

PHYS1013

Energy and Matter

$U_i (n_i, P_i, V_i, \dots)$ \rightarrow $U_f (n_f, P_f, V_f, \dots)$

$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right)$

$H = U + pV$ $T(K) = T(^{\circ}C) + 273.15$

$dH = dU + d(pV)$ $dH = dU + pdV + Vdp$

$C_p = (\Delta H / \Delta T)_p$ $\Delta U = Q - W$


$C_p = \left(\frac{\partial H}{\partial T}\right)_p$ $W = P \Delta U$ $\Delta S = nRT \ln\left(\frac{V_f}{V_i}\right)$

$dU = dq + dw$ $dH = dq - pdV + Vdp$ $W = \int_{V_1}^{V_2} P dV$


$H = U + P V$ $dH = C_p dT$ $\Delta H = q_p = C_p \Delta T$ $C_v = (\Delta U / \Delta T)_v$

$dw = -pdv$ $\Delta S = \frac{\Delta_{\text{rev}} H}{T}$ $ds \geq \frac{dq}{T}$

$C_v = \left(\frac{\partial U}{\partial T}\right)_v$



$\Delta U = m(u_2 - u_1) \Delta KE$
 $= \frac{1}{2} m (v_2^2 - v_1^2) \Delta PE$
 $= mg(z_2 - z_1)$



$W_b = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$ $\eta_{th} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$

$dH = dq + Vdp$ $\Delta H = \Delta U + V \Delta p$


$Q = \Delta U + P \Delta V$

$dH = (dq)_p$ $\Delta H = q_p$ $T_R = \frac{T}{T_{cr}}$ $dU = C_v dT$

$dU = (dq)_v$ $\Delta U = q_v$ $\Delta U = q_v = C_v \Delta T$

$P_{cr} = \frac{P}{P_{cr}}$ $W_b = P_1 V_1 \ln \frac{V_2}{V_1}$ $= P_1 V_1 \ln \frac{P_1}{P_2}$ $= RT_1 \ln \frac{P_1}{P_2}$

$\Delta U = U_f - U_i = q(\text{heat}) + w(\text{work})$

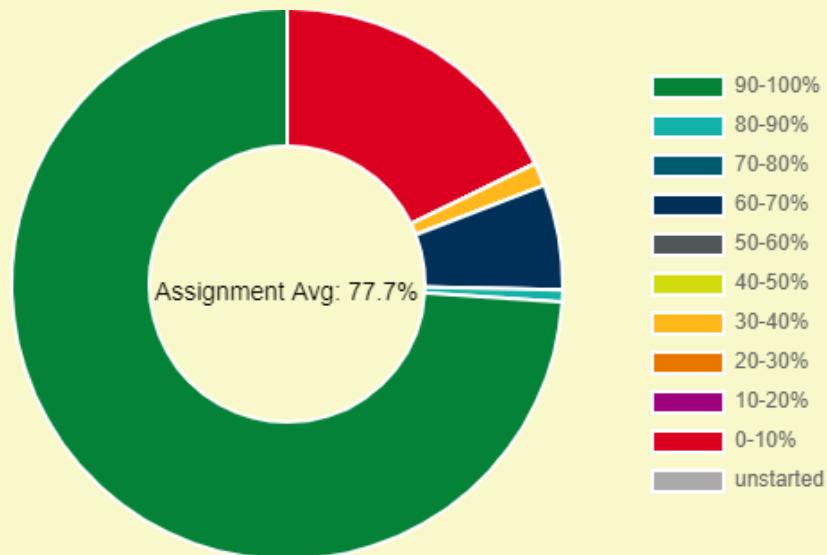
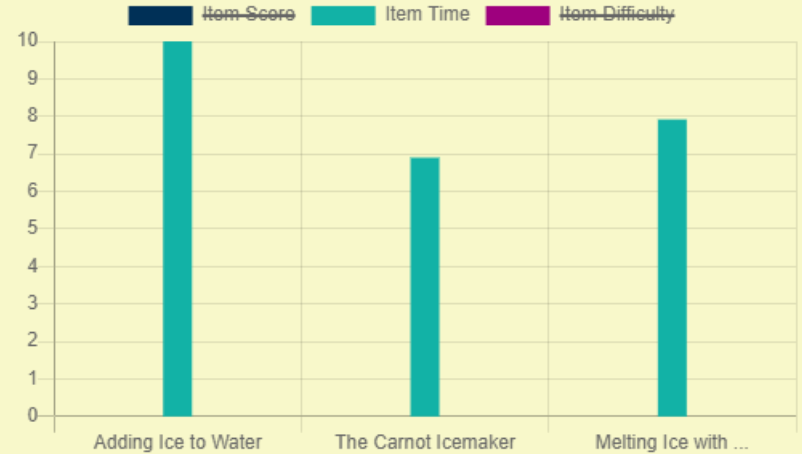
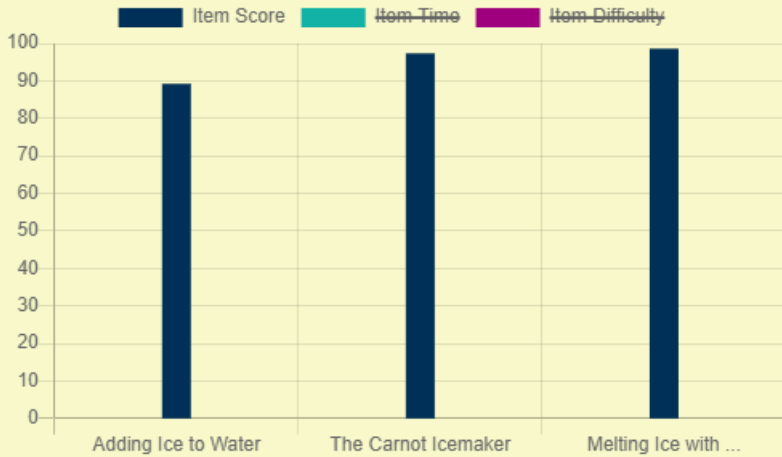


$\gamma_k = \frac{V_{cr}}{RT_{cr}}$

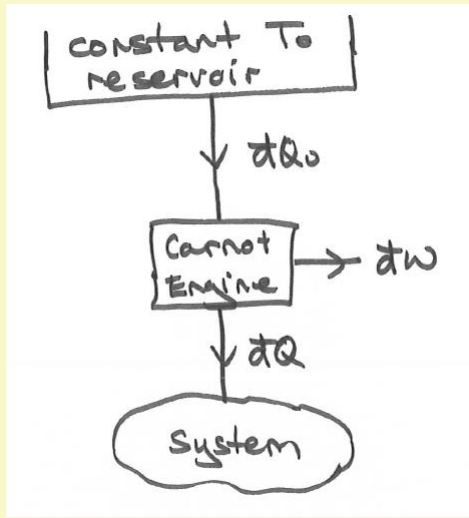
Thermodynamics

MP Week 8 - average score 77.7%
(last year 78.7%)

Average time 25 min
(last year 25 min)



ENTROPY



$$dQ_0 = T_0 \frac{dQ}{T}$$

do many steps

Then we reverse to HP mode & extract energy from the system to put it back exactly as it was at the beginning.

$$Q_0 = \int dQ_0 = T_0 \int \frac{dQ}{T} \leq 0$$

Clausius' Inequality

2ND law

The integral is independent of the path.

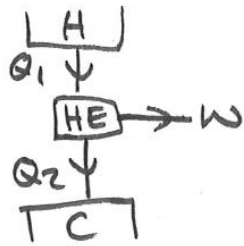
new function of state

$$dS = \frac{dQ_R}{T}$$

Clausius' Proposed 2ND Law: entropy always rises ($S \geq 0$)
in any process

Entropy Changes

Heat Engines



$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

Phase Change

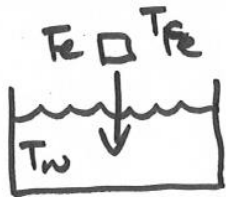
$$Q = mL$$

$$\Delta S = \frac{mL}{T_m}$$

Isothermal Gas Expansion

$$\begin{aligned} \Delta S_{\text{gas}} &= \int_{V_1}^{V_2} \frac{P dV}{T} \quad PV = n_m RT \\ &= \int_{V_1}^{V_2} n_m R \frac{dV}{V} \\ &= n_m R \ln V_2/V_1 \end{aligned}$$

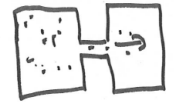
Cooling In Water



$$\Delta S_{\text{water}} = m_{\text{Fe}} C_{\text{Fe}} \frac{(T_{\text{Fe}} - T_w)}{T_w}$$

$$\begin{aligned} \Delta S_{\text{Fe}} &= \int_{T_{\text{Fe}}}^{T_w} m_{\text{Fe}} C_{\text{Fe}} \frac{dT}{T} \\ &= - m_{\text{Fe}} C_{\text{Fe}} \ln T_{\text{Fe}}/T_w \end{aligned}$$

Joule Expansion



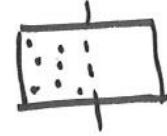
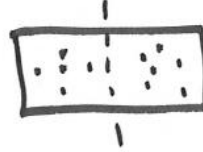
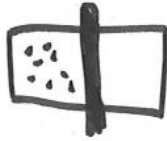
However, we can compute ΔS for the gas by finding an alternative reversible route from initial \rightarrow final state. Entropy is a function of state!

Eg isothermal expansion from $V_1 \rightarrow V_2$. T fixed $\Rightarrow \Delta U = 0$.

$$\Delta S_{\text{gas}} = n_m R \ln V_2/V_1$$

Statistical Interpretation

Npt Joule expansion



$$P = \left(\frac{1}{2}\right)^N$$

microstates

$$\frac{W_2}{W_1} = \left(\frac{V_2}{V_1}\right)^N$$

If you double V
each of N pts gets
 $2 \times$ as many ω

$$\ln \frac{W_2}{W_1} = N \ln \frac{V_2}{V_1}$$

$$S = k \ln W$$

Gibb's Entropy Formula

$$S = -k \sum_{\text{states}} p_i \ln p_i$$

↑
prob of being in state

Central Equation

1st Law: $dQ = dU - dW$

For reversible processes

$$T dS \quad ? \quad -P dV$$

$$\Rightarrow \boxed{T dS = dU + P dV}$$

Entropy of An Ideal Gas

For one mole $P = RT/V$ & $dU = C_v dT$

$$\Rightarrow dS = C_v \frac{dT}{T} + R \frac{dV}{V}$$

We integrate &

$$S = S_0 + C_v \ln T + R \ln V$$

HELMHOLTZ FREE ENERGY

constant volume (no work)

$$Q = \Delta U$$

$$\Delta S_{\text{UNIVERSE}} = \Delta S_{\text{SYST.}} + \Delta S_{\text{SURR.}} \geq 0$$
$$? \quad -\frac{Q}{T_0} = -\frac{\Delta U}{T_0}$$

$$\boxed{F = U - TS} \quad \& \quad \Delta F \leq 0$$

ENTHALPY

constant pressure

$$H = U + PV$$

If $\Delta H \leq 0$ a reaction will occur.

GIBBS FREE ENERGY

$G = H - TS$ & for a reaction to occur $\Delta G \leq 0$

$$G = U - TS + PV$$

$$dG = \underbrace{dU + PdV - TdS}_{0} + VdP - SdT$$

NATURAL VARIABLES

$$dU = TdS - PdV$$

$$U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \& \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

A1. 1 L of water is heated from temperature $T_1 = 17\text{ }^\circ\text{C}$ to temperature $T_2 = 90\text{ }^\circ\text{C}$ in a pan placed on a heating element (taken as a heat reservoir) at $T_H = 500\text{ }^\circ\text{C}$. Assuming negligible thermal expansion and that the heat capacity remains constant at $c = 4.18\text{ kJ K}^{-1}\text{ kg}^{-1}$, find

- (a) the entropy change in the water during this process,
- (b) the entropy change in the heating element,
- (c) the total entropy created. Does your result comply with the second law of thermodynamics? What sort of process is this? [5]

A1. Consider mixing together a mole of a chemical species A and a mole of a chemical species B:

- (a) Define, in words, what the activation energy of a chemical reaction is. [2]
- (b) Define the Gibbs free energy of a reaction. [2]
- (c) State what condition needs to be met for a reaction to occur spontaneously. [1]

- B3.** (a) Explain what it means to say that entropy is a function of state. Write down an expression for the differential change dS in the entropy of a system to which heat dQ is transferred in a reversible process at temperature T . [4]
- (b) Derive an expression for the internal energy of 1 mol of an ideal gas whose molecules have f degrees of freedom. State any theorem that you use and define degree of freedom. [4]
- (c) Derive an expression for the increase in entropy ΔS of the gas in (b) when its temperature is raised from T_1 to T_2 at constant volume. Explain qualitatively why ΔS is larger for gases with more degrees of freedom. [4]
- (d) Suppose that the same gas undergoes a free (Joule) expansion from volume V_1 into volume V_2 ; no work is done pushing on a piston in this process. Explain why the temperature of the gas stays the same and its entropy increases in this process. [4]
- (e) By considering a reversible process that will take the gas between the same initial and final states as the free expansion of part (d), find an expression for the increase in entropy $\Delta S'$ that accompanies the free expansion. Explain why $\Delta S'$ does not depend on f . [4]