

Problem #1

Carnot cycle improve  $\eta = 1 - \frac{T_c}{T_H}$

\* make sure you can do all the calculations on your own.

$$|W| = nRT_H \ln\left(\frac{V_B}{V_A}\right) + nRT_C \ln\left(\frac{V_D}{V_C}\right)$$

$$|q_{H+}| = nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$q = 0 \Rightarrow \Delta U = \delta W$$

$$\frac{3}{2} nR \Delta T = C_V dT \quad \rightarrow -P \Delta V = -\frac{nRT}{V} dV$$

$$\text{so, } \frac{3R}{2T} dT = -\frac{R}{V} dV$$

$$\int_{T_1}^{T_2} \frac{3R}{2T} dT = -\int_{V_1}^{V_2} \frac{R}{V} dV \Rightarrow \frac{3}{2} \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)$$

$$\text{so, } \ln \frac{V_A}{V_B} = \ln \frac{V_D}{V_C} \Rightarrow \ln V_A - \ln V_B = \ln V_D - \ln V_C$$

$$\text{so, } \ln\left(\frac{V_A}{V_B}\right) = -\ln\left(\frac{V_D}{V_C}\right)$$

$$\text{so, } \frac{|W|}{|q_{H+}|} = \eta = 1 + \frac{T_C}{T_H} \cdot \frac{\ln\left(\frac{V_D}{V_C}\right)}{\ln\left(\frac{V_B}{V_A}\right)} = 1 - \frac{T_C}{T_H}$$

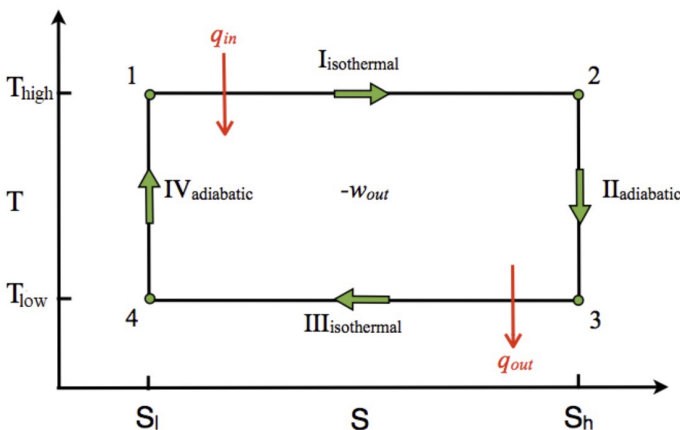
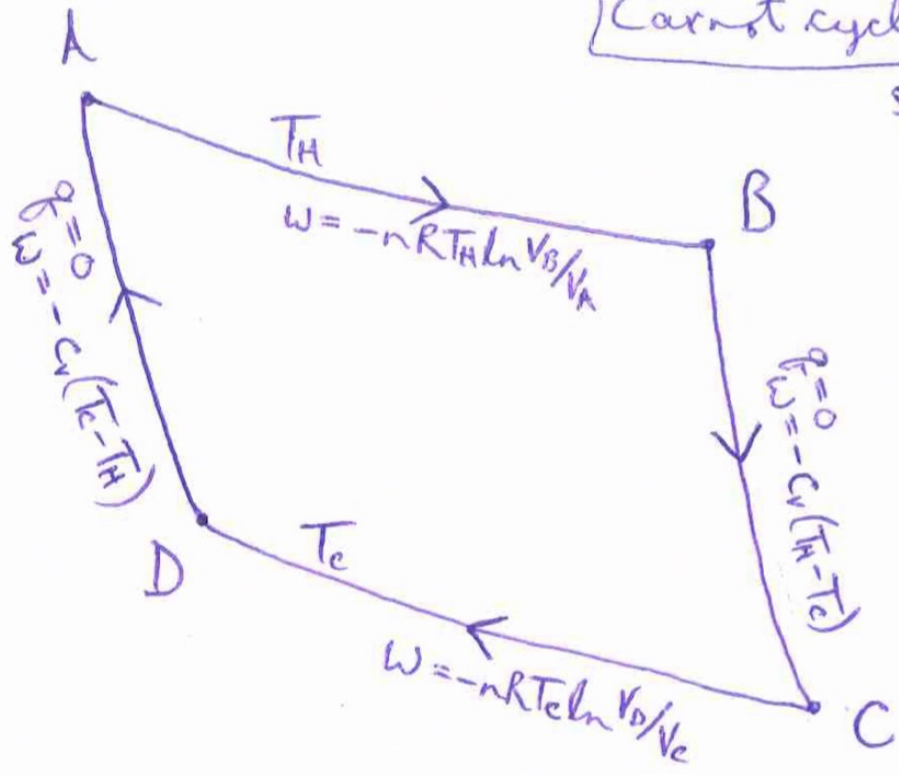


Figure 3: A T-S diagram of the Carnot Cycle. (CC BY 4.0; XiSen Hou via Hope College)

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Carnot cycle

system is an ideal gas



- D → A adiabatic compression
  - A → B isothermal expansion
  - B → C adiabatic expansion
  - C → D isothermal compression
- } all reversible

V

$$\eta = \text{thermal efficiency} = \frac{|W|}{|q_H|} = 1 - \frac{|q_C|}{|q_H|}$$

$$\ln\left(\frac{V_A}{V_D}\right) = \ln\left(\frac{V_B}{V_C}\right)$$

For the Carnot cycle:

28a

$$|w| = nRT_H \ln V_B/V_A + nRT_C \ln V_D/V_C$$

$$|q_H| = nRT_H \ln V_B/V_A = \text{energy supplied as heat from the hot reservoir}$$

Need to work out the relationship between  $T$  and  $V$  for a reversible adiabatic process (section 19-5).

$$q=0 \Rightarrow dU = \delta w \quad \rightarrow \quad -PdV = -\frac{nRT}{V} dV$$

$$\frac{3}{2} nR dT = C_V(T) dT$$

$\rightarrow$  monoatomic ideal gas

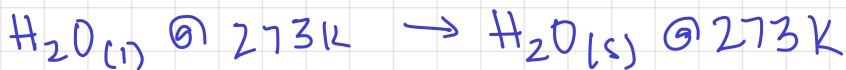
$$\Rightarrow \int_{T_1}^{T_2} \frac{3R}{2T} dT = - \int_{V_1}^{V_2} \frac{R}{V} dV \quad \text{divide both sides by } nT$$
$$\Rightarrow \int_{T_1}^{T_2} \frac{3R}{2T} dT = - \int_{V_1}^{V_2} \frac{R}{V} dV \Rightarrow \frac{3}{2} \ln T_2/T_1 = \ln V_1/V_2$$

$$\text{Therefore } \ln V_A/V_D = \ln V_B/V_C \Rightarrow \ln V_A - \ln V_D = \ln V_B - \ln V_C$$
$$\Rightarrow -\ln V_D/V_C = \ln V_B/V_A$$

$$\text{Thus } \frac{|w|}{|q_H|} = \eta = 1 + \frac{T_C}{T_H} \frac{\ln V_D/V_C}{\ln V_B/V_A} = 1 - T_C/T_H .$$

## Problem #2

$$T_{\text{interior}} = 0^\circ\text{C} = 273\text{K}$$



$$T_{\text{room}} = 300\text{K}$$

$$W = 0.50\text{hp}$$

$$q_c = \frac{T_c}{T_H - T_c} |w|$$

\* fridge is perfectly isolated  
; works at  $\eta_{\text{max}}$ .

\* work has to be in J  
use conversion  
1hp = 746 J/s

need: mass produced in one day (Time)

answer should be  
in J/s

$$\frac{\text{J/s}}{\text{kJ/mol}} q_c \underbrace{(24 \times 3600\text{s})}_{\text{time}} \underbrace{(18.02\text{g/mol})}_{\text{mol}} = \text{Answer in Kg}$$

\* use this to  
get mass

$$\text{where } \Delta H_{\text{fusion}} = 6.008\text{ kJ/mol}$$

convert to J

$$\Delta T = 0$$

↑

Find  $\Delta U, \Delta H, \Delta S, \Delta A, \Delta G$  for isothermal expansion of ideal gas

$$V_i = 1\text{L} \quad V_f = 100\text{L} \quad P = 1\text{atm} \quad T = 25^\circ\text{C} = 298\text{K}$$

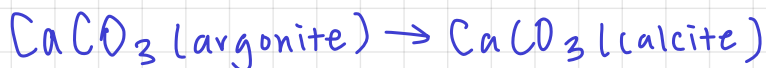
$$\Delta U = \cancel{\int nRdT} \quad \Delta H = \cancel{\int nRdT} + \cancel{\Delta PV}^{\text{const}}$$

$$\Delta T = \Delta U = \Delta H = 0 \quad \text{so, } \Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

$$\frac{PV}{RT} = \frac{nRT}{RT} \Rightarrow n = \frac{PV}{RT}$$

$$A = \cancel{H} - TS \quad \text{and} \quad G = \cancel{H} - TS$$

## Problem #4



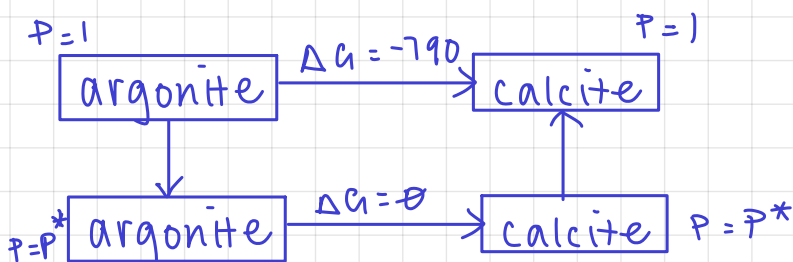
At what  $P$  is aragonite stable if  $T = 25^\circ\text{C}$

$$\Delta G = -790\text{ J/mol}$$

$$\Delta V = 2.75\text{ mL/mol}$$

$$T = 25^\circ\text{C}$$

\* assume  $\Delta V$  is ind.  
of Pressure  
(Notation  $^\circ$  means at 1 atm)



from notes:

$$dG = VdP - SdT \Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow \Delta G = \int_1^{P^*} VdP = V(P^* - 1)$$

$$\Delta G = V_a(P^* - 1) + 0 + V_c(1 - P^*)$$

$$\Delta G = (P^* - 1)(V_a - V_c) \quad * \Delta V \text{ is the change from } V_c \text{ to } V_a, \text{ so use the neg.}$$

$\uparrow$  in J/mol                       $\uparrow$  in mL·mol

use conversion  $0.101 \text{ J} = 1 \text{ mL} \cdot \text{atm}$

Problem #5 Problem 5 is a question, before going to part (a), (b).

TABLE 19.2

Standard molar enthalpies of formation,  $\Delta_f H^\circ$ , for various substances at 25°C and one bar.

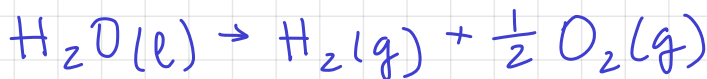
Substance	Formula	$\Delta_f H^\circ / \text{kJ} \cdot \text{mol}^{-1}$
Water	H <sub>2</sub> O(l)	-285.83
	H <sub>2</sub> O(g)	-241.8

TABLE 21.2

Standard molar entropies ( $\bar{S}^\circ$ ) of various substances at 298.15 K.

Substance	$\bar{S}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
H <sub>2</sub> O(g)	188.8
H <sub>2</sub> O(l)	70.0
O <sub>2</sub> (g)	205.2
H <sub>2</sub> (g)	130.7

\* This is not in kJ



$$\Delta G = \Delta H - T\Delta S$$

endothermic, so raise T to drive forward = Le Chatelier

$$T = 298 \text{ K}$$

$$\Delta_{\text{rxn}} S = \left( \Delta S_{\text{H}_2(g)} + \frac{1}{2} \Delta S_{\text{O}_2(g)} \right) - \Delta S_{\text{H}_2\text{O}(l)} \quad (\text{convert to kJ before plugging into } \Delta G \text{ eq.})$$

$$\Delta H = 285.83 \text{ kJ} \cdot \text{mol}^{-1}$$

← positive

spontaneous?  $\Delta G = 0?$

a) At what temp would reaction become favorable assuming  $\Delta_{\text{rxn}} H^\circ_{298}$  and  $\Delta_{\text{rxn}} S^\circ_{298}$  are independent of temp?

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G < 0$ : spont  
 $\Delta G > 0$ : non-spont  
 $\Delta G = 0$ : equilibrium

$$0 = \Delta H - T\Delta S \Rightarrow T = \frac{\Delta H}{\Delta S}$$

$$\bar{C}_v \text{ diatomic} = \frac{5}{2} R$$

b)  $\Delta P = 0$   
 $n = 1$   
 diatomic  
 $T_f = ?$   
 $T_i = 298 \text{ K}$

what is  $\Delta S?$

$$\Delta S = \bar{C}_v \cdot n \cdot \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT \quad \text{or}$$

$$\frac{\Delta S(\text{calculated})}{\Delta S_{\text{rxn}}(\text{table})} \times 100 = \%$$

you can use both to see if you get same result