P. Chem I Lecture 5 2/3/23

2^{nd} Law Thermodynamics

* from last class

isolated system : $q = \emptyset = w$

Definition : $dS > 0$ for a spontaneous process in an isolated system
$dS = 0$ for a reversible process in an isolated system

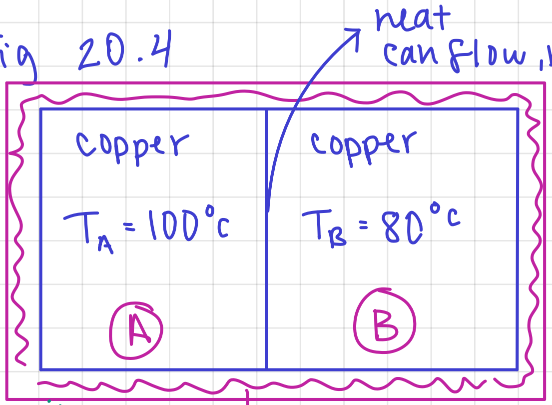
Section 20.9 (not responsible) :
$S = k_B \ln W$ is equivalent to : $dS = \frac{\delta q_{rev}}{T}$ and S = state function

Ideal gas : $dU = \delta q + \delta w$ 1^{st} law
$= \delta q_{rev} + \delta w_{rev}$ 1^{st} law : U is a state function

$\Rightarrow \delta q_{rev} = dU - \delta w_{rev} = \frac{3}{2} nR\,dT + P\,dV$

Fig 20.4

heat can flow, but irreversible



*not ideal gas rigid insulator

what is entropy change in first ms? (initially)

$q = \emptyset$
$w = \emptyset$

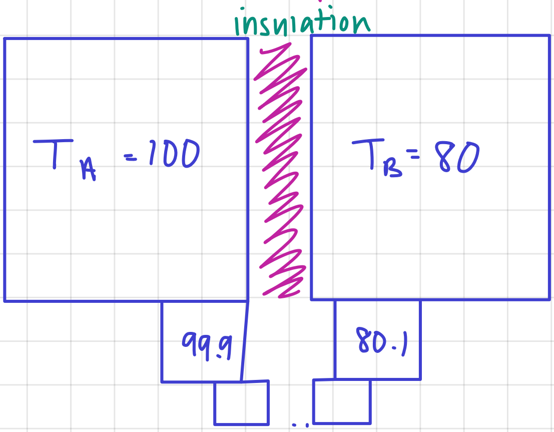
dS at first?

$dS = \frac{dq_{rev}}{T}$ * our system is not reversible change path so it becomes reversible

$dU = \emptyset$
$dw = \emptyset$

use reversible path

insulation



get heat to flow

diff in reversible and irreversible is surrounding

We are doing this because we need to be able to use $dS = \frac{dq_{rev}}{T}$

Allowed to change path for state functions b/c they're path independent, so we change surroundings to use $dS = \frac{dq_{rev}}{T}$

We will develop other formulas throughout course, but so far this is all we have

$dU = 0 = d(U_A + U_B)$

from $dS = \frac{\delta q_{rev}}{T}$

* combination of 1st & 2nd Law

$\Rightarrow \; dU_A = -dU_B$

$dU_A = \delta q_{rev} + \delta w_{rev} = \delta q_{rev} = T_A\, dS_A = dU_A$, where $\delta w_{rev} \rightarrow 0$

$T_B\, dS_B = dU_B$

$dS = d(S_A + S_B) = \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$

$dS = dU_B\left(-\frac{1}{T_A} + \frac{1}{T_B}\right) = dU_B\left(\frac{1}{T_B} - \frac{1}{T_A}\right) = dS > 0$

* since T_A is greater than T_B

math is simple, concept not so much

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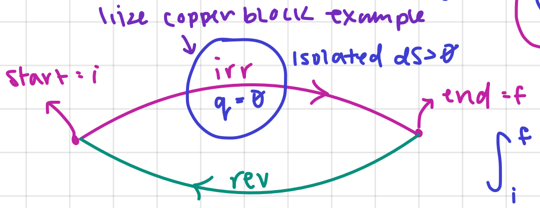
different 2nd Law formulation

Clausius inequality $\oint \frac{dq}{T} \leq 0$

cycle $\Rightarrow$ same initial & final state



$\int_i^f \frac{dq_{irrev}}{T} + \int_f^i \frac{dq_{rev}}{T} \leq 0$, where $\frac{dq_{rev}}{T} \rightarrow S$

$\int_i^f \frac{dq}{T} + \int_f^i dS \leq 0 \Rightarrow \int_i^f \frac{dq}{T} + S_i - S_f \leq 0$

$\int_i^f \frac{dq}{T} \leq \underbrace{S_f - S_i}_{\Delta S} \Rightarrow dS \geq \frac{\delta q}{T}$

$\Rightarrow dS \geq$ for isolated system

Next few lectures : Heat $\rightleftharpoons$ Work

chapter 20 notes on his website

As preparation for our discussion of cycles (and as a foreshadowing of the second law), we examine two types of processes that concern interactions between heat and work. The first of these represents the conversion of work into heat. The second, which is much more useful, concerns the conversion of heat into work. The question we will pose is how efficient can this conversion be in the two cases.

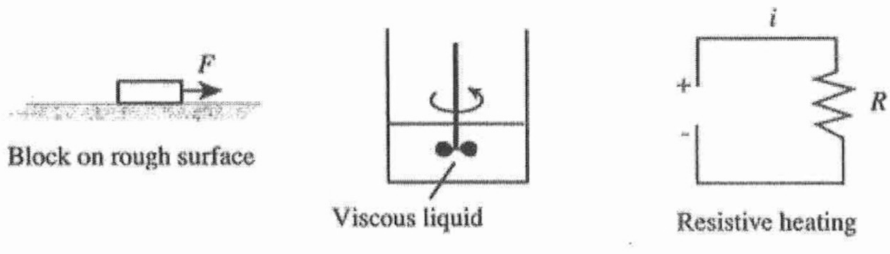


Figure 3.1: Examples of the conversion of work into heat