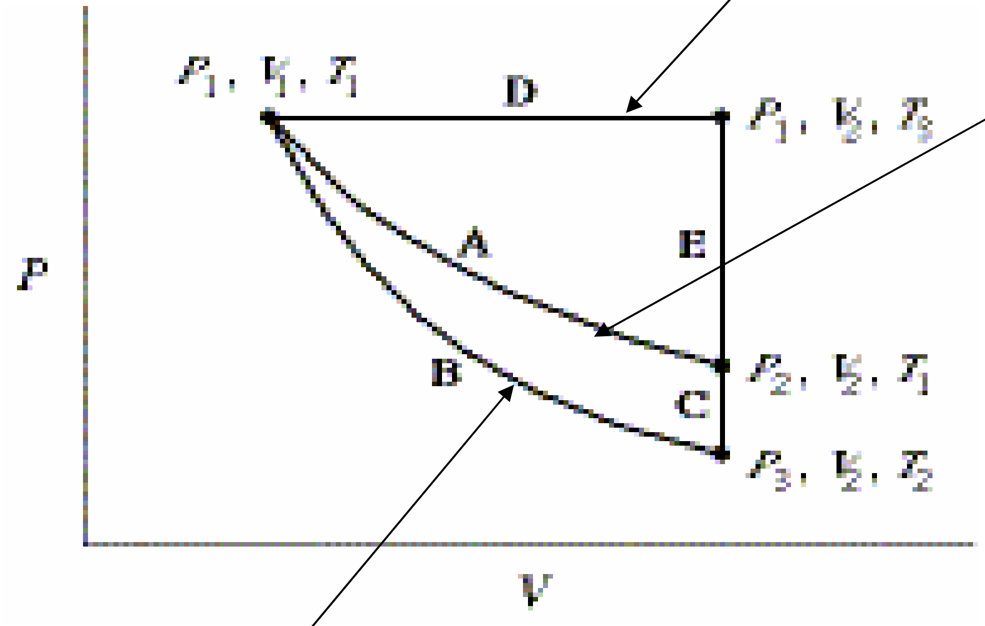
$$q_{rev,D+E} = q_{rev,D} + q_{rev,E} = P_1(V_2 - V_1)$$

$$w_{rev,D+E} = w_{rev,D} + w_{rev,E} = -P_1(V_2 - V_1)$$

$$\Delta U_{D+E} = q + w = 0$$

Summary… q, w, ΔU

$$w_{rev,D+E} = -P_1(V_2 - V_1) \qquad q_{rev,D+E} = P_1(V_2 - V_1) \qquad \Delta U_{rev,D+E} = 0$$



$$w_{rev,A} = -nRT_1 \ln\frac{V_2}{V_1}$$

$$q_{rev,A} = nRT_1 \ln\frac{V_2}{V_1}$$

$$\Delta U_A = 0$$

$$w_{rev,B+C} = \int_{T_1}^{T_2} C_V(T)\,dT \qquad q_{rev,B+C} = \int_{T_2}^{T_1} C_V(T)\,dT \qquad \Delta U_{rev,B+C} = 0$$

ΔU, state function, is same for all paths but q_{rev} and w_{rev}, path functions, differ based on path.