

Equation of state (EoS): $F(p, \alpha, T) = 0$

$$\alpha = \frac{V}{M} \quad | \text{ Specific Volume; } \alpha_m = \frac{V}{n} \quad | \text{ Molar specific Volume}$$

$V = \text{vol. occupied by } n \text{ moles}$

Boyle's Law: (req closed sys & T const): $pV = \text{constant}$ or $p_1V_1 = p_2V_2$

Charles' Law: (req closed sys & p const)

$$dv = \alpha V_0 dt \Rightarrow \alpha = \frac{1}{V_0} \frac{dv}{dt} \quad | \quad p = \text{constant; } V_0 \text{ at } 0^\circ\text{C}$$

$t \Rightarrow ^\circ\text{C}; T \Rightarrow \text{K}$

$$\int_{V_0}^V dv = \int_0^t \alpha V_0 dt \Rightarrow V(t) = V_0(1 + \alpha t) \quad | \quad \alpha = \frac{1}{273.16} \text{ Vol. coefficient}$$

of thermal expansion

$$p_{\text{const}} \Rightarrow \frac{V_1}{V_2} = \frac{T_1}{T_2}, \quad V_{\text{const}} \Rightarrow \frac{p_1}{p_2} = \frac{T_1}{T_2}, \quad \left(\frac{V}{T}\right)_{\text{const}} \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Universal Gas Constant - The point of convergence, i.e. the numerical

limit of the ratio $\frac{p\alpha_m}{T} = R^*$ as $p \rightarrow 0$ $R^* = 8.3143 \times 10^3 \text{ J} \cdot (\text{kg} \cdot \text{mol})^{-1} \text{ K}^{-1}$

Ideal Gas: A gas for which $\frac{p\alpha_m}{T} = R^*$ exactly, regardless of T & p

Equation of State for an Ideal Gas: $p\alpha_m = R^*T$ or $pV = nR^*T$

Differential of the EoS: $p d\alpha + \alpha dp = R dT$

Specific Gas Constant: The numerical limit of the ratio of $\frac{p\alpha}{T}$

$R = \frac{p\alpha}{T}$ R is constant for any gas, but is a different constant for different gases. To the extent that it acts like an ideal gas:

$$p\alpha = RT \Rightarrow \frac{pV}{mT} = R \Rightarrow p = \frac{m}{V} RT$$

$R = \frac{R^*}{M}$ **Specific Gas Constant:** Use when need to calculate 'specific' values such as specific volume, spec. heat... Note: $M [\text{amu}] = M [\text{g mol}^{-1}]$

$$\otimes R_{\text{Argon}} = \frac{R^*}{M_{\text{Ar}}} = \frac{8.3134 \text{ J mol}^{-1} \text{ K}^{-1}}{39.95 \text{ g mol}^{-1}} = 0.208 \text{ J g}^{-1} \text{ K}^{-1} = 208 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\alpha = \frac{R_{\text{Ar}} T}{p} = \frac{(208 \text{ N m kg}^{-1} \text{ K}^{-1})(283 \text{ K})}{10^5 \text{ N m}^{-2}} = 0.589 \text{ m}^3 \text{ kg}^{-1}$$

$$c_{v(\text{Ar})} = \frac{5R_{\text{Ar}}}{2}, \quad c_{p(\text{Ar})} = \frac{7R_{\text{Ar}}}{2}, \quad \kappa_{\text{Ar}} = \frac{R_{\text{Ar}}}{c_{p(\text{Ar})}} \quad \{\text{For Poisson Gas Eqn.}\}$$

$$pV = mRT \quad | \quad \{R = \mathfrak{R}_d\}. \text{ Since } \rho = \frac{m}{V} \quad \left[\frac{\text{kg}}{\text{m}^3}\right] \Rightarrow$$

$$m = \frac{pV}{R_d T} = \left[\frac{\text{N m}^{-2} \text{ m}^3}{\text{N m kg}^{-1} \text{ K}^{-1} \text{ K}}\right] = [\text{kg}] \quad | \text{ For dry air for example}$$

$$p = \rho RT \text{ or } \rho = \frac{p}{RT} \quad | \text{ Since } \alpha = \frac{1}{\rho} \Rightarrow$$

$$p = \frac{RT}{\alpha} \quad \alpha = \frac{RT}{p} \quad p\alpha = RT \quad d(p\alpha) = R dT$$

$$P = \rho \cdot \mathfrak{R}_d \cdot T_v \quad | \text{ Eq. of state: Ideal Gas Law (IGL) for dry air}$$

$V \propto \rho, V \propto T, V \propto \frac{1}{P}$

$$R^* = 8314.3 \text{ J} \cdot \text{kmole}^{-1} \cdot \text{K}^{-1} = 8.3143 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \quad | \text{ Universal gas constant}$$

$$\mathfrak{R}_d = R^*/M_d = 8314.3/28.97 = 287.053 \text{ J/kg} \cdot \text{K} \quad | \quad M_d = \text{Molecular weight of dry air}$$

Dalton's Law of Partial Pressures: $p_{A1}\alpha_A = p_{A2}(\alpha_A + \alpha_B), p_{\text{Tot}} = p_{A2} + p_{B2}$

Molar Volume: $V_0 = \frac{R^* T_0}{p_0} = 22.4136 \text{ liter} = 2.24136 \times 10^{-2} \text{ m}^3$

Molar specific volume: $\alpha_m = \frac{V}{n}$ where V is vol occupied by n mols of a gas

$$m = nM \quad | \quad m = M_0 N_0 \quad \text{or} \quad n = \frac{M_0 N_0}{M} = \frac{m}{M}$$

$$\otimes n = 311 \text{ mol} \left(\frac{\text{kg mol}}{1000 \text{ g mol}}\right) = 0.311 \text{ kg-mol}$$

$M = [\text{g mol}^{-1}]$ = molecular weight of a gas; m = total mass of gas present

M_0 = mass of one molecule;

$N_0 = N_A = 6.0220943 \times 10^{23} \text{ mole}^{-1}$; # of molecules in 1 mole

\therefore 1 gram-mole of any gas contains 6.0220943×10^{23} molecules

$$M_{\text{H}_2\text{O}} = 18 \text{ amu} \Rightarrow m = nM \Rightarrow m = (2 \text{ mol})(18 \text{ g mol}^{-1}) = 36 \text{ g}$$

\otimes If there are 3 kg-moles of O_2 in a tank, how many kg's are there?

$$3 \text{ kg-mole} \times 32.00 \frac{\text{kg}}{\text{kmol}} = 99.7 \text{ kg}$$

$$\otimes M_d(\text{dry air}) = \frac{28.97 \text{ g}}{\text{mol}} \cdot \frac{1000 \text{ mol}}{\text{kmol}} \cdot \frac{\text{kg}}{1000 \text{ g}} = 28.97 \frac{\text{kg}}{\text{kmol}}$$

Potential Temperature: When a unit parcel rises and the environmental pressure decreases, the parcel expands and performs work against the env. p . If the ascent is adiabatic, the energy required for doing this work is obtained from the internal energy of the parcel. This causes a cooling of the parcel. The converse is true for a sinking parcel which is compressed by the env. p forces. The parcel's temp change during adiabatic ascent or descent can be obtained from $T_1 p_1^{-\kappa} = T_2 p_2^{-\kappa}$ or $T p^{-\kappa} = \text{const}$

$$\therefore T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{\kappa} \quad \theta = T \left(\frac{p_0}{p}\right)^{\kappa} = T \left(\frac{1000 \text{ mb}}{p}\right)^{\kappa}$$

Specific Entropy:

In an adiabatic process, where $\delta q = 0$ & $d\theta = 0, ds = 0$
 $ds = \frac{\delta q}{T} = d(c_p \ln \theta)$ \therefore Specific entropy is constant in an adiabatic process.
 This is called an isentropic process.

$$ds = \frac{\delta q}{T} + \frac{\delta q'}{T} \text{ (general eqn for specific entropy)}$$

$$\Delta s = \int_1^2 ds = \int_1^2 d(c_p \ln \theta) \Rightarrow \Delta s = s_2 - s_1 = c_p \ln \left(\frac{\theta_2}{\theta_1}\right) \Rightarrow \Delta s = c_p \ln \left(\frac{\theta_2}{\theta_1}\right) \quad [\text{J K}^{-1}]$$

$$\otimes c_{v1} T_1 + c_{v2} T_2 = c_{v1} T + c_{v2} T \Rightarrow T = T_1 \left(\frac{c_{v1} m_1}{c_{v1} m_1 + c_{v2} m_2}\right) + T_2 \left(\frac{c_{v2} m_2}{c_{v1} m_1 + c_{v2} m_2}\right)$$

Entropy

$$\Delta s = c_v \ln \left(\frac{T_2}{T_1}\right) + R \ln \left(\frac{\alpha_2}{\alpha_1}\right), \quad \Delta s = c_p \ln \left(\frac{T_2}{T_1}\right) - R \ln \left(\frac{p_2}{p_1}\right)$$

$$T ds = du + p dV \Rightarrow \Delta s = p \frac{\Delta V}{T} = nR^* \ln \left(\frac{V}{V_0}\right), \quad s(T, \alpha) \quad ds = \left(\frac{\partial s}{\partial T}\right)_\alpha dT + \left(\frac{\partial s}{\partial \alpha}\right)_T d\alpha$$

Heat Engines

$$\eta = \frac{w_{\text{output}}}{Q_{\text{input}}} = \frac{w_{\text{net}}}{\text{total } Q \text{ added}} = \frac{W}{Q_1} = \frac{Q_1 - Q_3}{Q_1} = 1 - \frac{Q_3}{Q_1}, \quad \eta < 1$$

Carnot cycle

$$\eta_c = 1 - \frac{T_3}{T_1}, \quad \left\{ \frac{T_3}{T_1} = \left(\frac{\alpha_1}{\alpha_2}\right)^{\gamma-1} \right\}, \quad \frac{Q_3}{Q_1} = \frac{T_3}{T_1}, \quad \frac{Q_1}{T_1} - \frac{Q_3}{T_3} = 0$$

NOTE: If only have α can use $(\alpha_1/\alpha_2)^{\gamma-1}$ instead of T , for both Carnot & Otto

The entropy of the heat absorbed = the entropy of the heat rejected

Calculate the work done & heat absorbed when IG is subjected to Carnot cycle:

$$[1 \rightarrow 2] \text{ isothermal } T_1 = \text{const}, \quad w_{12} = \int_{\alpha_1}^{\alpha_2} p d\alpha = nR^* T_1 \ln \frac{\alpha_2}{\alpha_1}$$

$u_{12} = c_v \Delta T = 0, \quad q_{12} = w_{12}$, since $\alpha_2 > \alpha_1 \Rightarrow q_{12} > 0$ (heat was absorbed by the gas from the heat source at T_1)

$$[2 \rightarrow 3] \text{ adiabatic, } \theta_1 = \text{const}, \quad q_{23} = 0, \quad \Delta u_{23} = c_v (T_2 - T_1) < 0$$

$$w_{23} = -\Delta u_{23} = -c_v (T_2 - T_1) > 0$$

$$[3 \rightarrow 4] \text{ isothermal } T_2 = \text{const}, \quad w_{34} = \int_{\alpha_3}^{\alpha_4} p d\alpha = nR^* T_2 \ln \frac{\alpha_4}{\alpha_3}, \quad \Delta u_{34} = 0, \quad q_{34} = w_{34}$$

since $\alpha_4 < \alpha_3 \Rightarrow q_{34} < 0$ (heat was given away by the gas to the heat source at T_2)

$$[4 \rightarrow 1] \text{ adiabatic, } \theta_2 = \text{const}, \quad q_{41} = 0, \quad \Delta u_{41} = -\Delta u_{41} = -c_v (T_1 - T_2) < 0$$

$$\text{Total work: } w = w_{12} + w_{23} + w_{34} + w_{41} = nR^* T_1 \ln \frac{\alpha_2}{\alpha_1} + nR^* T_2 \ln \frac{\alpha_4}{\alpha_3}$$

Transformations $2 \rightarrow 3$ & $4 \rightarrow 1$ are adiabatic $\Rightarrow T_1 \alpha_2^{\gamma-1} = T_2 \alpha_3^{\gamma-1}$ &

$$T_1 \alpha_1^{\gamma-1} = T_2 \alpha_4^{\gamma-1} \Rightarrow \frac{\alpha_2}{\alpha_1} = \frac{\alpha_3}{\alpha_4} \quad \& \quad w = nR^* T_1 \ln \frac{\alpha_2}{\alpha_1} - nR^* T_2 \ln \frac{\alpha_2}{\alpha_1} = nR^* \ln \frac{\alpha_2}{\alpha_1} (T_1 - T_2)$$

The total amount of heat absorbed during the cycle is:

$$q = q_{12} + q_{34} = w_{12} + w_{34} \Rightarrow q = w = nR^* \ln \frac{\alpha_2}{\alpha_1} (T_1 - T_2)$$

$$\text{Let } q_{12} = Q_1, Q_1 > 0, \quad q_{34} = Q_2, Q_2 < 0, \quad \Rightarrow \eta = 1 + \frac{Q_2}{Q_1}$$

2ND LAW OF THERMODYNAMICS $Q_1 = Q_2 + W, \quad \delta q = T ds$

Combined 1st & 2nd Laws $T ds = du + (\delta w)_{\text{tot}} \Rightarrow (\delta w)_{\text{tot}} = -d(u - Ts)$

If δw refers to expansion work ($p d\alpha$) only, it can be written as: $T ds = du + p d\alpha$

General Ideal Gas (IG)

$$T ds = du + \delta w \quad T ds = du + \delta w$$

$$T ds = du + p d\alpha \quad T ds = c_v dT + p d\alpha$$

$$T ds = c_p dT - \alpha dp$$

$$p + \left(\frac{\partial u}{\partial \alpha}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_\alpha \quad T ds = dh - \alpha dp$$

Helmholtz Free Energy Function (AKA Helmholtz potential) $f = u - Ts$

The function $u - Ts$ (a function of state only) is a free energy function.

Specific Gibbs function (AKA Gibbs potential)

$$g = u - Ts + p\alpha = f + p\alpha = h - Ts \quad (\leftarrow \text{a function of state only}) \quad dg = -s dT + \alpha dp$$

$$dg = du - T ds - s dT + p d\alpha + \alpha dp \quad \text{since } (\delta w)_{\text{tot}} = T ds - du, \Rightarrow$$

$(\delta w)_{\text{tot}} = -dg - s dT + p d\alpha + \alpha dp$ where $-dg - s dT + \alpha dp$ represent the w over & above the expansion work $p d\alpha$. $T ds = du + p d\alpha$ (since func remains const for proc

which take place at const T & p . $\therefore dg = du - du - p d\alpha + p d\alpha = 0$ & specific Gibbs function is constant during this process.

Function	Independent variable	Fundamental Equations
u	s, α	$du \leq T ds - p d\alpha$
h	s, p	$dh \leq T ds - \alpha dp$
f	T, α	$df \leq -s dT - p d\alpha$
g	T, p	$dg \leq -s dT - \alpha dp$
$=$	\Rightarrow Reversible process,	$> <$ \Rightarrow Irreversible process

WORK IN THERMODYNAMICS $dW = \vec{F} \cdot d\vec{r}$

The work done by a force \vec{F} when a mass parcel changes position

by an amount $d\vec{r}$. The work done depends on the parcel's path. $W = \int_1^2 \vec{F} \cdot d\vec{r}$

represents the total work done from point 1 \rightarrow 2. $[dw = p d\alpha]$ is the fundamental expression for specific expansion w . General: does not depend on the substance. $dw > 0$ if the system does work on the env. $\Rightarrow d\alpha > 0 \Rightarrow$ expansion
 $dw < 0$ if the env does work on the system. $\Rightarrow d\alpha < 0 \Rightarrow$ compression
 Total w is the area under the curve ($p\alpha$ diagram). Amount of work and its sign are path dependent. $w = \int_1^2 p d\alpha = \int_1^2 p d\alpha$ (General - any substance)

When working with an IG, we can use alternate form by diff both sides of State Eq:

IGE: $p\alpha = RT$, $\Rightarrow p d\alpha + \alpha dp = R dT$, $\therefore [dw_{IG} = R dT - \alpha dp]$ (work - IG)

w in Cyclic process: $w_{net} = \oint p d\alpha =$ Area enclosed by process curve

Thermodynamic $p\alpha$ diagram: Clockwise $\Rightarrow w_{net}$; CCW $\Rightarrow -w_{net}$

Meteorological ($\alpha, -p$) diagram: CW $\Rightarrow w_{net} < 0$; CCW $\Rightarrow w_{net} > 0$

w in Isobaric process: $w_{12} = \int_1^2 p d\alpha = p_1 \int_1^2 d\alpha$, (since $p = p_1 = \text{const.}$) \Rightarrow

$w_{12} = p_1 (\alpha_{final} - \alpha_{initial}) \Rightarrow$ work in an isobaric process is proportional to the diff between the final & initial specific volumes. (General - any substance)

w in Isothermal process: $w_{23} = \int_2^3 p d\alpha$; If ideal gas, Eq of State: $p = RT/\alpha$, \Rightarrow

$w_{23} = \int_2^3 RT \frac{d\alpha}{\alpha} = RT_2 \int_2^3 \frac{d\alpha}{\alpha} = RT_2 \ln \left(\frac{\alpha_3}{\alpha_2} \right)$, or $w_{23} = RT_2 \ln \left(\frac{\alpha_3}{\alpha_2} \right)$ | $\alpha_3 = \text{final}$
 $\alpha_2 = \text{initial}$

Since $\alpha_3 > \alpha_2, w_{23} > 0$. However $w_{41} = RT_1 \ln \left(\frac{\alpha_1}{\alpha_4} \right) < 0$ (Ideal Gas only w_{23} & w_{41})

w in Isotheric process (constant specific volume): $w_{34} = w_{41} = 0$ (General)

Since $d\alpha = 0$, no volume change, no work done by or on the system.

Net work: $w_{net} = \oint p d\alpha = \int_1^2 p d\alpha + \int_2^3 p d\alpha + \int_3^4 p d\alpha + \int_4^1 p d\alpha =$

$w_{12} + w_{23} + w_{34} + w_{41}$, or $w_{net} = p_1 (\alpha_2 - \alpha_1) + R \left[T_2 \ln \left(\frac{\alpha_3}{\alpha_2} \right) + T_1 \ln \left(\frac{\alpha_1}{\alpha_2} \right) \right]$

Since the path is a CW cycle in the $p\alpha$ -diagram, $w_{net} > 0$ & sys does w on env.

1st LAW OF THERMODYNAMICS: $[dq = du + dw]$ (Any subst. in equilibrium)

Principle of conservation of energy: Types of energy:

(a) u , internal energy (the kinetic energy of the random molecular motions)

(b) kinetic energy of the mean motion, $v^2/2$ (the kinetic energy of the motion of the center of the center of mass of the system.) (c) potential energy, ϕ , (energy associated w/ the field of gravity). Accordingly, $[de = du + d(v^2/2) + d\phi]$ (General)

Internal Energy: $\oint du = 0 \Rightarrow du$ is exact differential. The specific internal energy u is a function of state, ie. $u = u(p, \alpha, T)$, though since diff is exact, can eliminate p :

$du = \left(\frac{\partial u}{\partial T} \right)_\alpha dT$ For an IG, u is a function of T & does not depend on α .

Heat $W = QJ$, where W is mech. work dissipated. (1 calorie = 4.18684 Joule)

(Q) is energy in transit. When heat is added or taken from a homogenous system, T_{sys} changes proportionally: $dQ = CdT$, where C is heat capacity of substance.

To work w /unit masses, let $q = Q/m, c = C/m, \Rightarrow dq = cdT, c =$ specific heat capacity.

Specific heat capacities allow us to write 1st Law in different forms:

$[dq = du + p d\alpha]$, (General form, any substance in equilibrium)

$dq = \left(\frac{\partial u}{\partial T} \right)_\alpha dT + \left[p + \left(\frac{\partial u}{\partial \alpha} \right)_T \right] d\alpha = dq = c_v dT + \left[p + \left(\frac{\partial u}{\partial \alpha} \right)_T \right] d\alpha$ General Eqs. - any substance

1st Law - isotheric process: $d\alpha = 0, \therefore dq = (\partial u / \partial T)_\alpha dT_\alpha = c_v dT_\alpha, \Rightarrow [dq = c_v dT_\alpha]$

$\therefore c_v = (\partial u / \partial T)_\alpha$ where c_v is the specific heat at const. specific V . We can replace $(\partial u / \partial T)_\alpha$ by c_v in any eqn, for any substance, even if α is not constant in the process.

$[R = c_p - c_v]$, for monoatomic IG $c_p = 7R/2 = 1004.64J \text{ kg}^{-1} \text{ deg}^{-1}, c_v = 5R/2 = 717.6$

Poisson constants: $\gamma = c_p / c_v = 7/5 = 1.4$, value for IG or dry air.

γ represents the fraction of q used to increase the u during an isobaric process:

$$\frac{\Delta u}{q_{12}} = \frac{c_v(T_2 - T_1)}{c_p(T_2 - T_1)} = \frac{c_v}{c_p} = \frac{1}{\gamma}$$

κ represents the fraction of heat used to do work during an isobaric process is:

$$\frac{w_{12}}{q_{12}} = \frac{p(\alpha_2 - \alpha_1)}{c_p(T_2 - T_1)} = \frac{R(T_2 - T_1)}{c_p(T_2 - T_1)} = \frac{R}{c_p} = \kappa \quad \kappa = \frac{c_p - c_v}{c_p} = 1 - \frac{c_v}{c_p} = 1 - \frac{1}{\gamma}$$

$\kappa = 2/7 = 0.286$ (for dry air/IG) Above: relationship between κ & γ

1st Law for an Isobaric process: ($dp = 0$)

$dq_p = \left[\left(\frac{\partial u}{\partial T} \right)_p + p \left(\frac{\partial \alpha}{\partial T} \right)_p \right] dT_p \Rightarrow [dq_p = c_p dT_p]$ General; $c_p =$ specific heat @ const p
 NOTE: $\left(\frac{\partial u}{\partial T} \right)_p \neq c_p$

1st Law for an Isotheric process: ($d\alpha = 0$)

$dq_\alpha = \left(\frac{\partial u}{\partial T} \right)_\alpha dT_\alpha \Rightarrow [dq_\alpha = c_v dT_\alpha], \therefore c_v = \left(\frac{\partial u}{\partial T} \right)_\alpha$ ($c_v =$ specific heat @ v_{const})

Specific Enthalpy: $[h = u + p\alpha] \Rightarrow dh = d(u + p\alpha) \Rightarrow dh = du + d(p\alpha) \Rightarrow$

$dh = du + p d\alpha + \alpha dp$ $[d(p\alpha) = R dT] \therefore p d\alpha + \alpha dp = R dT$ $[dq = dh - \alpha dp]$

$\Rightarrow dh = du + R dT \Rightarrow [dh = R dT]$ If $du = 0$ **Sensible heat:** $[dh = c_p dT]$

$\therefore h_{net} = \int_1^2 R dT + \int_2^3 R dT + \int_3^4 R dT \Rightarrow R(T_2 - T_1 + T_3 - T_2 + T_1 - T_3)$

1st Law for all processes of an IG: $[dq = c_v dT + p d\alpha]$, since $du = c_v dT$ for IG
 $p d\alpha + \alpha dp = R dT$, (differential form of the Eq. of State), leads to:

$dq = p d\alpha + c_v dT = R dT - \alpha dp + c_v dT$, which gives: $dq = (c_v + R) dT - \alpha dp$, or $[dq = c_p dT - \alpha dp]$

NOTE: $dq = c_p dT - \alpha dp$ does not permit these identities: $du \neq c_p dT, \bar{d}w \neq -\alpha dp$

All we can say is that the sum $du + \bar{d}w = c_p dT - \alpha dp$

Comparison of various thermodynamic relationships for substances

General	Ideal Gas (IG)
$dq = du + \bar{d}w$	$dq = du + \bar{d}w$
$dq = du + p d\alpha$	$dq = du + p d\alpha$
$dq = c_v dT + \left[p + \left(\frac{\partial u}{\partial \alpha} \right)_T \right] d\alpha$	$dq = c_v dT + p d\alpha$
$dq = c_p dT + \left[\left(\frac{\partial h}{\partial p} \right)_T - \alpha \right] dp$	$dq = c_p dT - \alpha dp$
$du = c_v dT + \left(\frac{\partial u}{\partial \alpha} \right)_T d\alpha$	$du = c_v dT$
$dh = c_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp$	$dh = c_p dT$
$dh = d(u + p\alpha)$	$dh = d(u + p\alpha)$
$c_p = c_v + \left[p + \left(\frac{\partial u}{\partial \alpha} \right)_T \right] \left(\frac{\partial \alpha}{\partial T} \right)_p$	$c_p = c_v + R$

$$w = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{nR^* T}{V} dV = nR^* T \ln \left(\frac{V_2}{V_1} \right)$$

$$\otimes dw = p dV = p \left(\frac{\partial V}{\partial T} \right)_p dT + p \left(\frac{\partial V}{\partial p} \right)_T dp, \quad V = V(T, P)$$

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp, \quad V = mRT/p \Rightarrow \left(\frac{\partial V}{\partial T} \right)_p = mR/p,$$

$$\left(\frac{\partial V}{\partial p} \right)_T = \frac{(p)(0) - (mRT)(1)}{p^2} = -\frac{mRT}{p^2}, \quad dw = p dV, \quad dw = p \left[\frac{mR}{p} dT - \frac{mRT}{p^2} dp \right]$$

$$dw = mR dT - \frac{mRT}{p} dp, \therefore \frac{\partial}{\partial p}(mR) = 0; \frac{\partial}{\partial T} \left(\frac{mRT}{p} \right) = -\frac{mR}{p}, \therefore \frac{\partial}{\partial p} \left(\frac{\partial w}{\partial T} \right) \neq \frac{\partial}{\partial T} \left(\frac{\partial w}{\partial p} \right)$$

$$\otimes dV, \quad V = V(T, P), \quad dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial P} \right)_P dP: \quad \frac{\partial}{\partial T} \left(\frac{nRT}{p} \right) = \frac{nR}{p} \Rightarrow$$

$$\Rightarrow \left(\frac{nR}{p} \right) dp = \left[-\frac{nR p^{-2}}{dp} \right] \parallel \frac{\partial}{\partial p} \left(\frac{nRT}{p} \right) = -nRT p^{-2} \Rightarrow (-nRT p^{-2}) dT = \left[-\frac{nR p^{-2}}{dp} \right] dp$$

$\otimes i \rightarrow f$ • isobaric expan & isochoric cool. • vice versa: $w_i = \int_{V_i}^{V_f} p dV + \int_{V_i}^{V_f} p dV$,

$w_i = \int_{V_i}^{V_f} p dV = p_i (V_f - V_i), w_2 = \int_{V_i}^{V_f} p dV + \int_{V_i}^{V_f} p dV \Rightarrow p_f (V_f - V_i), \therefore p_f \neq p_i, w_i \neq w_2$

PROCESSES OF AN IDEAL GAS

Isothermal process: $du = c_v dT = 0$, since $dT = 0$, and $\Delta u = u_2 - u_1 = 0$
 i.e. the internal energy remains unchanged during an isothermal process.

From the 1st law, $dq = du + \bar{d}w = \bar{d}w$, $q_{12} = \int_1^2 dq = w_{12} = RT \ln \left(\frac{\alpha_2}{\alpha_1} \right)$

and all the heat absorbed by the system during an isothermal process is used by the system to do work. Finally, $dh = c_p dT = 0$ and $\Delta h = h_2 - h_1 = 0$, i.e. the specific enthalpy of the system remains unchanged during an isothermal process.

Isotheric process: $\Rightarrow \alpha_1 = \alpha_2, \quad du = c_v dT, \quad \Delta u = u_2 - u_1 = \int_1^2 c_v dT = [c_v (T_2 - T_1)]$

if c_v is constant, and $dh = c_p dT \Rightarrow \Delta h = h_2 - h_1 = \int_1^2 c_p dT = [c_p (T_2 - T_1)]$ if c_p is const.

From the 1st Law, $dq = du + \bar{d}w = du$, since $\bar{d}w = 0$ here. $\therefore [q_{12} = \Delta u = c_v (T_2 - T_1)]$

and all the q absorbed by the sys during an isotheric proc. is used to \uparrow the specific u of the sys.

Isobaric process: $\Rightarrow du = c_v dT$ & $\Delta u = u_2 - u_1 = \int_1^2 c_v dT = [c_v (T_2 - T_1)]$ if c_v is const.

From the 1st Law, $dq = du + \bar{d}w \Rightarrow [q_{12} = (c_v + R)(T_2 - T_1)]$ or $[q_{12} = c_p (T_2 - T_1)]$

$dh = c_p dT$ & $\Delta h = h_2 - h_1 = \int_1^2 c_p dT = [c_p (T_2 - T_1)]$ if c_p is constant. \therefore since $\Delta h = q_{12}$ all

the heat absorbed by the system during an isobaric process is used to increase the specific enthalpy of the sys. \therefore we can think of enthalpy as a measure of the "heat content" of a sys.

$\bar{d}w = p d\alpha \Rightarrow w = p(\alpha_2 - \alpha_1)$ {if proc is unknown, may make it isobaric by finding/using \bar{p} }

Adiabatic process: by def: $dq = 0 \Rightarrow dq = c_v dT + p d\alpha = 0, \bar{d}q = c_p dT - \alpha dp = 0$ | **Remember:**

$[p\alpha^\gamma = \text{constant}], [T p^{-\kappa} = \text{constant}], [T \alpha^{\gamma-1} = \text{constant}], [T_1 p_1^{-\kappa} = T_2 p_2^{-\kappa}]$ **Poisson Gas Eq** {- $\hat{e}!!$ }

w done during an adiabatic proc (w_i): since $dq = 0, 0 = du + \bar{d}w \Rightarrow \bar{d}w = -du = -c_v dT$

or $w_{12} = -c_v (T_2 - T_1)$ or $w_i = -c_v (T_f - T_i)$ or $w_{12} = \frac{p_2 \alpha_2 - p_1 \alpha_1}{1 - \gamma}$ Also: $[d\theta = 0 \& ds = 0]$

$\otimes p_i \rightarrow p_f$, • specific w - adiabatic • specific w - isothermal.

• adiab $\Rightarrow dq = 0$, so $dw = -du = -c_v dT, T_i p_i^{-\kappa} = T_f p_f^{-\kappa} \Rightarrow T_f = T_i (p_i / p_f)^{\kappa}$

$dw = -c_v dT \Rightarrow w = -c_v (T_f - T_i) = -c_v T_i \left((p_i / p_f)^{\kappa} - 1 \right) \cdot dw = p d\alpha = (RT/\alpha) d\alpha$

$\int dw = RT \int (1/\alpha) d\alpha, \Rightarrow w = RT \ln (\alpha_f / \alpha_i) = RT \ln (p_i / p_f)$ {via Boyle's Law: $p_1 V_1 = p_2 V_2$ }

Quantities and units

Quantity	Derived unit	MKS
Force	Newton [N]	kg · m · sec ⁻²
	Dyne [Dyn]	gm · cm · sec ⁻²
Pressure	Pascal [Pa]	N · m ⁻² OR kg · m ⁻¹ · sec ⁻²
Energy	Joule [J]	N · m OR kg · m ² · sec ⁻²
	Erg	Dyne · cm
Power	Watt [W]	J · sec ⁻¹ OR kg · m ² · sec ⁻³

The ratio between a CGS unit and the corresponding MKS unit is usually a power of 10. A newton accelerates a mass 1000 times greater than a dyne does, and it does so at a rate 100 times greater, so there are 100 000 = 10⁵ dynes in a newton.

Numerical values

N_A is Avogadro's number = 6.022 × 10²³ molecules mol⁻¹ = 6.022 × 10²⁶ molecules kmol⁻¹

1 gram-mole of any gas contains 6.0220943 × 10²³ molecules

1 mole = .001 kilomole

$R^* = 8314.3 \text{ J} \cdot \text{kmole}^{-1} \cdot \text{K}^{-1}$ | Universal gas constant

$R^* = 8.314.3 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$

Reference values (dry air)

$p_0 = 1.01325 \times 10^5 \text{ Pa}$

$\rho_0 = 1.225 \text{ kg} \cdot \text{m}^{-3}$

$c_p = 1004 \text{ J kg}^{-1} \text{ K}^{-1} = 1.00464 \text{ J gm}^{-1} \text{ K}^{-1}$ (const for IG)

$c_v = 717 \text{ J kg}^{-1} \text{ K}^{-1} = 0.7176 \text{ J gm}^{-1} \text{ K}^{-1}$, $c_v = \left(\frac{\partial u}{\partial T} \right)_\alpha$ (for any substance)

$\kappa = 2/7 = 0.286$ (for dry air or IG)

$\gamma = c_p/c_v = 7/5 = 1.4$, value for IG or dry air.

⊗ A sample of 1000 grams of dry air has an initial temp of 270K & pressure 900mb.

During an isobaric process heat is added and the volume expands by 20% of its initial volume. Estimate: a) the final temp of the air. b) the amount of heat added

c) the work done against the env. $m = 1 \text{ kg}$, $T_1 = 270 \text{ K}$, $P_1 = P_2 = 9 \times 10^4 \text{ Pa}$

$$V_2 = (1.2) \cdot V_1 = \frac{1.2 \cdot mRT_1}{p} = \frac{1.2 \cdot (287)(270)}{9 \times 10^4} \Rightarrow V_2 = 1.0332 \text{ m}^3$$

$$V_1 = V_2/1.2 = 0.861 \text{ m}^3 \Rightarrow a) T_f = \frac{pV_f}{mR} = 323 \text{ K}$$

b) $dq = c_p dT - \alpha dp \Rightarrow dq = c_p dT$ (since there is no change in p)

$$dq = c_p (T_f - T_i) = c_p (324 - 270) = 54250.5 \text{ J kg}^{-1} \text{ (1 kg)} = 54250.5 \text{ J}$$

c) $\vec{d}w = p d\alpha \Rightarrow w = p(\alpha_2 - \alpha_1) = 15498 \text{ J}$

CONVERSION FACTORS**Temperature :**

$$\left(\frac{9}{5} \times ^\circ\text{C} \right) + 32 = ^\circ\text{F}; \quad (^\circ\text{F} - 32) \times \frac{5}{9} = ^\circ\text{C}; \quad \text{K} = ^\circ\text{C} + 273.15$$

Area :

$$1 \text{ cm}^2 = 10^{-4} \text{ m}^2 \Leftrightarrow 1 \text{ m}^2 = 10^4 \text{ cm}^2$$

Volume :

$$1 \text{ liter} = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3$$

$$1 \text{ m}^3 = 10^6 \text{ cm}^3 \Leftrightarrow 1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

Force :

$$1 \text{ Dyn} = 10^{-5} \text{ N} \Leftrightarrow 1 \text{ N} = 10^5 \text{ Dyn}$$

Energy :

$$1 \text{ calorie} = 4.18684 \times 10^7 \text{ erg} = 4.18684 \text{ Joule}$$

$$1 \text{ Joule} = 10^7 \text{ erg} \Leftrightarrow 1 \text{ erg} = 10^{-7} \text{ J}$$

$$1 \text{ J gm}^{-1} = 1000 \text{ J kg}^{-1}$$

Pressure :

$$1 \text{ atm} = 1013.25 \text{ mb} = 1013.25 \text{ hPa} = 101.325 \text{ kPa} = 1.01325 \times 10^5 \text{ Pa} = 1.01325 \text{ bar}$$

Density :

$$1 \text{ gm cm}^{-3} = 1000 \text{ kg m}^{-3}$$

⊗ Entropy

$$\Delta s = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right), \quad R = c_p - c_v \Rightarrow c_p = R + c_v$$

$$\Delta s = R + c_v \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{T_2}{T_1} \right) \quad \left\{ \begin{array}{l} \text{System as a whole} \\ \left\{ \leftarrow \text{check on this algebra} \right\} \end{array} \right.$$

$$\left\{ \Delta s = R^* - c_v \ln \left(\frac{T_2}{T_1} \right) - R^* \ln \left(\frac{T_2}{T_1} \right) \right\} \quad \left\{ \leftarrow \text{Version from my notes} \right.$$

$$Tds = du + dw, \quad du = c_p dT$$

$$Tds = c_v dT + p d\alpha \quad (\text{const vol so } p d\alpha \text{ goes to zero})$$

$$ds = \frac{c_v}{T} dT \Rightarrow \Delta s = c_v \ln \left(\frac{T}{T_0} \right)$$

$$\Delta s_1 = \Delta s_{1T} + \Delta s_{1V}, \quad \Delta s_2 = \Delta s_{2T} + \Delta s_{2V},$$

$$\Delta s = \Delta s_1 + \Delta s_2 \quad \{*\} \quad (\text{for system as a whole:})$$

$$\Delta s_{1T} = c_{v1} \ln \left(\frac{T}{T_1} \right), \quad \Delta s_{2T} = c_{v2} \ln \left(\frac{T}{T_2} \right),$$

$$\Delta s_{1V} = m_1 R_1 \ln \left(\frac{V_1 + V_2}{V_1} \right), \quad \Delta s_{2V} = m_2 R_2 \ln \left(\frac{V_1 + V_2}{V_2} \right)$$

In Eq. $\{*\}$, $\Delta s_v > 0$ & Δs_T is either > 0 or $= 0$. If $T_1 = T_2 \Rightarrow \boxed{\Delta s > 0} \Rightarrow$ the process of mixing is irreversible. Irreversible, ie. can't be reversed naturally.

⊗ Assume 2 ideal gases separated by membrane. Both gases have the same temp, but different pressures (p_1 & p_2). Find entropy before mixing, after mixing, and determine a change in s due to mixing.

$$\theta_1 = T_1 \left(\frac{1000 \text{ mb}}{p_1} \right)^{\kappa}, \quad \theta_2 = T_1 \left(\frac{1000 \text{ mb}}{p_2} \right)^{\kappa} \quad ds = c_p d(\ln \theta)$$

$$\Delta s_{\text{before}} = c_p \ln \frac{\theta_2}{\theta_1} \Rightarrow \{ \text{subst from above} \} \Rightarrow \Delta s_{\text{before}} = c_p \ln \left(\frac{p_1}{p_2} \right)^{\kappa}$$

$$\text{After mixing, } p = \frac{p_1 + p_2}{2} \Rightarrow \Delta s_{\text{after}} = c_p \ln \left[T \left(\frac{1000 \text{ mb}}{p_1 + p_2} \right)^{\kappa} + T \left(\frac{1000 \text{ mb}}{p_1} \right)^{\kappa} \right] \Rightarrow$$

$$\Delta s_{\text{after}} = c_p \ln \left[T \left(\frac{2000 \text{ mb}}{p_1 + p_2} \right)^{\kappa} \cdot \frac{1}{T} \left(\frac{p_1}{1000 \text{ mb}} \right)^{\kappa} \right] = c_p \ln \left(\frac{2p_1}{p_1 + p_2} \right)^{\kappa}$$

∴ change in entropy due to mixing:

$$\Delta s = \Delta s_{\text{after}} - \Delta s_{\text{before}} = c_p \ln \left(\frac{p_1}{p_2} \right)^{\kappa} - c_p \ln \left(\frac{2p_1}{p_1 + p_2} \right)^{\kappa} = c_p \ln \left(\frac{2p_2}{p_1 + p_2} \right)^{\kappa}$$

THERMODYNAMICS OF THE WATER SUBSTANCE
VAPOR PHASE - Assumption: H₂O vapor behaves like an Ideal Gas (as long as it's unsaturated).
Eqn. of state for water vapor $\left[e\alpha_v = R_v T \right]$ & $\left[e\alpha_g = R_g T \right]$ where $\alpha_v = V_v/M_v$, & $R_v = R^*/M_v$
 Since $M_v = 18.016$ amu, $R_v = 461.5 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. e is the max p attainable by H₂O vapor for a given T
 Also $e\alpha_v = \left(\frac{M_d}{M_v} \right) R_g T \Rightarrow e\alpha_v = \frac{R_g T}{\varepsilon}$ where $\varepsilon = \frac{M_v}{M_d} = 0.62197$
 By convention, the gaseous phase of a substance is called a vapor if $T < T_s$, & a gas if $T > T_c$.
 When a liquid boils, its temp is that temp at which the saturation vapor pressure = external p .
 $e = 1013.25$ mb when $T_{H_2O} = 100^\circ\text{C}$. \therefore @ sea level H₂O boils @ 100°C ; e is limited by e_s .

LIQUID & ICE PHASE - Both are incompressible. Ice is less dense than H₂O. Opposite of most substances

Eqn. of state for liquid water: $\left[\alpha_w = 1 \text{ cm}^3 \text{ gm}^{-1} = 10^{-3} \text{ m}^3 \text{ kg}^{-1} = \text{constant} \right]$
Eqn. of state for ice: $\left[\alpha_i = 1.091 \text{ cm}^3 \text{ gm}^{-1} = 1.091 \text{ m}^3 \text{ kg}^{-1} = \text{constant} \right]$
Specific Heats of Water Substance
 $c_{pv} = 4R_v = 1846 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, where c_{pv} = specific heat of H₂O vapor at constant pressure
 $c_{vw} = 3R_v = 1384.5 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, where c_{vw} = specific heat of H₂O vapor at constant volume
 $c_w = 4187 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, where c_w = specific heat of liquid water
 $c_i = 2106 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, where c_i = specific heat of ice

Note that for water vapor, $c_{pv} - c_{vw} = R_v$, in analogy with the difference of specific heats of dry air
CHANGES OF HEAT, PHASE etc. Phase changes are always accompanied by changes in α . $\therefore w$ must be done on or by the sys undergoing a phase change, and heat will be liberated or absorbed by the sys.

$ds = \frac{du}{T} + \frac{p}{T} d\alpha$ We can relate the heat of transformation (heat which must be added to the system or liberated by it) to other thermo variables by means of the 1st Law or the Tds eqn.
 u also changes in above situation. If the phase change occurs at constant T , it also occurs at constant p .
Latent Heat (LH)

$T(s_{II} - s_I) = \int_I^{II} dq \Rightarrow l_{II} = T(s_{II} - s_I) \Rightarrow \left[l_{II} = h_{II} - h_I \right]$ Latent heat is = to the diff in enthalpies
 Note: The heat absorbed/liberated by the system when it phase changes from I to II is liberated/absorbed when its phase changes from II to I. $\therefore \left[l_{II} = -l_{II} \right]$
 l_v (0°C) = $2.83 \times 10^6 \text{ J} \cdot \text{kg}^{-1}$; latent heat of sublimation (ice \leftrightarrow vapor);
 l_w (0°C) = $3.34 \times 10^5 \text{ J} \cdot \text{kg}^{-1}$; latent heat of fusion (ice \leftrightarrow water)
 l_w (0°C) = $2.50 \times 10^6 \text{ J} \cdot \text{kg}^{-1}$; latent heat of vaporization (water \leftrightarrow vapor)
 l_w ($T^\circ\text{C}$) = $2.50 \times 10^6 \text{ J} \cdot \text{kg}^{-1} - 2.38 \times 10^3 \cdot T$ ($^\circ\text{C}$); latent heat of vaporization (water \leftrightarrow vapor)
 For most purposes we can treat these as constants, although LHs of transformation are temp dependent.
 When the transformation takes place in a direction from a phase of low molecular activity (MA) to one of higher MA, the heat of transformation must be added to the system. The same amount of heat is liberated by the system when the phase transition takes place in the reverse direction.
 At cons T the heat of sublimation is equal to the sum of the heat of fusion & the heat of vaporization.
 $l_v = h_v - h_i$; $l_w = h_w - h_i$; $l_{vw} = h_w - h_v$; $\Rightarrow l_w = l_{vw} + l_{vw}$

Heat required for temp change of mass $m \Rightarrow Q = mc\Delta T$ Δ Entropy: $\left[\Delta s = mc \int_{T_1}^{T_2} \frac{dT}{T} \right]$ [$\text{J} \cdot \text{K}^{-1}$]

Heat transfer in a phase change. $Q = \pm ml$ **Entropy change in phase change**: $ds = \frac{dq}{T} \Rightarrow$
 $\dots \Delta s$ (Δ phase) $\Rightarrow \Delta s = \int_w^v ds = \int_w^v \frac{dq}{T} \Rightarrow \frac{q_{wv}}{T}$; $\{q_{wv} = l_{wv}\}$ $\Delta s = \frac{Q}{T}$ or $\left[\Delta s = m \frac{l_{wv}}{T} \right]$ [$\text{J} \cdot \text{K}^{-1}$]

$\Delta s_{tot} = \Delta s_1 + \Delta s_2$ etc.
Work in phase change (ex: $w \rightarrow v$): $w_{wv} = \int_w^v p d\alpha = p(\alpha_v - \alpha_w)$. In the conversion from water to steam, the vapor pressure at the boiling point = the external p , i.e. $p = p_{atm} = e$. $\therefore w_{wv} = p\alpha_v - p\alpha_w = w_{wv} = e\alpha_v - e\alpha_w$. {Neglect $e\alpha_w$, since $\alpha_w \ll \alpha_v$.} \therefore From State Eq: $e\alpha_v = R_v T$, $\left[w_{wv} = R_v T \right]$ {Remember to \times by m @ end!}

Internal energy change (ex: $w \rightarrow v$): The best way to compute Δu is to use: $Tds = dq = du + dw \Rightarrow$
 $du = Tds - dw \Rightarrow \Delta u = \int_w^v Tds - \int_w^v dw \Rightarrow \left[\Delta u = T\Delta s - w_{wv} \right]$ [J]

Enthalpy change (ex: $w \rightarrow v$): $dh = d(u + p\alpha) \Rightarrow dh = du + p d\alpha + \alpha dp \Rightarrow \left[dh = du + dw \right]$ | b/c $dp = 0$
 $\left[\Delta h = \Delta u + w_{wv} \right]$ [J] {Note: this is equal to l_{wv} .} \therefore Alternate eqn: $\left[\Delta h = ml_{wv} \right]$ [J] = 2256.71 J

Heat added: $Tds = dq = du + dw \Rightarrow q_{wv} = \int_w^v Tds \Rightarrow \left[q_{wv} = T\Delta s \right]$ [J] $\Rightarrow q_{wv} = l_{wv} = 2256.71 \text{ J}$

Clausius - Clapeyron Equation (CCE):
 $\frac{dp}{dT} = \frac{l_{II}}{T(\alpha_{II} - \alpha_I)}$ Gives the slope of the equilibrium curves in the pT -plane. If $l_{II}, \alpha_I, \alpha_{II}$ are known as functions of abs. temp T , the CCE can be integrated to give e_s as a function of T .

$e_{sw} = (e_s) \exp \left[\frac{l_{sv}}{R} \left(\frac{1}{T_s} - \frac{1}{T} \right) \right]$ | Eqn for the saturation vapor pressure line w/ respect to water
 $\frac{de_{sw}}{dT} = \frac{l_{sv}}{T(\alpha_v - \alpha_w)}$ | Slope of the water-vapor line (vaporization); $\frac{de_{sw}}{dT} = \frac{l_{sw}}{T^2}$ | If l is const.
 $\frac{de_{si}}{dT} = \frac{l_{sv}}{T(\alpha_v - \alpha_i)}$ | Slope of the vapor-ice line (sublimation curves)
 $\frac{dp_{iw}}{dT} = \frac{l_{iw}}{T(\alpha_w - \alpha_i)}$ | Slope of the water-ice line (melting curve)

Empirical formula of Magnus: e_s (mb) = $6.11 \times 10^{a/T} \exp(b/T)$, useful where e_s is given in mb & T is in $^\circ\text{C}$
 $a = 7.567$ $b = 239.7^\circ$ ($T > 0$) } over water
 $a = 7.744$ $b = 245.2^\circ$ ($T < 0$) }
 $a = 9.716$ $b = 271.5^\circ$ ($T < 0$) } over ice

Wet Bulb & Equivalent Temperature
Psychrometric formula: $T_w = T - \frac{l}{c_{pd}} (w_{sw} - w)$ | T_w = wet bulb temp.
 $w_{sw} = \frac{e_{sw}}{p - e_{sw}}$, $e_{sw} = e_s$ @ the wet bulb temp
Equivalent Temp: $T_e = T + \frac{l}{c_{pd}} w$ | Comparing above eqns: $T_w < T$, & $T_e > T$

Thermodynamics of Moist Air (The absence of a subscript in CAR indicates moist air parameters)
 ** Take care to use gm/gm when necessary
 Below LCL: Adiabatic, can use Poisson Eqn, need to adjust constants. Above LCL: Saturated, l
Equation of state for dry air: $p_d V = m_d R_g T$
Equation of state for unsaturated H₂O vapor: $eV = m_v R_v T$; $e\alpha_v = R_v T$; $\alpha_v = V_v/m_v$;
 $m_v = \frac{V e e}{R_d T}$; $\rho_v = e/R_d T$; $e\alpha_v = R_v T/\varepsilon$
Equation of state for saturated vapor: $e_s \alpha_s = R_s T$, $R = \text{gas "const" for moist air}$

Equation of state for moist air: $p = \rho \left(\frac{R^*}{M} \right) T \Rightarrow p = \rho R_d T^*$ | variable due to variable amounts of H₂O vapor which make up moist air
 since $R = R_d (1 - \mu + \mu/\varepsilon)$, $\Rightarrow p = \rho R_d T^* (1 - \mu + \mu/\varepsilon)$ | Avoid calculations for R .

$p \approx \rho R_d (1 + 0.608 \mu)$ $\Rightarrow p = \rho R_d T^* \Rightarrow$ since $\alpha = \frac{1}{\rho} \Rightarrow \left[\alpha_m = \frac{R_d T^*}{p} \right]$
 $R_d = \frac{R^*}{M_d}$; $R_v = \frac{R^*}{M_v}$; $\frac{R_v}{R_d} = \left(\frac{R^*}{M_v} \right) \left(\frac{M_d}{R^*} \right) = \frac{M_d}{M_v} = \frac{1}{\varepsilon}$; $\left[R = R_d (1 - \mu + \mu/\varepsilon) \right]$
 $\left[R = R_d (1 + 0.608 \mu) \right]$ $\varepsilon = \frac{M_v}{M_d} = 0.62197$ Also note for pressure: $\left[p_{tot} = p_d + e_s \right]$

a) Vapor pressure (e, e_s): Use above eqns, &: $e = \frac{w p}{\varepsilon + w}$; $e = e(\alpha_v, T)$; $e_s = e_s(T)$
 For e_s , can use Magnus: e_s (mb) = $6.11 \times 10^{a/T} \exp(b/T)$ (see other sheet for values of a & b)

b) Mixing ratio (w, w_s): $w = \frac{m_v}{m_d} \left[\frac{\text{gm}}{\text{kg}} \text{ or } \frac{\text{gm}}{\text{gm}} \right] = \frac{m_v/V}{m_d/V} = \frac{\rho_v}{\rho_d} = \frac{e \cdot e}{p - e} \rightarrow$ Complete Eqn.
 $w \approx \frac{\varepsilon \cdot e}{p}$ \rightarrow Approximate Eqn. $w = \frac{\mu}{1 - \mu}$; $w_s = \frac{e_s \cdot e_s}{p - e_s}$; $w_s = w_s(p, T)$

When using above formulae, answer will come out "unitless" i.e. \rightarrow gm gm⁻¹
c) Specific Humidity (μ, μ_s): $m_T = m_v + m_d =$ Total mass of moist air.

$\mu = \frac{m_v}{m_T} \Rightarrow \mu = \frac{w}{w+1} \Rightarrow \mu \approx w$ (w & μ usually $\leq 0.04 \frac{\text{gm}}{\text{gm}}$) $\left[\mu_s = \frac{w_s}{w_s+1} \right]$ $\left[\mu = \frac{\varepsilon \cdot e}{p - (1 - \varepsilon)e} \right]$

d) Relative Humidity (r): $r = \frac{e}{e_s} = \frac{w}{w_s} = \frac{\mu}{\mu_s}$, $0 \leq r \leq 1$, $r(\%) = 100 \cdot \frac{e}{e_s}$
e) Absolute Humidity (ρ_v, ρ_s): $\rho_v = \frac{e}{R_v T}$

Dalton's Law of partial pressures: $p = p_d = e$
Virtual Temperature (T^*): $T^* = T(1 - \mu + \mu/\varepsilon)$ or $T^* = \frac{T(1 + 0.608 \mu) - T(1 + 0.608 w)}{1}$
 NOTE: Numerical values for μ & w in T^* Eqn. must be in gm/gm. i.e. they are non-dimensional

$t^* \sim t + \frac{W}{6}$ Practical eqn, where t^* = virtual temp in $^\circ\text{C}$. $W = 1000w$ (i.e. W must be in $\frac{\text{g}}{\text{kg}}$)

Isobaric specific heat of moist air (c_p): $c_p = c_{pd} \left[1 + \mu \left(\frac{8}{\varepsilon} - 1 \right) \right] = c_{pd} (1 + 0.837 \mu)$
Isosteric specific heat of moist air (c_v): $c_v = c_{vd} \left[1 + \mu \left(\frac{6}{5\varepsilon} - 1 \right) \right] = c_{vd} (1 + 0.929 \mu)$

ADIABATIC PROCESSES OF MOIST AIR:
(A) Dry Stage: $\theta_d = T \left(\frac{p_0}{p_d} \right)^{\kappa_d}$, $p_d \alpha_d^{\gamma_d} = \text{constant}$, $\kappa_d = \frac{R_d}{c_{pd}}$, $\gamma_d = \frac{c_{pd}}{c_{vd}}$ | Can use mb in θ_d eqn.
Potential temperature of unsaturated moist air (UMA):
 $\theta_m = T \left(\frac{p_0}{p_d} \right)^\kappa \Rightarrow \theta_m = T \left(\frac{p_0}{p_d} \right)^{\kappa_d (1 - 0.299 \mu)}$, $\kappa = \frac{R}{c_p} = \frac{R_d (1 + 0.680 \mu)}{c_{pd} (1 + 0.837 \mu)} \Rightarrow \left[\kappa = \kappa_d (1 - 0.299 \mu) \right]$
 $\gamma_m = \frac{c_p}{c_v} = \gamma_d (1 - 0.092 \mu)$, $p \alpha^{\gamma_d (1 - 0.092 \mu)} = \text{constant}$. | For practical purposes for UMA, we can use $p_d \alpha_d^{\gamma_d} = \text{const}$ instead, w/ p_d & α_d replaced by p & α
 $\theta_m < \theta_d$ due to the greater heat capacity of the water vapor component.

Adiabatic Isobaric Mixing (Horizontal mixing)
 $\bar{T} \cong \frac{m_1 T_1 + m_2 T_2}{m_{tot}}$; $\bar{e} \cong \frac{m_1 e_1 + m_2 e_2}{m_{tot}}$; $\bar{w} = \frac{\varepsilon \bar{e}}{p - \bar{e}}$; find e_s ; $w'_s = \frac{\varepsilon e_s}{p - e_s}$ | If $\bar{w} > w'_s \Rightarrow$ air is saturated
 If $\bar{e} > e_s \Rightarrow$ air is saturated
 If so, \Rightarrow condensation \Rightarrow latent heat release $\Rightarrow T_{parcel} \uparrow$. need to compute ΔT due to condensation
 $\Rightarrow \Delta T = \frac{l \cdot \Delta w}{c_{pd}}$; $T_s = \bar{T} + \Delta T$; $dc = -\frac{e_s - e}{R_s T_s}$ = liquid water content. {Note: $\bar{w} \cong \frac{m_1 w_1 + m_2 w_2}{m_{tot}}$ }

Pseudo-adiabatic process: A saturation adiabatic process of moist air in which the condensed water substance is removed from the system.
 $m_m = m_d + m_v$ = mass of moist air in the AP; m_w = mass of liquid water
 $m_{tot} = m_m + m_w = m_d + m_v + m_w$ = total mass of the AP
 $m_{H_2O} = m_v + m_w$ = total mass of H₂O substance in the AP $\Rightarrow \frac{m_w}{m_d} = \frac{m_{H_2O}}{m_d} - \frac{m_v}{m_d}$

$\left[(1 + w_s) (c_p dT - \alpha dp) + l_{wv} dw_s = 0 \right]$ Pseudo-adiabatic (or saturated) process of moist air.
 or $\left[c_{pd} dT - R_d T \frac{dp}{p} + l_{wv} dw_s = 0 \right]$ Diff. eqn. of a family of lines on met diagrams: moist adiabats, sat adiabats, pseudo adiabats.

The 2nd eqn above is a simplification of the first based on the assumption that the latent heat released during condensation (sublimation) is used exclusively to heat the dry air component of the air parcel.

Thermodynamic Diagrams

1) $p\alpha$ diagram

Slope: $m_\eta = \frac{dp}{d\alpha} = -\frac{(\partial\eta/\partial\alpha)_p}{(\partial\eta/\partial p)_\alpha}$ $\eta =$ any parameter in diagram which is constant. This is for diagrams w/ $p \uparrow$ upward; If p increases downward, the slope is the negative of this eqn.

$m_T = \frac{dp}{d\alpha} = -\frac{p}{\alpha}$ $m_T =$ slope of an isotherm ($dT = 0$) in a regular $p\alpha$ diagram. Met diagram: $m_T = p/\alpha$; Differential of EoS: $p d\alpha + \alpha dp = R dT$

$m_\theta = \frac{dp}{d\alpha} = -\frac{\gamma p}{\alpha}$ $m_\theta =$ slope of an adiabat; Met diagram: $m_\theta = \gamma p/\alpha$ from fact that $p\alpha^\gamma = \text{constant}$ along any adiabat. Since $\gamma = 1.4$, we note that the adiabats on a $p\alpha$ diagram have a steeper slope than the isotherms.

2) Emagram ($\ln p$ vs T): Isobars & isotherms are the only straight lines.

Assuming an IG: $p\alpha = RT \Rightarrow \alpha = RT/p$; $p = e^{\ln p}$; $\Rightarrow \alpha = RTe^{-\ln p}$

$J\left(\frac{\alpha, p}{T, \ln p}\right) = \begin{vmatrix} Re^{-\ln p} & -RTe^{-\ln p} \\ 0 & e^{\ln p} \end{vmatrix} = R$ $|J| = J = R = \text{const} \Rightarrow$ proportional-area transformation of the $p\alpha$ diagram \Rightarrow eq areas in diff parts represent equal amounts of work (energy) (If $J = 1$, \Rightarrow equal area diagram)

Hence $(w)_{p\alpha} = R(w)_{\ln p}$, where $w =$ work done, & \therefore the Emagram is a proportional-area transformation of the $p\alpha$ diagram.

$m_\theta = -\frac{d \ln p}{dT} = -\frac{1}{\kappa T}$ Slope of an adiabat, where $\theta =$ adiabat, & $\kappa = \kappa_d$ $\theta = T(P_0/P)^\kappa \Rightarrow \ln \theta = \ln T + \kappa \ln P_0 + \kappa \ln P \Rightarrow$

$\ln p = \frac{1}{\kappa} \ln T + \text{const}$, ($\text{const} = \ln P_0 - \frac{1}{\kappa} \ln \theta$).

$m_\alpha = -\frac{d \ln p}{dT} = -\frac{1}{T}$ Slope of an isotherm. IGL: $p\alpha = RT \Rightarrow \ln p + \ln \alpha = \ln R + \ln T \Rightarrow \ln p = \ln T + \text{const}$. ($\text{const} = \ln R - \ln \alpha$)

Comparing above 2 eqns, note that slope of the adiabat is $>$ than slope of isotherm since $\kappa < 1$

$m_{w_s} = -\frac{d \ln p}{dT} = -\frac{1}{R_v T^2}$ Slope of the saturation mixing ratio lines. This slope is independent of any particular w_s -line, i.e., all the saturation-mixing ratio lines have the same slope.

$w_s = \frac{e_s}{p}$, $\Rightarrow e_s = \frac{w_s}{\epsilon} p \Rightarrow \ln e_s = \ln \frac{w_s}{\epsilon} + \ln p$. From the approximate integral of the CCE for

$e_s \Rightarrow \ln e_s = \ln(e_{s,i}) + \frac{l}{R_v} \left(\frac{1}{T_i} - \frac{1}{T} \right) \Rightarrow \ln p = -\frac{l}{R_v T} + \text{const}$ ($\text{const} = \ln(e_{s,i}) + \frac{l}{R_v T_i} - \ln \frac{w_{s,i}}{\epsilon}$)

$m_\theta = -\frac{d \ln p}{dT} = -\frac{1}{\kappa_d T} \left(\frac{1 + w_{s,i}^2 / R_v c_{pd} T^2}{1 + w_{s,i} l / R_v T} \right)$ Slope of the θ_s -lines. Comparison with m_θ shows that sat adiabats have steeper slopes than dry adiabats. At large altitudes, $w_s \rightarrow 0$ & $m_\theta \rightarrow m_\theta$

3) Tephigram (s vs. T or $\ln \theta$ vs. T)

Specific entropy $s = c_p \ln \theta$ or $\ln \theta$ is the vertical coordinate, & K is the horizontal coordinate.

$m_\eta = \frac{ds}{dT} = -\frac{(\partial\eta/\partial T)_s}{(\partial\eta/\partial s)_T}$ or $m_\eta = \frac{d \ln \theta}{dT} = -\frac{(\partial\eta/\partial T)_{\ln \theta}}{(\partial\eta/\partial \ln \theta)_T}$

Most of the slopes can be computed quite readily from the Tds -equations $Tds = c_p dT + p d\alpha$

or $Tds = c_p dT - \alpha dp$, or from $\theta = T \left(\frac{p_0}{p} \right)^\kappa$. To check on the equality of areas, Jacobians can

be cumbersome, better to use Tds eqn realizing that Tds is an element of area in the Tephigram.

$Tds = du + p d\alpha \Rightarrow$ for a cyclic process: $\oint T ds = \oint du + \oint p d\alpha$, ($\oint du = 0$), $\therefore (w)_\alpha = (w)_{T_s}$

\therefore Tephigram (s vs. T) is an equal-area transformation of $p\alpha$ diagram. Equal areas in different portions of the Tephigram represent equal amounts of energy.

4) Stueve Diagram (p^{κ_v} vs. T)

Isobars, Isotherms

5) Log p Skew T Diagram ($\ln p$ vs. T).

As in Emagram, equal areas in different portions of the Skew- T diagram represent equal amounts of energy, i.e. the Skew- T diagram is a proportional-area transformation of the $p\alpha$ -diagram.

Temperature and Humidity Parameters

Dry Temperatures: $T_v = T^* =$ Virtual Temp; $T_e = T_{ie} =$ (isobaric) equivalent Temp;

$T_{ae} = T_{se} =$ adiabatic equivalent, or pseudo-equiv., Temp;

Saturation Temperatures: $T_d =$ Dew point Temp; $T_{sw} = T_{sw} =$ (isobaric) wet-bulb Temp;

$T_{sw} = T_{sw} =$ adiabatic wet-bulb, or pseudo wet-bulb, Temp; $T_s =$ Saturation Temp;

Potential Temperatures: $\theta_e = \theta_{ie} =$ (isobaric) equivalent potential Temp;

$\theta_{ae} =$ adiabatic equivalent, or pseudo-equivalent, potential Temp; $\theta_w = \theta_{sw} =$ (isobaric)

wet-bulb potential Temp; $\theta_{sw} =$ adiabatic wet-bulb, or pseudo-wet-bulb, potential Temp;

Unsaturated: $T_s < T_d < T_{aw} < T_{sw} < T < T_v < T_{ie} < T_{ae}$

Saturated: $T_s = T_d = T_{aw} = T_{sw} = T < T_e < T_{se}$

U_w : NC, NC, NC, C

e or T_d : C, NC, NC, NC

q or r : C, NC, C, NC

T_{sw} or T_{ae} : NC, C, NC, NC

θ : NC, NC, C, NC

θ_{sw} or θ_{ae} : NC, C, C, C

CONVERSION FACTORS

Temperature:

$(\frac{9}{5} \times ^\circ\text{C}) + 32 = ^\circ\text{F}$; $(^\circ\text{F} - 32) \times \frac{5}{9} = ^\circ\text{C}$; $\text{K} = ^\circ\text{C} + 273.15$

Area:

$1 \text{ cm}^2 = 10^{-4} \text{ m}^2 \Leftrightarrow 1 \text{ m}^2 = 10^4 \text{ cm}^2$

Volume: $V = 1 \text{ liter} = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3$

$1 \text{ m}^3 = 10^6 \text{ cm}^3 \Leftrightarrow 1 \text{ cm}^3 = 10^{-6} \text{ m}^3$

Force:

$1 \text{ Dyn} = 10^{-5} \text{ N} \Leftrightarrow 1 \text{ N} = 10^5 \text{ Dyn}$

Energy:

$1 \text{ calorie} = 4.18684 \times 10^7 \text{ erg} = 4.18684 \text{ Joule}$

$1 \text{ Joule} = 10^7 \text{ erg} \Leftrightarrow 1 \text{ erg} = 10^{-7} \text{ J}$

$1 \text{ J gm}^{-1} = 1000 \text{ J kg}^{-1}$

Pressure:

$1 \text{ atm} = 1013.25 \text{ mb} = 1013.25 \text{ hPa} = 101.325 \text{ kPa} = 1.01325 \times 10^5 \text{ Pa} = 1.01325 \text{ bar}$

$1 \text{ hPa} = 100 \text{ Pa}$; $1 \text{ mb} = 10^2 \text{ Pa}$

Density: $\rho = \frac{m}{V}$; $\alpha = \frac{V}{m}$; $\Rightarrow V = \alpha m$; $\therefore \rho = \frac{m}{\alpha m} = \frac{1}{\alpha}$; $\Rightarrow \alpha = \frac{1}{\rho}$

$\rho_w = 1 \text{ gm} \cdot \text{cm}^{-3}$; $\Rightarrow \alpha_w = 1 \text{ cm}^3 \text{ gm}^{-1} = 10^{-3} \text{ m}^3 \text{ kg}^{-1} = \text{constant}$

$1 \text{ gm cm}^{-3} = 1000 \text{ kg m}^{-3}$

Quantities and units

Quantity	Derived unit	MKS	MKS	Derived unit	CGS	CGS
Specific Vol	α		$\text{m}^3 \cdot \text{kg}^{-1}$			
Force	Newton [N]		$\text{kg} \cdot \text{m} \cdot \text{sec}^{-2}$			
Force				Dyne [DYN]		$\text{gm} \cdot \text{cm} \cdot \text{sec}^{-2}$
Pressure	Pascal [Pa]		$\text{N} \cdot \text{m}^{-2}$ OR $\text{kg} \cdot \text{m}^{-1} \cdot \text{sec}^{-2}$		Barye (ba)	Dyne cm^{-2}
Pressure						
Energy	Joule [J]		$\text{N} \cdot \text{m}$ OR $\text{kg} \cdot \text{m}^2 \cdot \text{sec}^{-2}$		Erg	Dyne $\cdot \text{cm}$
Power	Watt [W]		$\text{J} \cdot \text{sec}^{-1}$ OR $\text{kg} \cdot \text{m}^2 \cdot \text{sec}^{-3}$			

⊗ Ice Crystal problem:

A) Initial conditions:

Determine the masses of: i) vapor, ii) Ice, iii) Dry air

B) Final conditions

1) Water substance: ice evaporates, Then max possible vapor pressure at 25C is (eqn of state)

$e_{final} = e_{max} = \frac{m_w R_v T_f}{V}$; since $e_{final} < e_s(25C) \Rightarrow$ all ice evaporates but vapor isn't saturated.

2) Dry air: Can use eqn of state or Charles' Law $p_{df}/T_f = p_{d0}/T_0$ since $v = \text{const}$ & $m_d = \text{const}$

3) Vapor: The last temp at which the vapor is saturated occurs for a temp when $e = e_s$ for the last

time. Can be found graphically or by trial & error. $e = \frac{m_w R_v T}{V}$

\therefore at 0C ice melts, vapor is initially saturated till 12.5C is reached. At end vapor is unsaturated.

-20C: Ice + vapor (sat)

Triple pt: ice + water + vapor

12.5C: all water substance in vapor

25C: moist air (unsat)