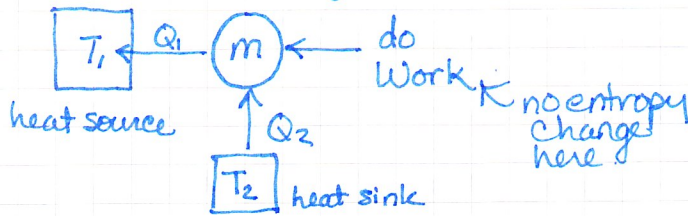# Lecture 9   Refrigeration Cycles

(A) If you run a heat engine in reverse, you get a refrigeration process

1ST Law: $Q_2 + W = Q_1$

2ND Law: $\Delta S_{TOT} \geq 0$ $\Delta S = \dfrac{+Q_1}{T_1} - \dfrac{Q_2}{T_2} \geq 0$ $\dfrac{Q_1}{T_1} > \dfrac{Q_2}{T_2}$ $\dfrac{Q_1}{Q_2} \geq \dfrac{T_1}{T_2}$

(B) What is the performance of a refrigerator?

Coefficient of performance $\eta_{Ref} = \dfrac{Q_2}{W} = \dfrac{Q_2}{Q_1 - Q_2}$

$\dfrac{1}{\eta_{Ref}} = \dfrac{Q_1 - Q_2}{Q_2} = \dfrac{Q_1}{Q_2} - 1$ $\dfrac{1}{\eta_{Ref}} \geq \dfrac{T_1}{T_2} - 1 = \dfrac{T_1 - T_2}{T_2}$

A reversible cycle takes an infinite amount of time

example: $\eta_{Ref}^{max} = \dfrac{T_2}{T_1 - T_2} = \dfrac{273K}{27K} = 10$

In an ideal refrigerator, for every KW of electricity you get 6 KW of heat.

(C) Inverse of this cycle is a heat pump.
It heats the reservoir

$\eta_{HP} = \dfrac{Q}{W} = \dfrac{Q_1}{Q_1 - Q_2}$ $\dfrac{1}{\eta_{HP}} = \dfrac{Q_1 - Q_2}{Q_1} = 1 - \dfrac{Q_2}{Q_1} \geq 1 - \dfrac{T_2}{T_1}$

Same cycle - want to get as much Q for input W

$\eta_{HP} \leq \dfrac{T_1}{T_1 - T_2}$ example: OAT = 273K   maximum coef $\eta_{HP}^{max} = \dfrac{298}{25} \sim 12$
                                            indoor = 298K   of hp performance

consider mechanism M as a frictionless piston
$\eta^{max} = \dfrac{T_1 - T_2}{T_1} =$

for a perfect gas temperature scale $PV = R\Theta$ got from triple point

So that is how to prove that the temperature scale
is the absolute temperature scale

Phase Equilibria

Mixing of entropies

$$S = S_1 + S_2 = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

now, not applying statistical mechanics — only classical thermodynamics.
System is isolated in some thermal insulating container

$$E_1 + E_2 = E_0 \qquad V_1 + V_2 = V_0 \qquad N_1 + N_2 = N_0$$

Note: N is NOT avagadro's number

$\therefore S(E_1, V_1, N_1) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$ can be expressed in terms of system parameters

$$\frac{\partial S}{\partial E_1} = 0 \Rightarrow \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} = 0 \Rightarrow \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2}\frac{\partial E_2}{\partial E_1} = 0 \Rightarrow \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0$$

$$\therefore \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \Rightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

$$\frac{\partial S}{\partial V_1} = 0 \Rightarrow \frac{\partial S}{\partial V_1} + \frac{\partial S_2}{\partial V_2} = 0 \Rightarrow \text{use } \frac{\partial S_2}{\partial V_2} = \frac{\partial S_2}{\partial V_1}\frac{\partial V_2}{\partial V_1} = -\frac{\partial S_2}{\partial V_2} \qquad \frac{\partial V_2}{\partial V_1} = -1$$

we had $\left(\frac{\partial S}{\partial V}\right)_{E,V} = \frac{P}{T}$ this equation leads to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$\therefore$ the pressures $P_1 = P_2$ of the two phases must be the same.

Find maximum entropy

$$\frac{\partial S}{\partial N_1} = 0 \qquad \frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_2}\frac{\partial N_2}{\partial N_1}^{-1} = 0 \Rightarrow \frac{\partial S}{\partial N_1} = \frac{\partial S}{\partial N_2} \quad \text{keep energy + volume fixed}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{\mu}{T} \quad \text{chemical potential}$$

$$-\frac{\mu_1}{T_1} = -\frac{\mu_2}{T_2} \quad \therefore \mu_1 = \mu_2 \quad \text{new condition of equilibrium}$$

$$\boxed{\mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}} \quad \text{chemical potential}$$

T, P = constant look at system another way G is a minimum

$$G = G_1 + G_2 \qquad \text{Gibb's free energy of the two phases.}$$

Fundamental Thermodynamic Energy

previously: $dE = TdS - PdV$ when $N = $ constant

$$S \equiv S(E, V, N)$$

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\boxed{TdS = dE + PdV - \mu dN}$$

Gibb's Free Energy

$$G \equiv G(P, T, N)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial N}\right)_{P,T} dN$$

$$\boxed{dG = VdP - SdT + \mu dN}$$

$$\left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu$$

$$G = \mu N + \chi(P, T)$$

$\hookleftarrow$ integration constant

$$\lim_{N \to 0} G = 0 = \chi(P, T) \quad \therefore \quad \chi(P, T) = 0$$

$$G = \mu N$$

$$\mu = \frac{G}{N} = g \qquad \text{Gibb's free energy per unit molecule}$$

$$\mu = g(T, P) \qquad \text{recall } T, P \text{ are intensive variables} \\ \text{not extensive variables}$$

$$G = N_1 g_1 + N_2 g_2$$

at equilibrium G is a minimum

$$dG = 0 \quad \text{@ minimum} \\ \text{@ equilibrium}$$

$$dG = g_1(T, P)\, dN_1 + g_2(T, P)\, dN_2 = 0$$

$$N_1 + N_2 = N_0 \quad \rightarrow \quad dN_1 = -dN_2$$

$$dG = \left[g_1(T,P) - g_2(T,P) \right] dN_1 = 0$$

since this has to be zero for any dN_1

$$g_1(T, P) = g_2(T, P)$$

$$G = N_1 g_1 + N_2 g_2$$

If $g_1 < g_2$ then all particles will go to $N_1 = N$ $N_2 = 0$
all particles go into phase 1

If $g_2 < g_1$ then to minimize g everything should
go into phase 2, $N_1 = 0$ $N_2 = N$

The important point is that they will always coexist.

$g_1 > g_2$

P

← phase equilibrium condition
$g_1(T, P) = g_2(T, P)$

$g_2 < g_1$

T