CHM 421/621
Statistical Mechanics

Lecture 16 Maximum Work Theorem

Introduction and Review

Lecture Plan

Review of Thermodynamics

Basic Formalism

Conditions of Equilibrium

Equilibrium Relations

Legendre Transformed Representations

Stability of Thermodynamic Systems

Equilibrium Relations

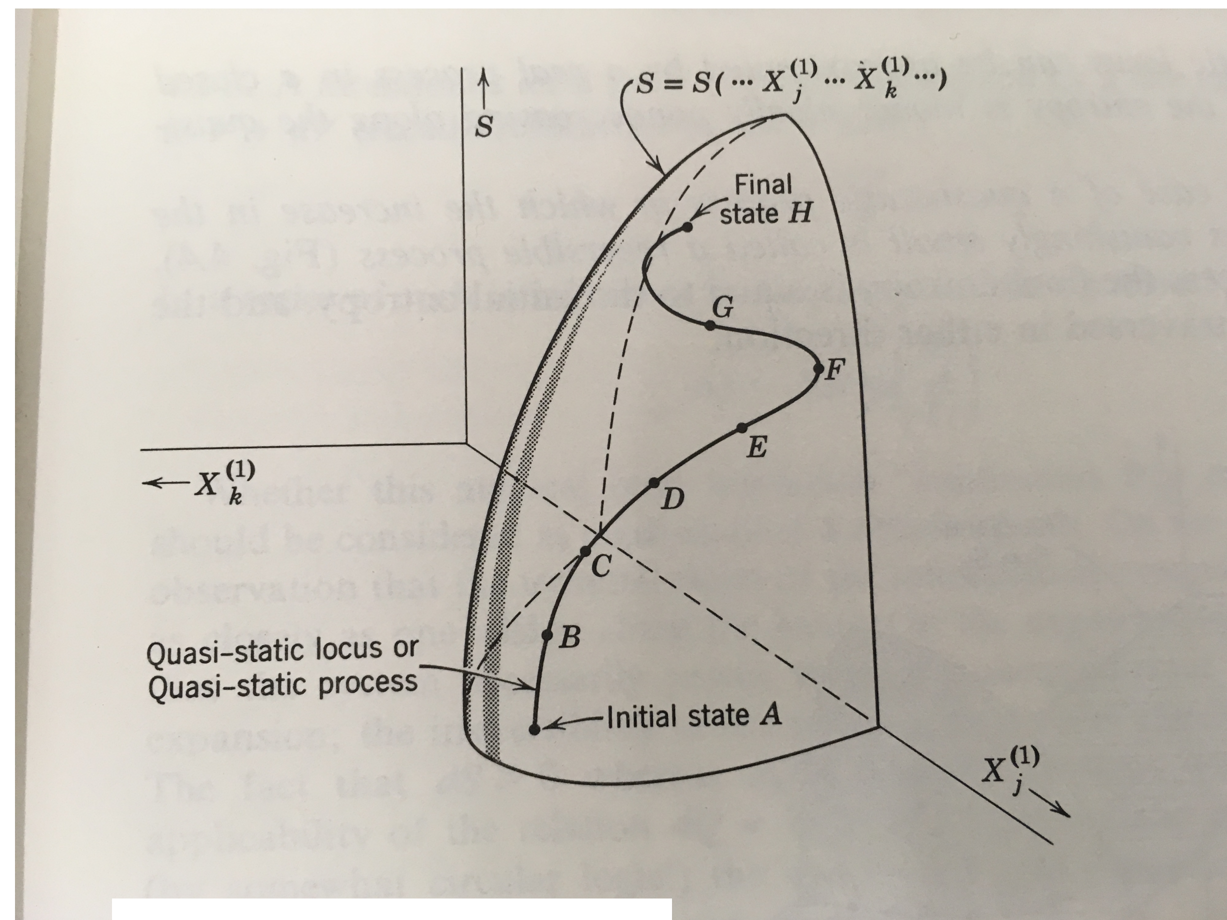
Quasi-static and reversible processes

A **quasi-static locus** or **process** is a curve drawn on the entropy surface in thermodynamic configuration space. (Goes only through equilibrium states)

Only for quasi-static processes can we write. $dQ = TdS$ and $dW = -PdV$

A real process can, at best, only closely mimic a quasi-static one since practically all systems always have some non-zero **relaxation time**.

Relaxation time - roughly, the time taken for a system to arrive at thermodynamic equilibrium following a change of state variables.



Composite system

Taken from Callen, Sec. 4-2.

Equilibrium Relations

Quasi-static and reversible processes

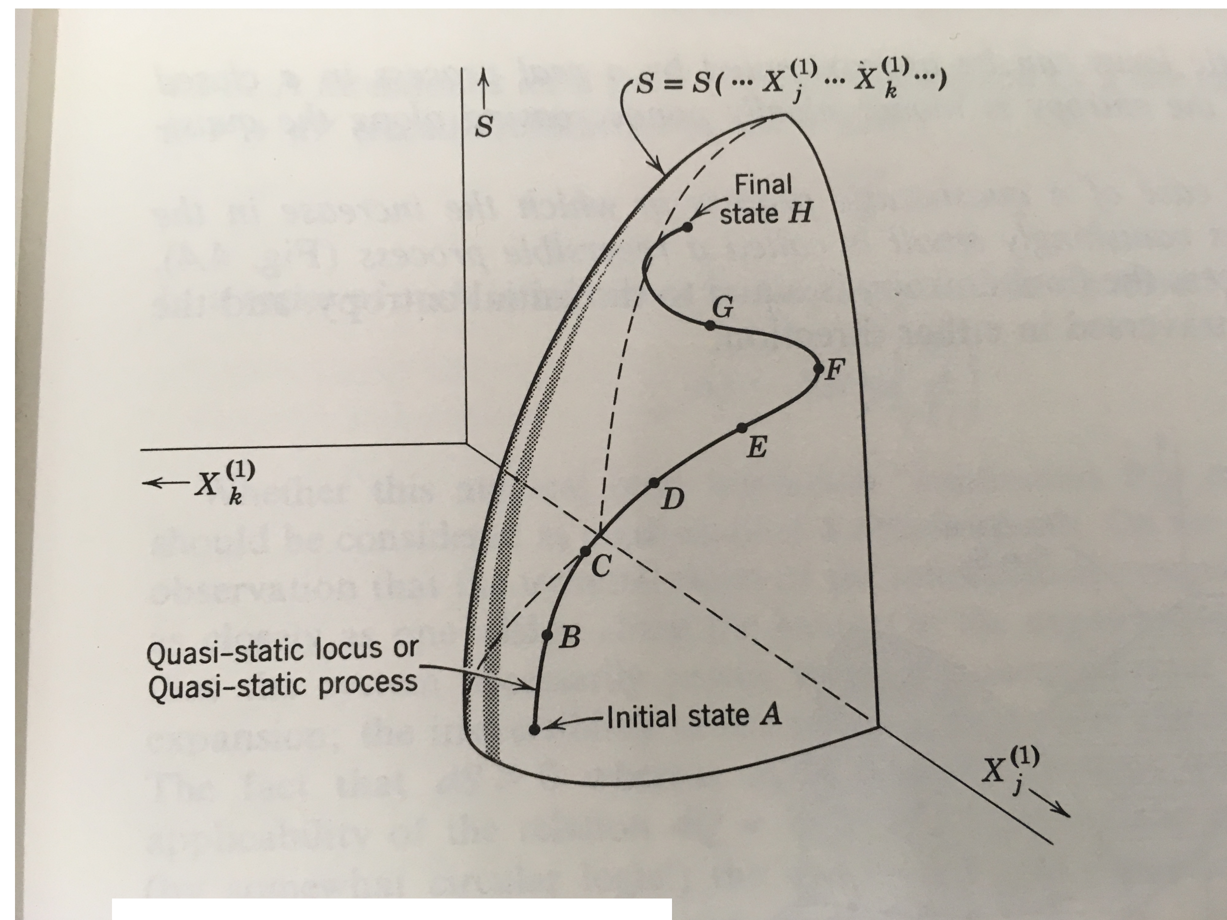
Suppose we start a closed system off at a state A on the curve.

The system is made to go to state B by relaxing a suitable internal constraint.

E.g. slightly relaxing a diathermal piston in a closed cylinder with two compartments of gas.

By postulate 2, state B will correspond to the maximum entropy among accessible configurations, including the one corresponding to state A.

i.e. $S_B > S_A$



Composite system

Taken from Callen, Sec. 4-2.

Equilibrium Relations

Quasi-static and reversible processes

Thus, the process A->B can be “realised”.

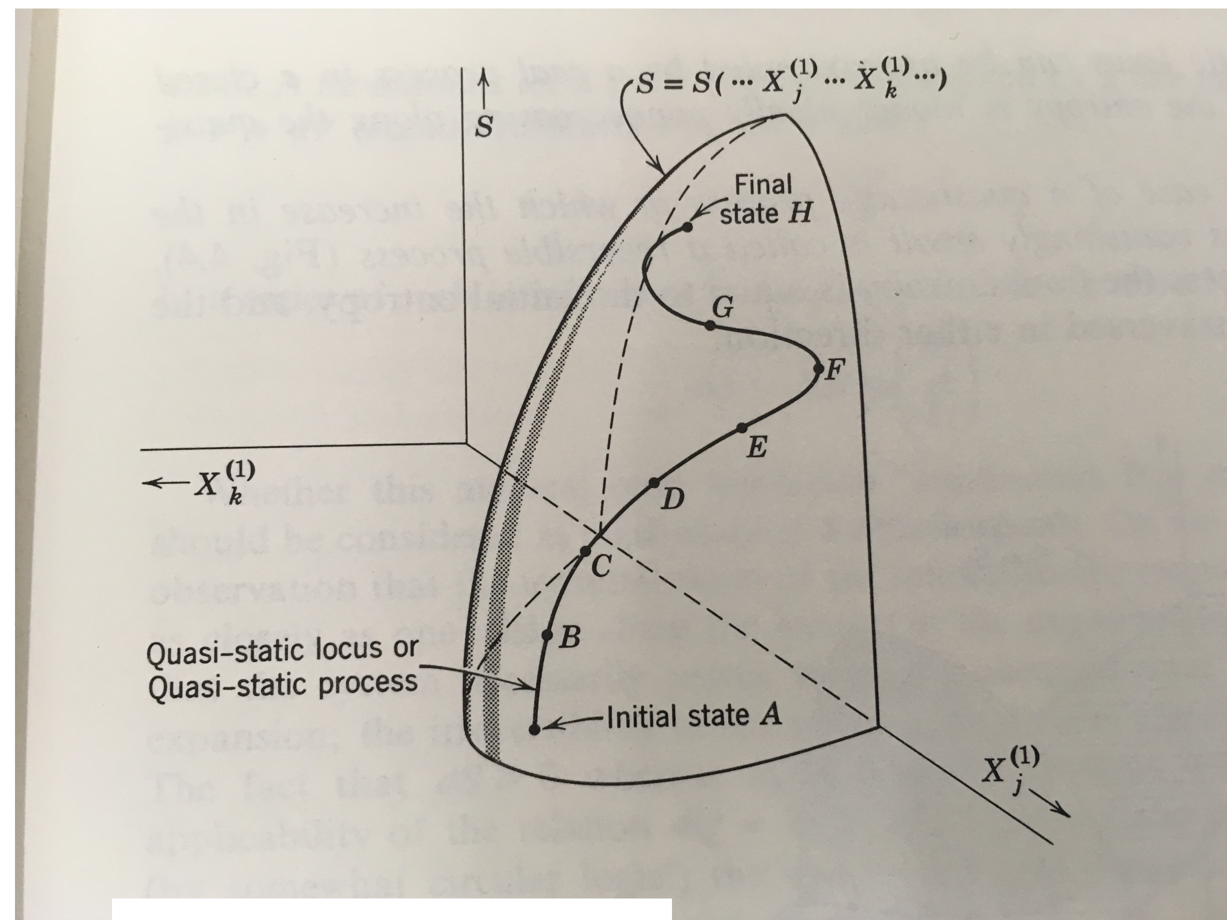
What about B->A?

No. Because entropy of the closed system cannot be lowered.

Thus, A->B is called an **irreversible** process.

The corresponding path can only be traversed one way.

Similarly, controlled release of the constraint can be used to travel along the locus from A to H. All the while, the entropy is strictly non-decreasing.



Composite system

Taken from Callen, Sec. 4-2.

Equilibrium Relations

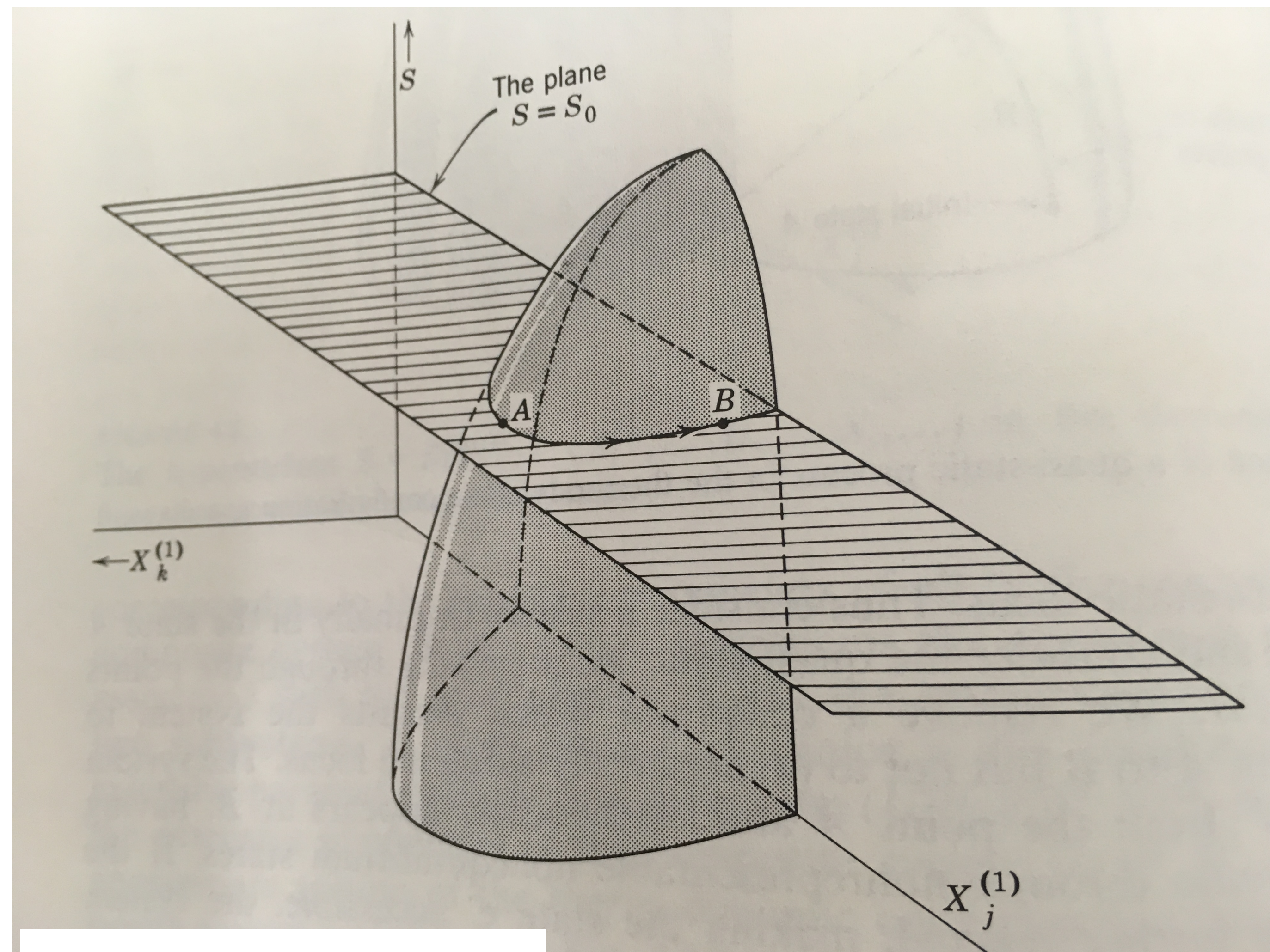
Quasi-static and reversible processes

What if, in a quasi-static process, the entropy does not change?

Such a process is called a **reversible** process.

E.g. quasi-static heat exchange between the two compartments at the same temperature.

What about quasi-static heat exchange between two compartments at different temperatures? (Spontaneity)



Reversible process

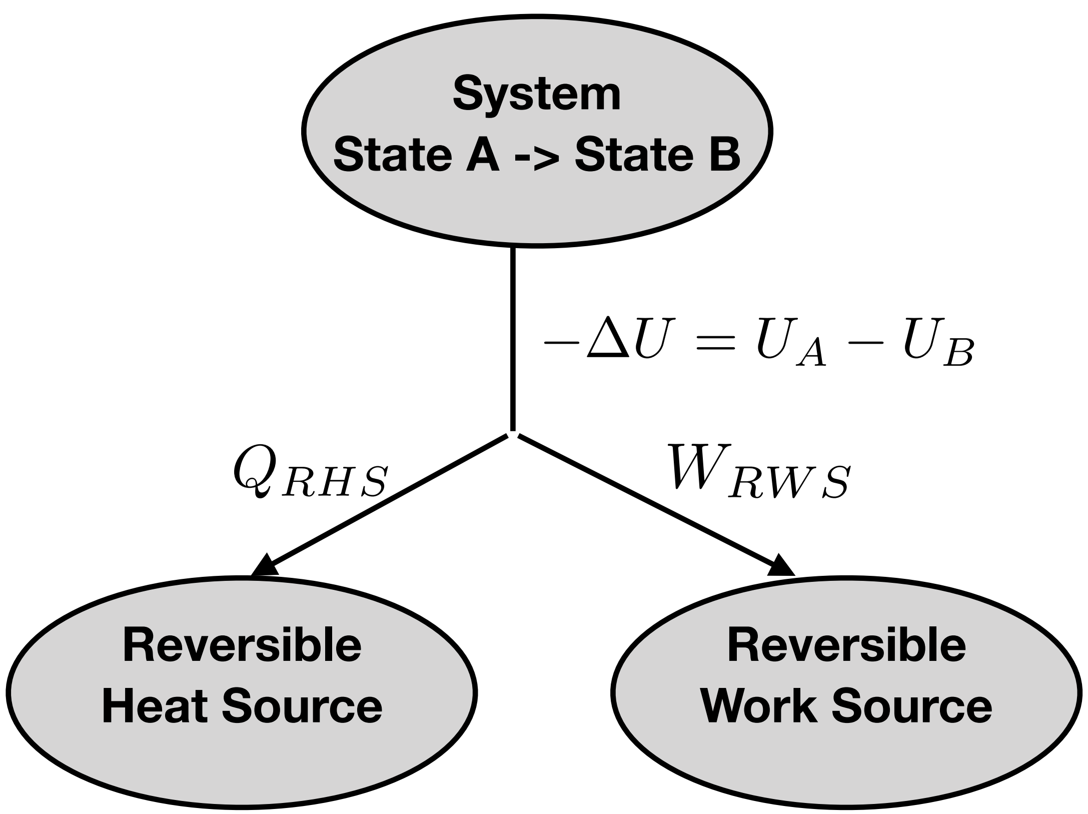
Taken from Callen, Sec. 4-2.

Equilibrium Relations

Maximum work theorem

Consider a system which is to undergo a process between two specified states. The system is in contact with a *reversible work source* and *reversible heat source*.

Then, for all processes connecting the initial to the final state of the primary system, the delivery of work is maximum (and the delivery of heat is minimum) for a reversible process.



Reversible Heat Source
Made of rigid, impermeable walls and v.v. low relaxation times. => All processes are essentially quasi-static.
dU = dQ = TdS = C(T) dT

Reversible Work Source
Made of adiabatic, impermeable walls and v.v. low relaxation times. => All processes are essentially quasi-static.
dU = dW

Equilibrium Relations

Maximum work theorem

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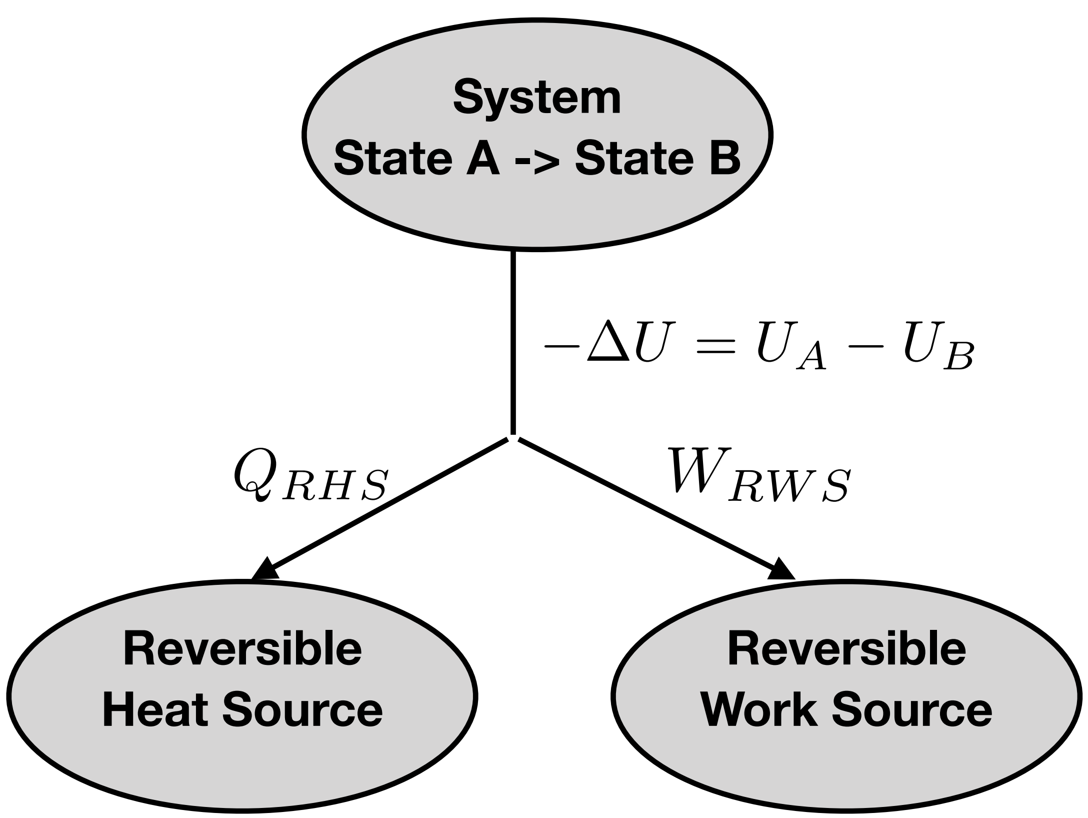
Then, for all processes connecting the initial to the final state of the primary system, the delivery of work is maximum (and the delivery of heat is minimum) for a reversible process.



$$\Delta U + W_{RWS} + Q_{RHS} = 0$$

$$\Delta S_{total} = \Delta S + \Delta S_{RHS}$$

Thus, maximum work => minimum heat flux => minimum entropy change for *RHS*

The extreme occurs for a reversible process $\Delta S_{total} = 0$

Equilibrium Relations

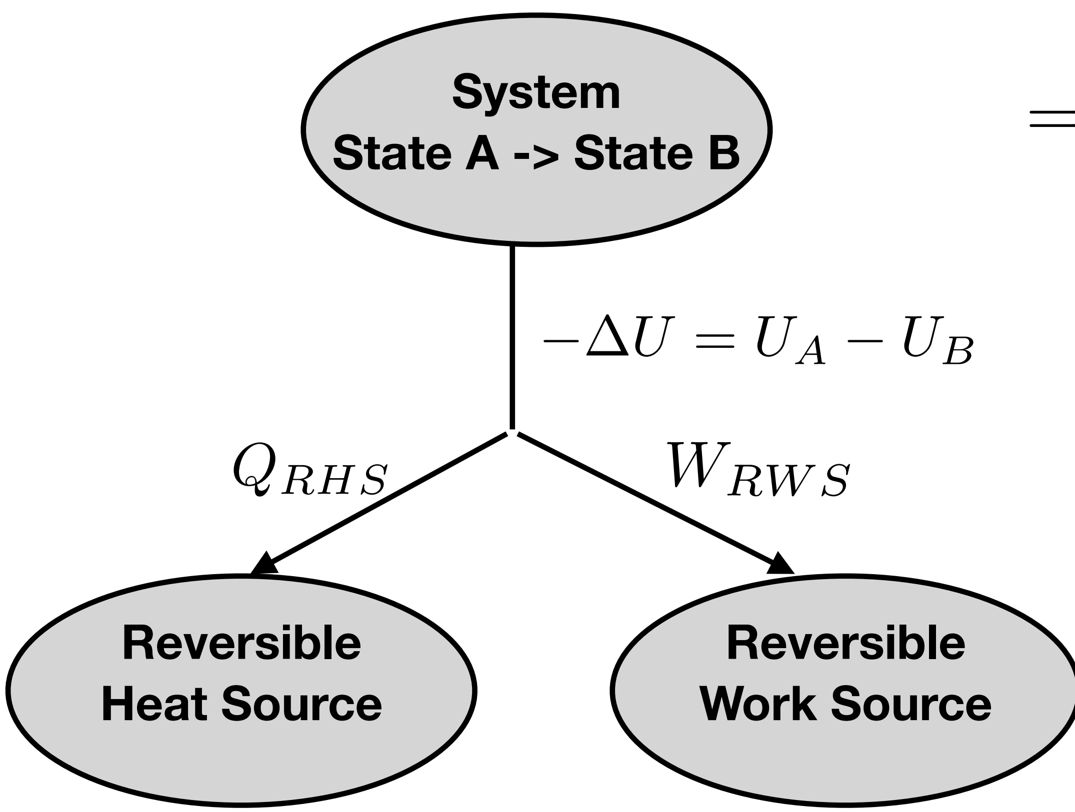
Maximum work theorem

For infinitesimally close terminal states

$$dU + \delta Q_{RHS} + \delta W_{RWS} = 0$$

$$dS_{tot} = dS + \frac{\delta Q_{RHS}}{T_{RHS}} \geq 0$$

$$\implies \delta W_{RWS} \leq T_{RHS} dS - dU$$



$$\delta W_{RWS}(\max) = \frac{T_{RHS}}{T}\delta Q - dU$$

$$= \left[1 - \frac{T_{RHS}}{T}\right](-\delta Q) + (-\delta W)$$

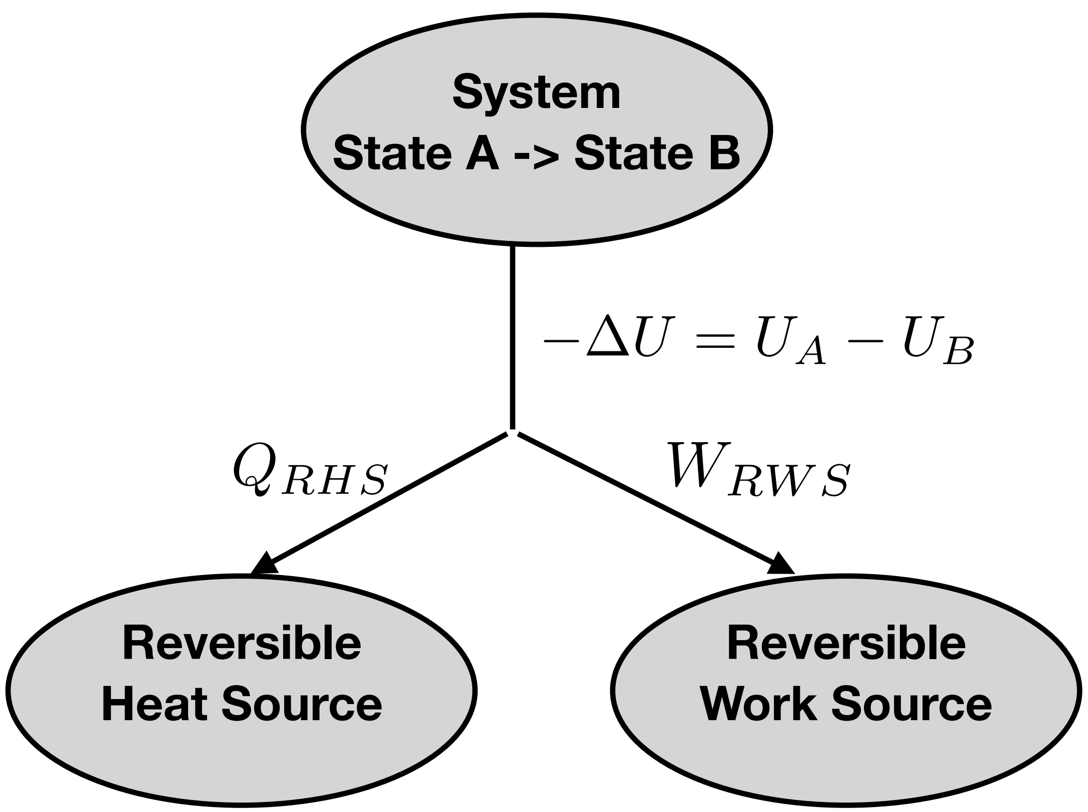
Fraction of heat to work

Equilibrium Relations

Maximum work theorem

Heat reservoirs - C is so large that T_{RHS} (=T_{res}) does not change.

$$\Delta U_{subsystem} + Q_{RHS} + W_{RWS} = 0$$



$$\Delta S_{total} = \Delta S_{subsystem} + \int \partial Q_{RHS}/T$$
$$= \Delta S_{subsystem} + Q_{res}/T_{res}$$

$$W_{RWS} = T_{res}\Delta S_{subsystem} - \Delta U_{subsystem}$$