⑦ APPLICATIONS OF ENTROPY AND THE SECOND LAW

1] ENTROPY CHANGES IN REVERSIBLE PROCESSES

FROM 1ST LAW WRITTEN IN TERMS OF ENTROPY, WE CAN COMPUTE ΔS (OR SPECIFIC ENTROPY, Δs) IN SPECIAL CIRCUMSTANCES

1) ADIABATIC PROCESSES

$$\delta Q = 0 \Rightarrow dS = \frac{\delta Q}{T} = 0 \Rightarrow S \text{ CONSTANT } (\Delta S = 0)$$

2) ISOTHERMAL PROCESSES

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} = \frac{\Delta Q}{T}$$

, WHERE ΔQ IS HEAT INPUT TO GO FROM STATE 1 TO 2 A CONSTANT TEMPERATURE T.

3) ISOCHORIC PROCESSES

USE $dU = TdS - PdV \overset{dV=0}{=} TdS$

AND $dU = C_V dT$

$$\Rightarrow \Delta S = \int_1^2 C_V \frac{1}{T} dT$$

IN PARTICULAR, IF C_V IS CONSTANT FOR TEMPERATURE BETWEEN T_1 & T_2

$$\Rightarrow \Delta S = C_V \,\mathrm{Ln}(T_2/T_1)$$

4) ISOBARIC PROCESSES

USE $dH = TdS + VdP \overset{dP=0}{=} TdS$

AND $dH = C_P dT$

$$\Rightarrow \Delta S = \int_1^2 C_P \frac{1}{T} dT \overset{C_P \approx \text{CONSTANT}}{\simeq} C_P \,\mathrm{Ln}(T_2/T_1)$$

5) PHASE CHANGE (AT CONSTANT TEMPERATURE AND PRESSURE)

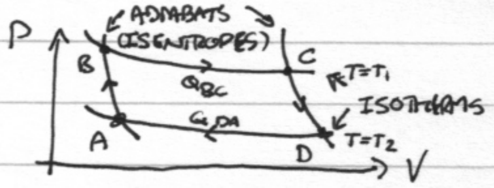
RECALL $\ell = \frac{\delta Q}{M} = \delta q$ IS LATENT HEAT (OF FUSION OR VAPORIZATION) WITH UNITS OF J/kg.

SO TO CHANGE THE PHASE OF A MASS M OF SUBSTANCE GIVES AN ENTROPY CHANGE $\Delta S = \pm(M\ell)/T$ (>0 FOR MELTING/EVAPORATION) (<0 FOR FREEZING/CONDENSATION)

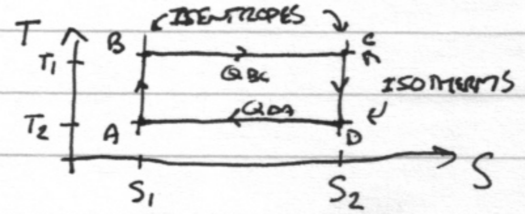
SPECIFIC ENTROPY CHANGE IS $\Delta s = \frac{\Delta S}{M} = \pm \ell/T$

2] CARNOT HEAT ENGINE REVISITED

EARLIER WE PLOTTED THE STAGES OF THE CARNOT ENGINE WITH A P-V DIAGRAM:



THIS CAN BE REPLOTTED ON A T-S DIAGRAM



BEING A REVERSIBLE PROCESS, WE KNOW THE CHANGE IN INTERNAL ENERGY GOING FROM $A \to B \to C \to D \to A$ IS ZERO: $\oint dU = U_{AB} + U_{CD} = 0$

So, FROM 1^{ST} LAW, $0 = \oint dU = \oint T dS - \oint P dV$

$$\Rightarrow W \equiv \oint P dV = \oint T dS = T_1(S_2 - S_1) + T_2(S_1 - S_2)$$
$$= (T_1 - T_2)(S_2 - S_1)$$

I.e. WORK IS THE AREA CONTAINED IN THE T-S DIAGRAM.

IN TERMS OF HEAT $Q_{BC} = T_1(S_2 - S_1)$ AND $Q_{DA} = T_2(S_1 - S_2)$

So $W = Q_{BC} + Q_{DA}$ AS BEFORE.

3] THE ENTROPY OF AN IDEAL GAS

BY DEFINITION, WE KNOW THAT S = CONSTANT FOR AN ISENTROPIC PROCESS. BUT SEPARATEL WE FOUND THAT THE POTENTIAL TEMPERATURE, $\theta \equiv T(P/P_0)^{-x}$, IS CONSTANT FOR A GAS THAT MOVES ADIABATICALLY INTO DIFFERENT PRESSURES. THIS SUGGESTS THE TWO ARE RELATED.

FROM 1^{ST} LAW IN TERMS OF SPECIFIC ENTHALPY, WE HAVE

$$\underbrace{T\,ds}_{\delta q} = \underbrace{c_p\,dT}_{dh} - \alpha\,dP \qquad \left(\alpha = \frac{1}{\rho} \text{ IS SPECIFIC VOLUME}\right)$$

$$\Rightarrow ds = c_p \frac{1}{T}\,dT - \frac{1}{\rho T}\,dP$$

$$= c_p \frac{1}{T}\,dT - \frac{R_g}{P}\,dP \qquad \left(\text{USING EQ}^{\underline{N}}\text{ STATE: } P = \rho R_g T\right)$$

$$= c_p\,d(\ln T) - R_g\,d(\ln P)$$

BUT $\ln\theta = \ln\left[T(P/P_0)^{-x}\right] = \ln T - x\ln P$ + CONSTANT

$$\Rightarrow c_p \ln\theta = c_p \ln T - R_g \ln P + \text{CONSTANT} \quad (\text{USING } x \equiv R_g/c_p)$$

BECAUSE c_p & R_g ARE CONSTANT FOR AN IDEAL GAS

$$\Rightarrow d(c_p \ln\theta) = c_p d(\ln T) - R_g d(\ln P) = ds$$

SO, TO WITHIN A CONSTANT (USUALLY TAKEN TO BE ZERO)

$$\boxed{S = c_p \ln\theta} \qquad ①$$

ONE CAN GO FURTHER AN CONSIDER AIR THAT ABSORBS OR CONDUCTS/RADIATES HEAT AS IT MOVES $\Rightarrow T\frac{ds}{dt} = \dot{q}$ ← HEATING RATE $\left[\frac{J}{kg\cdot s}\right]$

$$\Rightarrow \frac{ds}{dt} = \frac{1}{T}\dot{q}$$

SO ① $\Rightarrow \dfrac{d(c_p\ln\theta)}{dt} = \dfrac{1}{T}\dot{q} \Rightarrow c_p \dfrac{1}{\theta}\dfrac{d\theta}{dt} = \dfrac{1}{T}\dot{q} \Rightarrow \boxed{\dfrac{d\theta}{dt} = \dfrac{1}{c_p}\dfrac{\theta}{T}\dot{q}}$

THIS IS INTERNAL ENERGY EQUATION INCLUDING HEAT ABSORPTION/DISSIPATION

4] POTENTIAL DENSITY & POTENTIAL TEMPERATURE OF SEA WATER

FOR SIMPLICITY, IGNORE INFLUENCE OF SALINITY AND WILL ASSUME DENSITY AND TEMPERATURE CHANGE DUE TO PRESSURE THROUGH ADIABATIC PROCESSES. UNLIKE EXPRESSIONS FOR A GAS: $\rho_{POT} \equiv \rho (P/P_0)^{-1/\gamma}$, $\theta \equiv T(P/P_0)^{-\kappa}$; HERE WE CANNOT MAKE USE OF A "NICE" EQUATION OF STATE. INSTEAD MANIPULATE DIFFERENTIALS TO FIND COEFFICIENTS MEASURED TO BE APPROXIMATELY CONSTANT.

POTENTIAL DENSITY: SUPPOSE $s = s(\overset{\text{DENSITY}}{\rho}, \overset{\text{PRESSURE}}{p})$

$$\Rightarrow ds = \left(\frac{\partial s}{\partial \rho}\right)_p d\rho + \left(\frac{\partial s}{\partial p}\right)_\rho dp \qquad ①$$

USE $\left(\frac{\partial p}{\partial \rho}\right)_s = c_s^2$ WHERE $c_s \approx 1500$ m/s IS SPEED OF SOUND IN WATER

BUT $\left(\frac{\partial s}{\partial p}\right)_\rho = -\left(\frac{\partial s}{\partial \rho}\right)_p \left(\frac{\partial \rho}{\partial p}\right)_s$ ⇐ CYCLICAL RELATION: $\left(\frac{\partial s}{\partial \rho}\right)_p \left(\frac{\partial \rho}{\partial p}\right)_s \left(\frac{\partial p}{\partial s}\right)_\rho = -1$

$$= -\frac{1}{c_s^2}\left(\frac{\partial s}{\partial \rho}\right)_p$$

SO ① $\Rightarrow$ $ds = \left(\frac{\partial s}{\partial \rho}\right)_p \left[d\rho - \frac{1}{c_s^2} dp\right]$

FOR AN ADIABATIC PROCESS, $ds = 0 \Rightarrow d\rho - \frac{1}{c_s^2} dp = 0$

IN THE OCEAN IT IS CONVENIENT TO RECAST PRESSURE IN TERMS OF DEPTH THROUGH HYDROSTATIC BALANCE: $dp = -\rho g dz \simeq -\rho_0 g dz$

$$\Rightarrow d\left(\rho + \frac{1}{c_s^2}\rho_0 g z\right) = 0$$

SO DEFINE $\boxed{\rho_{POT} \equiv \rho + \rho_0 \frac{z}{H_\rho}}$ AS POTENTIAL DENSITY : $d\rho_{POT} = 0$

WITH $H_\rho = c_s^2/g$ $\left(\approx (1500\,\text{m/s})^2/(9.8\,\text{m/s}^2) \approx 200\,\text{km}\right)$

↖ DENSITY SCALE HEIGHT

ρ_{POT} IS DENSITY THAT FLUID WITH DENSITY ρ AT DEPTH z (<0) WOULD HAVE IF BROUGHT TO SURFACE (WHERE $z = 0$).

TYPICALLY, ρ_0 IS TAKEN TO BE THE DENSITY OF THE SURFACE WATER (1030 kg/m^3 IS TYPICAL)

EXAMPLE: FOR WATER BROUGHT ADIABATICALLY FROM SURFACE TO 5 km DEPTH TAKE $\rho_{POT} = \rho_0$ (DENSITY AT SURFACE). SO AT $z = -5$ km, ITS DENSITY IS $\rho = \rho_{POT} - \rho_0 \frac{z}{H_\rho} \simeq \rho_0 \left(1 - \frac{(-5\,\text{km})}{(200\,\text{km})}\right) \simeq 1.025\,\rho_0$.

NOT MUCH, BUT SIGNIFICANT COMPARED TO DENSITY RANGE IN OCEAN ($1025 - 1035\ \text{kg/m}^3$)

4] (CONT'D)

POTENTIAL TEMPERATURE (OF WATER)

SUPPOSE $s = s(T, p)$

$$\Rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

BUT $c_p = \frac{\delta q}{dT}\Big|_p = T\left(\frac{\partial s}{\partial T}\right)_p \Rightarrow \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$

$\swarrow \alpha = \frac{1}{\rho}$: SPECIFIC VOLUME

AND $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial \alpha}{\partial T}\right)_p$ ⇐ A MAXWELL RELATION (SEE p.42 OF NOTES)

$= \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_p$

THERMAL EXPANSION COEFFICIENT

$= \frac{1}{\rho^2}(-\beta_T \rho)$ USING $\beta_T \equiv -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

$= -\beta_T/\rho$

SO $ds = \frac{c_p}{T} dT - \frac{\beta_T}{\rho} dp$

FOR AN ADIABATIC PROCESS, $ds = 0 \Rightarrow \frac{c_p}{T} dT - \beta_T \frac{1}{\rho} dp = 0$

$\Rightarrow dT - \frac{\beta_T T}{c_p \rho} dp = 0$

AGAIN USE HYDROSTATIC BALANCE: $dp = -\rho g\, dz$

$$\Rightarrow dT + T \frac{\beta_T g}{c_p} dz = 0$$

FINALLY SUPPOSE $T \approx T_0$ IN COEFFICIENT AND THAT β_T & c_p ARE APPROXIMATELY CONSTANT

TEMPERATURE SCALE HEIGHT

$\Rightarrow d\left(T + T_0 \frac{z}{H_T}\right) = 0$ WITH $H_T \equiv \frac{c_p}{\beta_T g}$

DEFINE $\boxed{\theta \equiv T + T_0 \frac{z}{H_T}}$ THE "<u>POTENTIAL TEMPERATURE</u>"

IN OCEAN $c_p \approx 4 \times 10^3 \frac{J}{kg\,K}$, $\beta_T \simeq 2 \times 10^{-4} K^{-1}$, $g \simeq 9.8 m/s^2$

$\Rightarrow H_T \simeq 2000 km$.

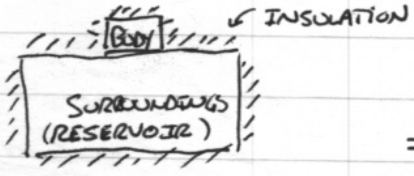
EXAMPLE: FOR WATER AT SURFACE BROUGHT ADIABATICALLY TO 5km DEPTH, ITS TEMPERATURE CHANGES FROM T_0 TO

$$T = \theta - T_0 \frac{z}{H_T} = T_0\left(1 - \frac{z}{H_T}\right) = T_0\left(1 - \frac{-5km}{2000km}\right) = 1.0025\, T_0$$

SO, IF $T_0 = 300K$, $T = 300.75 K$ (≃0.8°C INCREASE)

5] ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

CONSIDER ENTROPY CHANGE AS A BODY OF TEMPERATURE T_1 WARMS TO THE SURROUNDING TEMPERATURE T_2. IN DOING SO, SUPPOSE THE SURROUNDINGS ARE SO LARGE THAT TEMPERATURE REMAINS AT T_2.



$$\text{From } \delta q = c_p\,dT - \alpha\,dP \overset{\text{ISOBARIC}}{\approx} c_p\,dT$$
$$\Rightarrow ds = \frac{\delta q}{T} = \frac{c_p}{T}\,dT$$
$$\Rightarrow \Delta S_{BODY} = c_p \ln(T_2/T_1) \qquad (>0 \text{ IF } T_2>T_1)$$

BECAUSE BODY + SURROUNDINGS ARE INSULATED, ALL HEAT $c_p(T_2-T_1)$ COMES FROM SURROUNDINGS

$$\Rightarrow \Delta S_{RESERVOIR} = -\frac{1}{T_2}\left(c_p(T_2-T_1)\right) \qquad (<0 \text{ IF } T_2>T_1)$$

SO, THE TOTAL ENTROPY CHANGE OF THE BODY + RESERVOIR IS

$$\Delta S_{UNIVERSE} = \Delta S_{BODY} + \Delta S_{RESERVOIR}$$
$$= c_p\left[\ln(T_2/T_1) - \left(1 - \frac{1}{T_2/T_1}\right)\right]$$

NOTE $\Delta S_{UNIVERSE} = 0$ IF $T_2 = T_1$

SUPPOSE $T_2 = T_1 + \Delta T$ WITH $|\Delta T|/T_1 \ll 1$

$$\Rightarrow \ln(T_2/T_1) = \ln\left(1+\frac{\Delta T}{T_1}\right) \approx \frac{\Delta T}{T_1} - \frac{1}{2}\left(\frac{\Delta T}{T_1}\right)^2 + \frac{1}{3}\left(\frac{\Delta T}{T_1}\right)^3 - + \cdots$$
$$\frac{1}{T_2/T_1} = \left(1+\frac{\Delta T}{T_1}\right)^{-1} = 1 - \frac{\Delta T}{T_1} + \left(\frac{\Delta T}{T_1}\right)^2 - \cdots$$

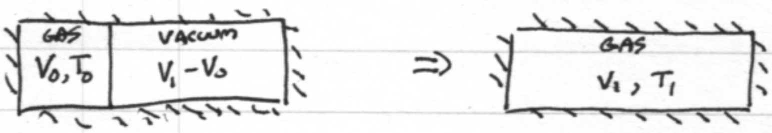
$$\text{So } \Delta S_{UNIVERSE} \simeq c_p\left[\left(\frac{\Delta T}{T_1} - \frac{1}{2}\left(\frac{\Delta T}{T_1}\right)^2\right) - 1 + \left(1 - \frac{\Delta T}{T_1} + \left(\frac{\Delta T}{T_1}\right)^2\right)\right]$$
$$\simeq c_p\left[\frac{1}{2}\left(\frac{\Delta T}{T_1}\right)^2\right]$$

SO $\Delta S_{UNIVERSE} \geq 0$ WITH EQUALITY ONLY IF $T_1 = T_2$

INDEED, THIS CIRCUMSTANCE IS IRREVERSIBLE – THE BODY WILL NOT SPONTANEOUSLY COOL DOWN

6] FREE EXPANSION OF AN IDEAL GAS

CONSIDER TWO CHAMBERS (ONE WITH A GAS, ONE IN VACUUM) ALL WITHIN AN INSULATED VESSEL. THE MEMBRANE SEPARATING THE CHAMBERS IS SUDDENLY POPPED ALLOWING THE GAS TO EXPAND TO FILL BOTH CHAMBERS



BECAUSE INSULATED $\delta Q = 0$.

ALSO, BECAUSE EXPANDING GAS MOVES INTO ZERO PRESSURE $\delta W = p\,dV = 0$

SO $dU = \delta Q - \delta W = 0 \Rightarrow C_V dT = 0 \Rightarrow T$ CONSTANT

$\Rightarrow \quad T_1 \approx T_0 \quad !$

[INDEED, ATTEMPTS BY JOULE TO MEASURE TEMPERATURE CHANGE GAVE NO DIFFERENCE]

BECAUSE THE SYSTEM CHANGES IRREVERSIBLY, THERE SHOULD BE AN ENTROPY INCREASE.

$$T\,dS = C_V \overset{dT \approx 0}{dT} + P\,dV \approx P\,dV$$

$$\Rightarrow dS \approx \frac{P}{T}\,dV = \frac{nR}{V}\,dV = nR\,d(\ln V)$$

SO $\Delta S = nR \ln(V_1/V_0) \qquad (>0 \text{ SINCE } V_1 > V_0)$ ①

NOTE, IF WE CONSIDERED WORK DONE IN A <u>REVERSIBLE</u> ISOTHERMAL PROCESS, WE GET [SEE P. 18 OF NOTES]

$$W = nRT \ln(V_1/V_0)$$

SINCE ISOTHERMAL $dU = 0 \Rightarrow \delta Q = \delta W$

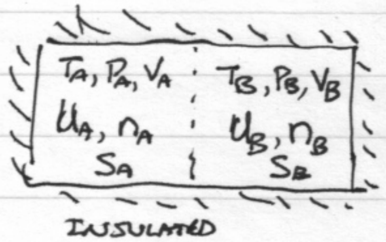
SO HEAT INTO SYSTEM WOULD BE $Q = W = nRT \ln(V_1/V_0)$

SO ENTROPY CHANGE IS $\Delta S = \int_0^1 \frac{\delta Q}{T} = \frac{1}{T}\int \delta Q = \frac{Q}{T} = nR \ln(V_1/V_0)$

THAT IS IRREVERSIBLE ENTROPY CHANGE IN ① IS THE SAME AS WOULD OCCUR FOR A REVERSIBLE PROCESS.

7] PHASE EQUILIBRIUM

CONSIDER 2 SYSTEMS IN EQUILIBRIUM WHICH CAN EXCHANGE THE SAME PARTICLES (e.g. ICE → WATER)



MUST HAVE:

$$(*)\begin{cases} n_A + n_B = n & \text{CONSTANT} \quad \text{(MASS CONSERVATION)} \\ V_A + V_B = V & \text{CONSTANT} \quad \text{(VOLUME CONSERVATION)} \\ U_A + U_B = U & \text{CONSTANT} \quad \text{(ENERGY CONSERVATION)} \\ S_A + S_B = S & \text{MAXIMUM} \quad \text{(AT EQUILIBRIUM)} \end{cases}$$

$$\text{So } 0 = dS_A + dS_B = \frac{1}{T_A}(dU_A + P_A dV_A - \mu_A dn_A) + \frac{1}{T_B}(dU_B + P_B dV_B - \mu_B dn_B)$$

$$(*) \Rightarrow \quad = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) dn_A$$

BECAUSE dU_A, dV_A AND dn_A ARE ARBITRARY

$$\Rightarrow \underbrace{T_A = T_B}_{\text{THERMAL EQ}^{\underline{\text{M}}}}, \quad \underbrace{P_A = P_B}_{\text{MECHANICAL EQ}^{\underline{\text{M}}}}, \quad \underbrace{\mu_A = \mu_B}_{\text{DIFFUSIVE EQ}^{\underline{\text{M}}}}$$

IF NOT IN EQUILIBRIUM, THEN $S_A + S_B$ MUST BE INCREASING TOWARD MAXIMUM (2^{ND} LAW OF THERMODYNAMICS)

$$\Rightarrow 0 < dS_A + dS_B = \underbrace{\left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A}_{①} + \underbrace{\left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A}_{②} - \underbrace{\left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)}_{③} dn_A$$

① ⇒ IF V & n FIXED BUT $T_A \neq T_B$ THEN $dU_A > 0$ IF $T_A < T_B$

i.e. HEAT ENERGY FLOWS FROM HOT TO COLD

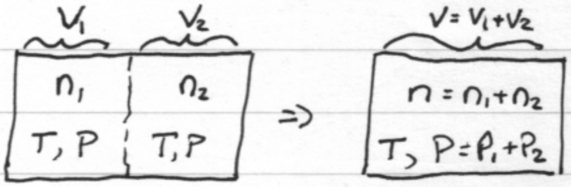
② ⇒ IF U & n FIXED (SO T FIXED) BUT $P_A \neq P_B$, THEN $dV_A > 0$ IF $P_A > P_B$

i.e. VOLUME GAINED AS HIGHER PRESSURE BODY EXPANDS

③ ⇒ IF T & P FIXED BUT $\mu_A \neq \mu_B$, THEN $dn_A > 0$ IF $\mu_A < \mu_B$

i.e. MASS FLOWS FROM BODY WITH HIGH CHEMICAL POTENTIAL TO LOW
(i.e. GIBBS FREE ENERGY APPROACHES MINIMUM)

8] MIXING PROCESSES



NOW CONSIDER 2 SYSTEMS EACH CONTAINING DIFFERENT TYPES OF PARTICLES (e.g. O_2 IN ONE, N_2 IN THE OTHER)

SPECIFICALLY WE WILL ASSUME THESE ARE IDEAL GASES SO THAT $PV_1 = n_1 RT$ & $PV_2 = n_2 RT$ BEFORE

AND $PV = nRT$

IN WHICH $P = P_1 + P_2$ WITH $P_1 = \frac{n_1}{n_1+n_2} P$, $P_2 = \frac{n_2}{n_1+n_2} P$

(DARCY'S LAW OF PARTIAL PRESSURES FOR GASES).

EXPECT ENTROPY TO INCREASE GOING FROM UNMIXED TO MIXED STATE. CALCULATE THIS USING GIBBS FREE ENERGY.

BECAUSE P AND n ARE CONSTANT IN TOTAL SYSTEM, $dG = -S dT$

I.e. $\Delta S = -\frac{\partial \Delta G}{\partial T}$, WITH $\Delta G = G_{\text{mixed}} - G_{\text{unmixed}}$

G ITSELF CHANGES BECAUSE PRESSURE OF EACH GAS GOES FROM P_i TO PARTIAL PRESSURE P_1 OR P_2.

FOR ISOTHERMAL PROCESS, FOR EACH GAS TYPE, HAVE

$$dG_i = -S\,dT + V_i\,dP_i - \mu_i\,dn_i = V_i\,dP_i$$

$$= \left(\frac{n_i RT}{P_i}\right) dP_i = n_i RT\, d(\ln P_i)$$

$$\Rightarrow G_i = n_i RT \ln P_i$$ (TO WITHIN AN ARBITRARY CONSTANT)

So $G_{\text{unmixed}} = n_1 RT \ln P + n_2 RT \ln P = nRT \ln P$

$$G_{\text{mixed}} = n_1 RT \ln P_1 + n_2 RT \ln P_2$$

$$= n_1 RT \ln\left(\frac{n_1}{n} P\right) + n_2 RT \ln\left(\frac{n_2}{n} P\right)$$

$$= n_1 RT \ln\left(\frac{n_1}{n}\right) + n_2 RT \ln\left(\frac{n_2}{n}\right) + nRT \ln P$$

$$\Rightarrow \Delta G = n_1 RT \ln\left(\frac{n_1}{n}\right) + n_2 RT \ln\left(\frac{n_2}{n}\right) = nRT(\alpha_1 \ln \alpha_1 + \alpha_2 \ln \alpha_2)$$

WITH $\alpha_i = \frac{n_i}{n}$

So $\Delta S = -nR(\alpha_1 \ln \alpha_1 + \alpha_2 \ln \alpha_2)$ //

E.g. IF $n_1 = n_2 = \frac{1}{2} n \Rightarrow \Delta S = -nR\left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right) = nR \ln 2 > 0$

NOTE: TWO GASES <u>MUST</u> BE DIFFERENT. IF BOTH ARE O_2, THEN $\Delta S = 0$