

Thermo Cheat Sheet (early class)

All systems are closed ($\Delta n=0$ mol)

In General: Work is defined as:

$$\partial w = -P_{\text{ext}} \cdot \partial V$$

and ∂q is the heat transaction between the exterior and interior.

Heat Capacities:

$$C = \frac{\partial q}{\partial T}$$

At constant volume: $\partial U = \partial q$ (no work is done) and thus:

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

At constant pressure: $\partial H = \partial q$ and thus $C_P = \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$

State functions, the changes of which are exact, have the same equations for each of the four types of transitions.

The Equipartition Theorem: Since $U = \frac{1}{2}RT \cdot \text{degrees of freedom}$, then:

$$\partial U = \partial w + \partial q = C_V \cdot \partial T$$

also

$$\partial U = -P \partial V + T \partial S$$

The Legendre transform of internal energy to remove the volume dependence is enthalpy $H(P, S) = U + PV$:

$$\partial H = \partial U + \partial(PV) = C_V \cdot \partial T + nR \cdot \partial T = C_P \cdot \partial T$$

also

$$\partial H = V \partial P + T \partial S$$

The Legendre transform of internal energy to remove the entropy dependence is the Helmholtz energy $A(T, V) = U - TS$:

$$\partial A = \partial U - \partial(TS) = -P \partial V - S \partial T$$

The Legendre transform of internal energy to remove the entropy and volume dependence is Gibbs energy $G(T, P) = U + PV - TS$:

$$\partial G = \partial U + \partial(PV) - \partial(TS) = V \partial P - S \partial T$$

The change in entropy is:

$$\Delta S = n \cdot C_{V,m} \cdot \ln\left(\frac{T_f}{T_i}\right) + nT \cdot \ln\left(\frac{V_f}{V_i}\right)$$

Maxwell Equations:

$$\partial U = -P \partial V + T \partial S \text{ therefore } \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\partial H = V \partial P + T \partial S \text{ therefore } \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\partial A = -P \partial V - S \partial T \text{ therefore } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\partial G = V \partial P - S \partial T \text{ therefore } -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Isothermal Reversible and Irreversible:

For all isothermal transitions ($\partial T = 0 \text{ K}$):

$$\partial U = \partial H = 0 \text{ J}$$

for the reasons expressed above. Since $\partial U = \partial w + \partial q$, then $\partial q = -\partial w$. $\partial A = -P \partial V$ which is the reversible work. $\partial G = V \partial P$, which oddly can be shown to be the same as reversible work.

Irreversible: $\Delta w = -P_{\text{ext}} \cdot \Delta V$ $\Delta S_{\text{tot}} > 0 \frac{\text{J}}{\text{K}}$ $\Delta S_{\text{ext}} > -\Delta S$

Reversible: Since $P_{\text{ext}} \cong P$: $\Delta w = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$ $\Delta S_{\text{tot}} = 0 \frac{\text{J}}{\text{K}}$ $\Delta S_{\text{ext}} = -\Delta S$

Adiabatic Reversible and Irreversible: Neither P, V nor T are constant!

$$\partial q = 0 \text{ J}$$

$$\Delta S_{\text{ext}} = 0 \frac{\text{J}}{\text{K}}$$

Irreversible: Since $\partial U = \partial w = C_V \cdot \partial T$, then

$$C_V \cdot \Delta T = -P_{\text{ext}} \cdot \Delta V$$

This gives the change in temperature, and you can then calculate:

$$\Delta U = \Delta w = C_V \cdot \Delta T$$

Also $\Delta H = C_P \cdot \Delta T$. After solving all the thermodynamic variables, usually starting with ΔT , you calculate the change in system entropy using:

$$\Delta S_{\text{tot}} = \Delta S = n \cdot C_{V,m} \cdot \ln\left(\frac{T_f}{T_i}\right) + nT \cdot \ln\left(\frac{V_f}{V_i}\right)$$

As for $\partial A = \partial U - \partial(TS)$ and $\partial G = \partial H - \partial(TS)$, we run into the problem that $\partial(TS)$ is very difficult to determine as both T and S are changing simultaneously.

Reversible: Since $P_{\text{ext}} = P$ then $C_V \partial T = -P \cdot \partial V = -\frac{nRT}{V} \cdot \partial V$, from here we derive the adiabatic equations of state:

$$\left(\frac{T_f}{T_i}\right) = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}} \quad \text{or} \quad \left(\frac{P_i}{P_f}\right) = \left(\frac{V_f}{V_i}\right)^{\frac{C_P}{C_V}}$$

With the change in temperature one can calculate $\Delta U = \Delta w = C_V \cdot \Delta T$ and $\Delta H = C_P \cdot \Delta T$. Also $\Delta S = 0 \frac{\text{J}}{\text{K}}$, $\Delta S_{\text{tot}} = 0 \frac{\text{J}}{\text{K}}$

As for $\partial A = \partial U - \partial(TS) = C_V \cdot \partial T - S \partial T$ and $\partial G = C_P \cdot \partial T - S \partial T$, while this is easier than the irreversible situation since $\Delta S = 0 \frac{\text{J}}{\text{K}}$, regardless, we need to know the absolute entropy of the gas in the cylinder. Furthermore, entropy is still a function of T, so integration of $S \partial T$ is nonetheless still complex. Generally we are not concerned with calculating ∂A or ∂G for these types of transitions.