Lecture 12: Thermodynamics

Work, Heat, Reversibility

How is PChem Thermo different than Gen Chem/Physics Thermo

- Rigorous derivation of formulas via calculus
- Some problems that can only be solved using calculus
- More challenging problems and different applications

Exam Advice: you need an equation sheet for this unit. There are a lot of equations to keep track of.

Definitions

Definitions

- System: what you are studying
- Surroundings: everything besides the system
- Universe: System + Surroundings
- Open System: Mass and energy can be transferred (soup in a pot)
- Closed System: Energy can be transferred, mass cannot (soup in covered pot)
- Isolated System: No mass and energy can be transferred (soup in thermos)
- Conservation of Energy: Energy cannot be created or destroyed
- State Function: Value that depends only on current state
- Path Function: Value where the path taken matters (work, heat)

Internal Energy, Work, Heat

Internal Energy: Total energy of a system

$$U = KE + PE$$

Work (w) and heat (q) are ways to add/remove energy, thus changing U:

Change in internal energy
$\Delta U = q + w$

Is internal energy related to temperature?

Temperature is a measure of **average kinetic energy**, not internal energy

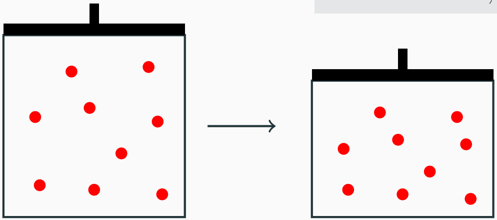
- A change in the amount of matter affects U, may or may not affects T
- A change in KE affects U and T
- A change in PE affects U but not T

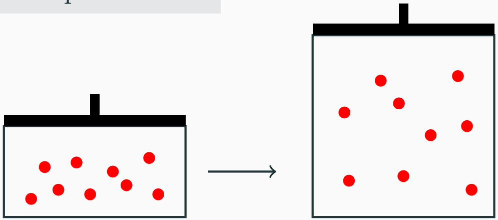
Isobaric Work

Isobaric: Constant Pressure

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

Indicated by a flexible container:
balloon, moveable piston





Compression

$\Delta V < 0 \qquad w > 0$

Work done **ON** the system

Expansion

$\Delta V > 0 \qquad w < 0$

Work done **BY** the system

Isochoric Work and Free Expansion

Isochoric: Constant Volume

$$\Delta V = 0 \implies w = 0$$

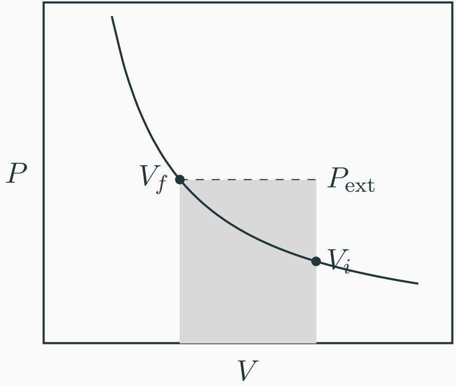
Indicated by a rigid container: rigid gas tank

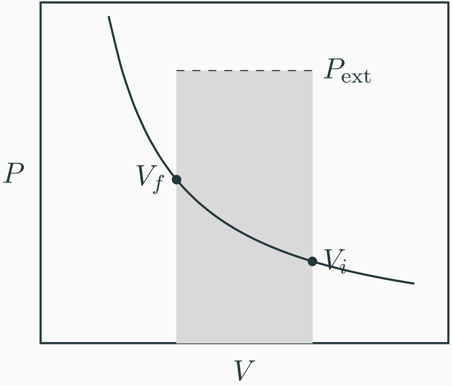
Free Expansion

$$P_{ext} = 0 \implies w = 0$$

No work done against a vacuum

Isothermal Work - Irreversible



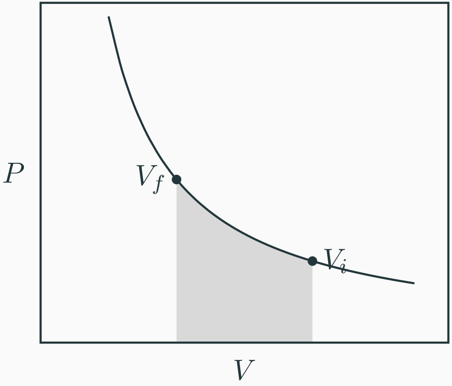


Irreversible Isothermal

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

Isothermal Work - Reversible

$$
\begin{aligned}
w &= -\int_{V_i}^{V_f} P_{ideal} dV \\
&= -\int_{V_i}^{V_f} \frac{nRT}{V} dV \\
&= -nRT \int_{V_i}^{V_f} \frac{dV}{V} \\
&= -nRT \ln \frac{V_f}{V_i}
\end{aligned}
$$



Reversible Isothermal

$$w = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

Comparing Magnitudes

$$|w_{irrev}| > |w_{rev}|$$

Heat

There could be no heat involved:

Adiabatic

$q = 0$

No heat exchange with surroundings.
Indicated by insulated container or very fast process

Heat energy could be used to increase kinetic energy and raise the T:

Change in T

$q = nC\Delta T = mc\Delta T$

Use equipartition to get heat capacity

All heat energy can be transferred to work, so there is no net T change:

Isothermal

$\Delta U = 0 \implies q = -w$

No change in temperature

Heat could break IMFs and cause a phase change:

Phase Change

$PE \uparrow, U \uparrow$

KE const, T const