

\* Recap from last time

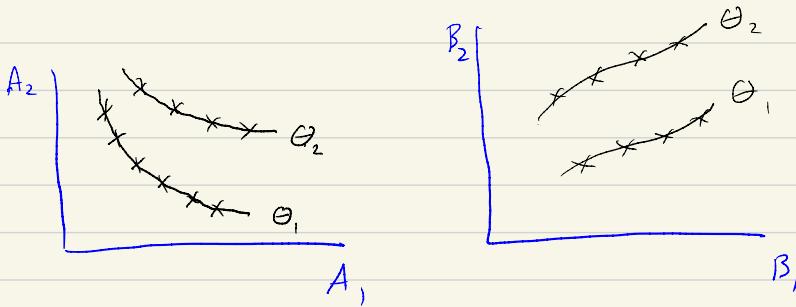
empirical observation

\* 0<sup>th</sup> Law: If 2 systems A & B are separately in equilibrium with C, then they are in equil. with each other. ( $\Rightarrow$  temperature)

\* Thermal equilibrium between systems is marked by all EOS functions having the same value  $\Theta$

$$\Theta_A(\{A_i\}) = \Theta_B(\{B_i\}) = \Theta_C(\{C_i\}) = \Theta$$

Leads to the notion of isotherms.

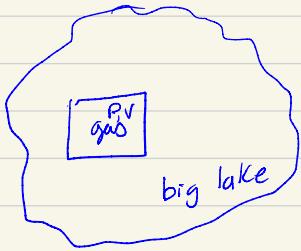


\* In general, an isotherm  $\Theta = \Theta_A(\{A_i\})$  specifies a surface of  $n-1$  dim. where  $n = \#$  of TD coords needed to specify the system.

\* Ideal Gas temperature Scale

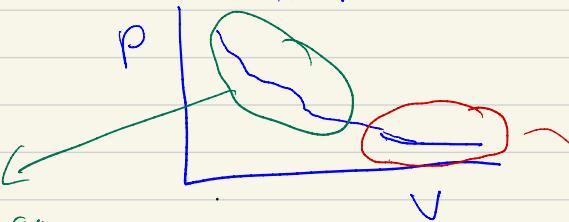
So far have not assigned a prescription to define different numerical  $\Theta$ -values (i.e., define a Temp. Scale)

## \* The Ideal Gas Temperature Scale



Put a piston of gas in a big lake  
(which we can assume stays @ constant  $\Theta$ )

↓  
fiddle around with  $P + V$  values  
to map out isotherm  $\Theta_{gas}(P, V) = \Theta$



here where gas  
is not dilute,  
the shaped isotherm  
will depend on  
details (e.g., Ar, H, O, etc.)

dilute limit  
 $P \rightarrow 0$   
 $V \rightarrow \infty$ ,

all gases  
have universal  
shape

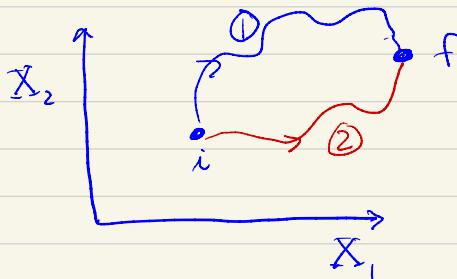
$$PV = \text{const}$$

Use this universal behavior of  
isotherms in dilute limit  
to define

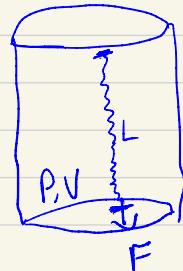
$$T(^\circ\text{K}) = 273.16 \lim_{V \rightarrow \infty} \frac{(PV)_{\text{sys}}}{(PV)_{\text{ice-water-vapor}}} \quad \begin{matrix} \text{ice-water-vapor} \\ \text{+ triple point} \\ \text{of water} \end{matrix}$$

\* Now that we've used the notion of equilibrium and its transitivity property to motivate temperature, let's similarly motivate the notion of Heat + construct the 1<sup>st</sup> Law of TD, which is basically energy conservation.

Empirical observation: The amount of work to change the state of an adiabatically isolated system depends only on initial + final states, and not on the method or path by which the work is done.



e.g.



\* Analogous to CM where the work in pushing a ball up a frictionless hill is independent of path (i.e., only depends on  $h_{\text{start}} + h_{\text{final}}$ )  $\Rightarrow \Delta W = U(h_2) - U(h_1)$



↑  
grav. PE function

Suggests an "Internal Energy"

State function  $E(\vec{x})$

( $\vec{x} = x_1, x_2, \dots = \text{all TD coords}$ )

∴  $\Delta W = E(\vec{x}_f) - E(\vec{x}_i)$

for isolated  
system w/ adiabatic  
walls

\* Now release the requirement of adiabatic walls. I.e., allow diathermic walls & repeat the experiment. Find

$$\Delta W \neq E(\vec{x}_f) - E(\vec{x}_i) \quad (\text{i.e., } \Delta W \text{ is path dependent})$$

$\therefore$  Since we believe conservation of energy is never violated, this suggests the introduction of a new form of energy Heat  $Q$  added to the system to balance the books.

$$\Rightarrow \boxed{\Delta Q = E(\vec{x}_f) - E(\vec{x}_i) - \Delta W}$$

Differential Form:  $dE(\vec{x}) = dW + dQ$

of 1st Law

depends      depends on  
on state      path

"exact" differential      "inexact" differential  
(hence the slash  $d$ )

Remarks: (1) In problem sets / group work, will touch a bit more on the difference of exact/inexact differentials

(2) Since  $W + Q$  not functions of state, it makes no sense to view  $\Delta W = W_f - W_i$  or  $\Delta Q = Q_f - Q_i$  as you can with energy.

(3) Beware of sign conventions. Some use  $dE = dQ - dW$  where  $dW = \text{work done by the system}$

\* Want to actually construct an explicit form for  $dE(\vec{x})$ .

To do this, it's useful to introduce another idealization

↓

Quasi-static processes: sufficiently slow so system always in equilibrium

Why do I want to consider quasi-static processes? Because otherwise I don't know where I am in my TD coordinate space  $\vec{x}$  (These are only defined in equilibrium!)

e.g. the mechanical example of trying to map out the PE function  $U(L)$  of a spring by doing work on it

$$\int dU = \int F dL$$



only works if I pull slowly so the work I do doesn't go into KE of the spring

\* Let's generalize the spring example to a general TD system.

\* Our TD coords  $\{\vec{x}\}$  can be split into

generalized forces  $\{\vec{J}\}$

generalized displacements  $\{\vec{x}\}$

$$\Rightarrow dW = \sum_{i=1}^n J_i dx_i$$

$n = \#$  of ways can do work on the system

X	J
1d wire	L
2d film	A
3d gas	V
Magnet	$\vec{M}$
electric field	$\vec{P}$

Note: the  $\sum J_i S$  is intensive

$\{\chi_i\} S$  is extensive

∴ The 1st Law becomes

$$dE = \sum_i J_i d\chi_i + dQ$$

Question: Is there some analog we can write for  $dQ$  as we did for  $dW$ ?

\* We can motivate a form for  $dQ$  via a bit of hand waving:

\* A system comprised of subsystems is in mechanical equilibrium when all the forces are balanced ( $J_i^{(1)} - J_i^{(2)}$ )

\* Likewise, we've shown that when 2 systems are in thermal equilibrium,  $T^1 = T^2$

∴ "guess" that  $\underline{dQ = T dS}$

This will lead us to the concept of entropy & the all important 2nd Law.

\* Before moving on to the 2<sup>nd</sup> Law and the new concept of Entropy, let's illustrate the 1<sup>st</sup> Law with a couple ideal gas examples:

Heat Capacities: example of a "response function"

T

heat capacity

perturb the system  
and look at how some TD  
property changes (linearly usually)

$$\textcircled{X} \quad \frac{dQ}{dt} = C \left|_{\substack{\text{path} \\ \text{perturbation}}} \right. \frac{dT}{dt}$$

response/change  
in the system

\* If looking at a gas ( $P, V$ ) are typical TD coords.

∴ Common to look at 2 paths in eq.  $\textcircled{X}$ :

$$\textcircled{1} \text{ Const. } V : C_V = \frac{dQ_V}{dT} = \frac{dE + PdV}{dT} \Big|_V$$

$$\textcircled{2} \text{ Const. } P : C_P = \frac{dQ_P}{dT} = \frac{dE + PdV}{dT} \Big|_P$$

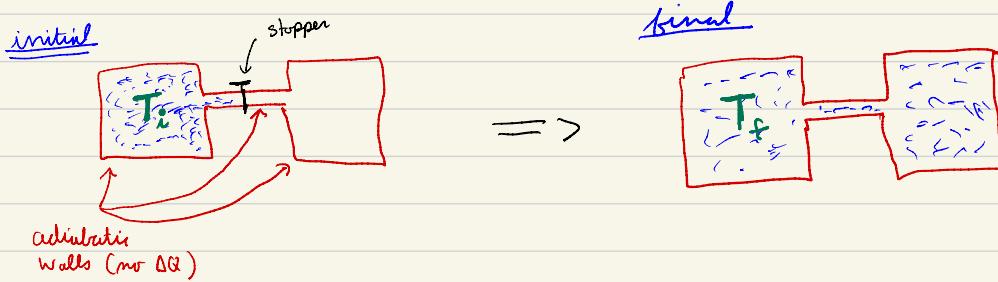
$$\therefore C_V = \frac{\partial E}{\partial T} \Big|_V$$

$$C_P = \frac{\partial E}{\partial T} \Big|_P + P \frac{\partial V}{\partial T} \Big|_P$$

general result.

Now let's apply  
to ideal gas ...

## Joule Free Expansion Experiment (ideal gas)



\* Joule finds  $T_i = T_f$

$$\begin{aligned} \Delta Q &= 0 \quad (\text{adiabatic walls}) \\ \Delta W &= 0 \end{aligned} \quad \left. \begin{array}{l} \Rightarrow \\ \text{Law} \end{array} \right\} \stackrel{\text{1st}}{\Rightarrow} \Delta E = E_f - E_i = 0$$

\* Now,  $E = E(P, V)$   $\stackrel{\substack{\text{ideal} \\ \text{gas}}}{=} [E(T, V) = E(T)]$   $\stackrel{\substack{\text{ideal} \\ \text{gas}}}{=}$

$PV \propto T$

↑

You will prove  
this "theoretically"  
in an exercise

(Since  $E(T_f, V_f) = E(T_i, V_i)$ )

$\left. \begin{array}{l} T_f = T_i \\ V_f \neq V_i \end{array} \right\} \therefore E = E(T)$

$$\Rightarrow \therefore C_p - C_v = \left. \frac{\partial E}{\partial T} \right|_P - \left. \frac{\partial E}{\partial T} \right|_V + P \left. \frac{\partial V}{\partial T} \right|_P \quad PV = \text{const. } T$$

$$\therefore \left. \frac{\partial V}{\partial T} \right|_P = \frac{\text{const}}{P}$$

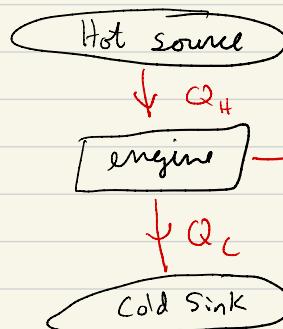
$\therefore C_p - C_v = \text{const}$

Moreover, this should be extensive  $\Rightarrow$

$$C_p - C_v = N \left( K_B \right)^{\text{universal constant (Boltzmann)}}$$

## The 2<sup>nd</sup> Law

- \* The historical (purely phenomenological) development of TD in the 19<sup>th</sup> century was largely driven by practical concerns (e.g., making efficient steam engines) yet will eventually lead to the abstract & deep concept of entropy.
- \* Let's follow the historical development and consider an idealized heat engine.

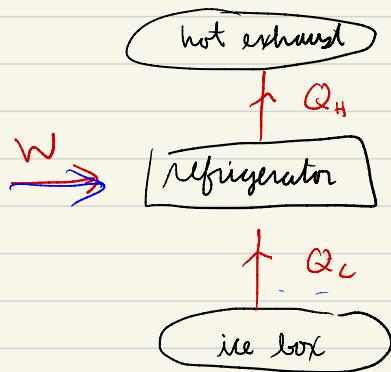


$$Q_H = Q_C + W \quad (\text{energy conservation})$$

Engine Efficiency:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq 1$$

- \* And an idealized refrigerator.



Refrigerator performance:

$$/\quad W = \frac{Q_C}{\dot{W}} = \frac{Q_C}{Q_H - Q_C}$$

(note no restriction for  
 $\dot{W} < 1$ )

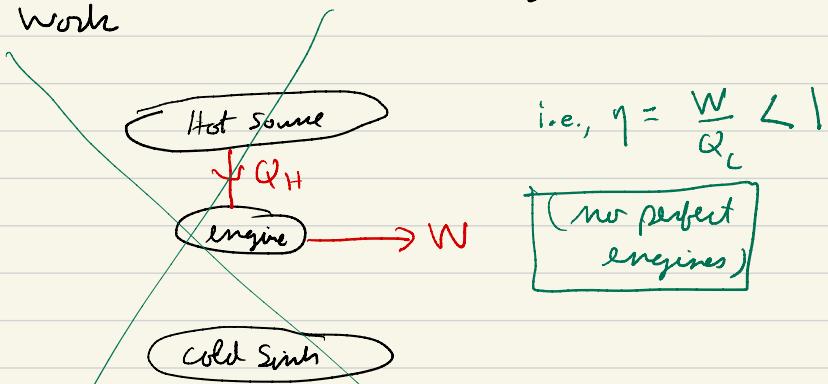
$$W + Q_C = Q_H \quad (\text{energy cons.})$$

\* 1<sup>st</sup> Law rules out "perpetual motion machines of the 1<sup>st</sup> kind"  
(e.g., engines that do work without consuming any energy)

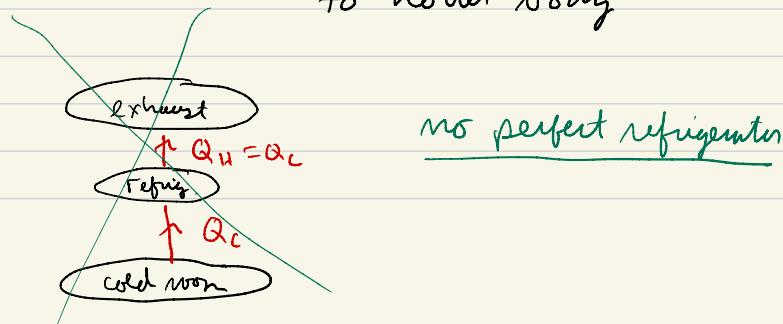
\* But it says nothing about a machine that (say) produces work by converting water to ice  
(i.e., converting heat entirely into work)

\* To rule out such a "perpetual motion machine of the 2<sup>nd</sup> kind," we turn now to 2 different statements of the empirical 2<sup>nd</sup> Law of TD:

Kelvin (K): No process possible whose sole result is the complete conversion of heat into work



Clausius (C): No process is possible where sole result is the transfer of heat from a colder to hotter body

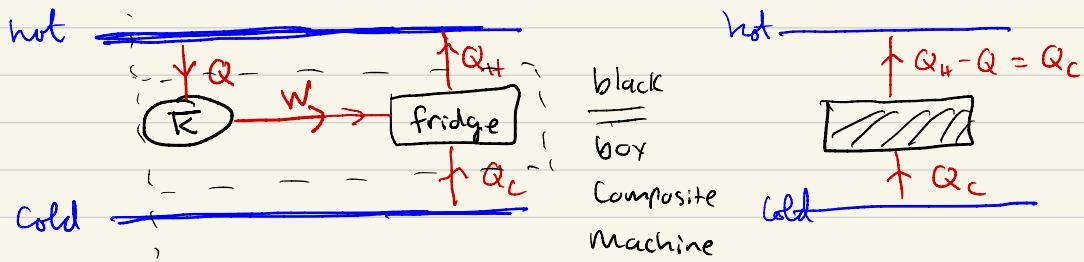


## Equivalence of K + C statements of 2<sup>nd</sup> Law.

We will do this by proving that a violation of the Clausius Statement implies a violation of the Kelvin Statement, and visa versa.

$$\text{i.e., } \bar{C} \Leftrightarrow \bar{K}$$

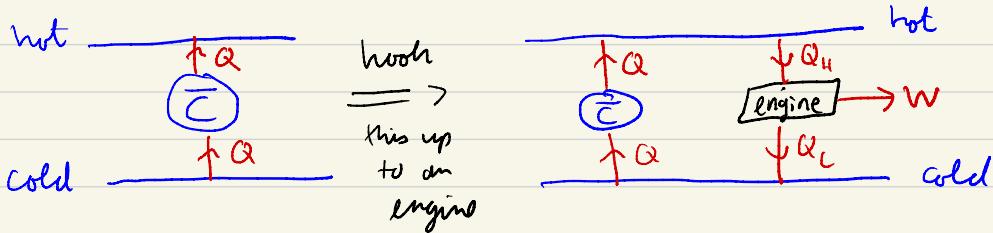
- a) Assume a perfect engine  $\bar{K}$  + use its work to run a refrigerator



$\therefore$  Violates Clausius

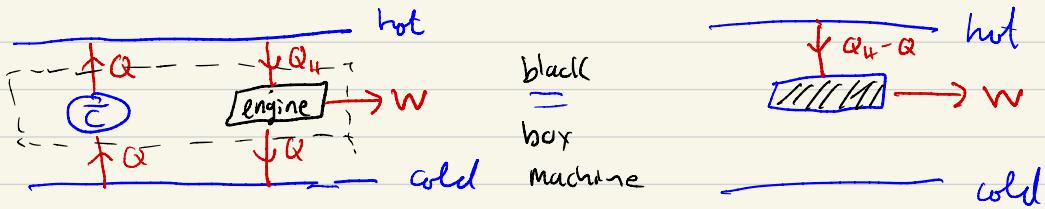
$$\bar{K} \Rightarrow \bar{C}$$

b) Assume a refrigerator  $\bar{C}$  that violates Clausius



\* Now run the engine enough cycles so that

$$Q_c = Q$$



Violates  
Kelvin

$$\bar{C} \Rightarrow \bar{K}$$

$\therefore K + C$  statements are equivalent

\* Carnot Engine  $\equiv$  any engine w/ the following properties

- 1) Reversible (Can go forward/backward by reversing inputs/outputs, analogy of frictionless motion.)
- 2) Operates in a cycle (Start/end points the same)
- 3) Operates between 2 temps  $T_H + T_C$

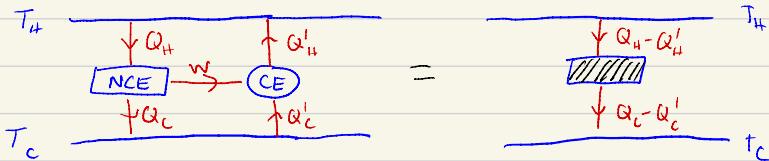
Carnot's theorem: No engine operating between  $T_H + T_C$  is more efficient than a Carnot engine

Proof: Use a non-Carnot engine to run a CE backward (reversible!)



\* By Clausius, must have  $Q_H - Q'_H \geq 0$

$$\therefore Q_H \geq Q'_H \Rightarrow \frac{Q_H}{W} \geq \frac{Q'_H}{W}$$



\* By Clausius, must have  $Q_H - Q'_H \geq 0$

$$\therefore Q_H \geq Q'_H \Rightarrow \frac{Q_H}{W} \geq \frac{Q'_H}{W}$$

$$\Rightarrow \frac{W}{Q_H} \leq \frac{W}{Q'_H}$$

$$\Rightarrow \eta_{NCE} \leq \eta_{CE} \quad \checkmark.$$

Corollary: all CE's have the same universal efficiency  $\eta_{CE} = \eta_{CE}(T_H, T_C)$

proof: Repeat the above argument with  $CE_1 + CE_2$

$$\Rightarrow \eta_{CE_1} \leq \eta_{CE_2}$$



Now repeat by interchanging  $CE_1 + CE_2$

$$\Rightarrow \eta_{CE_2} \leq \eta_{CE_1}$$

$$\therefore \eta_{CE_1} = \eta_{CE_2}$$

## Absolute TD Temp. Scale via Carnot Engines

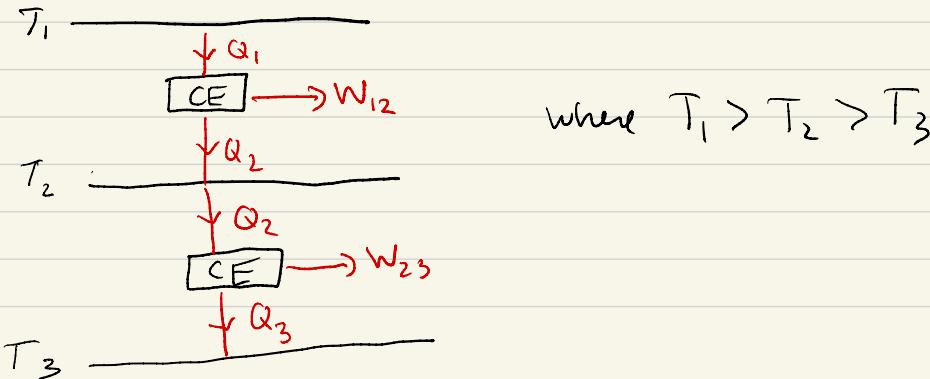
\* CE's are universal (don't depend on substance etc.)  
 ↗ only depends on  $T_A + T_C$  ! )

\* Suggests a theoretically pleasing way to define a Temperature Scale (compare vs. ideal gas T-scale, where we had to make use of specific properties of actual gases.)

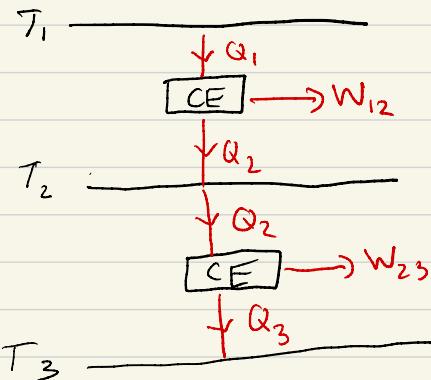
Side Remark: Kardas shows how using  $PV = n k_B T$ , you can at least "in principle" construct a CE using ideal gas as working substance.

More generally, (don't show this here), any substance characterized by 2 TD words works too "in principle" (modulo the fact that the reversible/quasi-static assumption is never 100% realized)

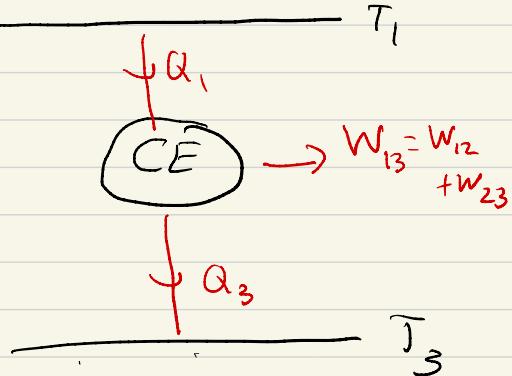
### Consider 2 CE's in Series



\* Consider 2 CE's in Series



block  
= box



$$\text{CE}_1: Q_2 = Q_1 - W_{12} = Q_1 [1 - \eta(T_1, T_2)] \quad (1)$$

$$\text{CE}_2: Q_3 = Q_2 - W_{23} = Q_2 [1 - \eta(T_2, T_3)] \quad (2)$$

$$Q_3 \stackrel{(1)}{=} Q_1 [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)] \quad (3)$$

$$\text{CE}_{\text{comp}}: Q_3 = Q_1 - W_{13} = Q_1 [1 - \eta(T_1, T_3)] \quad (4)$$

\* From (3) + (4) =>

$$1 - \eta(T_1, T_3) = [1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)]$$

Puts strong constraint on the form of  $\eta(T_H, T_C)$

\* Note that

$$1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1}$$

Moreover,  $1 - \eta(T_1, T_2) = \frac{1 - \eta(T_1, T_3)}{1 - \eta(T_2, T_3)}$  } the  $T_3$ -dep must cancel in the ratio!

$$\Rightarrow 1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} = \frac{f(T_2)}{f(T_1)}$$

\* Convention to pick  $f(T) = T$

$$\Rightarrow \boxed{1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} = \frac{T_2}{T_1}} \quad \textcircled{X}$$

∴  $\textcircled{X}$  defines temperature up to a constant of proportionality.

\* As with ideal gas T-Scale, we pick  $T_{\text{ref}} = 273.16^\circ\text{K}$

Remark: In HW #1, you will use the ideal gas  $PV = nK_B T$  to explicitly calculate  $W$  +  $Q$  for Carnot cycle, recovering  $\textcircled{X}$ .

$= T_{\text{H}_2\text{o triple Point}}$