THERMODYNAMICS NOTES

These notes give a brief overview of engineering thermodynamics. They are based on the thermodynamics text by Black & Hartley. Topics covered include: concepts; properties; conservation laws; second law statements; entropy; psychrometrics.

THERMODYNAMICS

SOME BASIC CONCEPTS

For thermodynamic calculations, the universe is broken down into two parts: the system and its surroundings. The system is the region of interest: the surroundings is the region external to the system. Thermodynamics deals with the interactions of the system with its surroundings. Heat and work are two types of interactions. Mass exchange is another. There are three types of systems. An open system is one that can exchange mass and energy with its surroundings. A closed system is one that can exchange only energy with its surroundings. An isolated system exchanges nothing with its surroundings.

For thermodynamic calculations, all working substances are assumed to be simple compressible pure substances. A pure substance is one having a homogeneous and fixed chemical composition. Examples are air and water. Simple compressible means that shaft work and volume change work are the only significant work modes. Shaft work devices include pumps and compressors. Systems are assumed to be always in a state of thermodynamic equilibrium. When disturbed from thermodynamic equilibrium, systems usually return rapidly to it because the rate of return is proportional to the molecular speed. To the molecules of a system, the system as a whole seems to be undergoing extreme slow motion. For engineering thermodynamic calculations, the molecular nature of matter is ignored. Matter is assumed to be continuous. This means that no matter how much you zoom in on a bit of matter you never see any molecules. This is known as the macroscopic approach to thermodynamics. The molecular or microscopic approach is used by chemists and physicists and is known as statistical thermodynamics.

Matter in a system or its surroundings can exist single phase as solid or liquid or vapor or multiphase as mixtures. In a solid, the molecules are closely packed and intermolecular forces are large: there is no large scale motion of molecules relative to each other. In a liquid, the molecules move large distances relative to each other: intermolecular forces are significant which tends to make a liquid hold itself together. In a vapor, molecules move large distances relative to each other: intermolecular forces are now insignificant which allows the vapor to expand into the surrounding space.

Any measurable characteristic of a system is known as a property. Properties include : (1) mass (2) volume (3) pressure (4) temperature (5) internal or microscopic energy (6) observable or macroscopic energy (7) enthalpy (8) entropy (9) exergy. The properties of a system determine its state. The state of a system can vary throughout the system. For example, the state at the inlet to a steam turbine is different from the state at the outlet. For a simple compressible pure substance, only 2 independent properties are needed to fix a state. This is known as the state postulate. When a substance exists as a liquid/vapor mixture, there is another property known as the mixture quality which must be considered. When a substance exists as a mixture, pressure and temperature are not independent.

Heat and work are not properties of systems. They are phenomena which occur at the boundary separating a system from its surroundings. Work is energy transfer across the boundary equivalent to a force acting through a distance. Work is considered positive when the system does work on its surroundings. Heat is a flow of energy caused by a difference in temperature between a system and its surroundings. Heat is considered positive when the flow of energy is into the system from the surroundings.

The transformation of a system from one state to another state is known as a process. Often restrictions are imposed on a system during a process. If there is no heat interaction with the surroundings, the process is known as adiabatic. If the process takes place at constant temperature, it is known as isothermal. If it takes place at constant pressure, it is known as isobaric. If it takes place at constant volume, it is known as isochoric or isometric. If it takes place at constant entropy, it is known as isentropic. An isentropic process is one that is frictionless and adiabatic. Flow through a turbine at its design operating point is approximately isentropic. At the operating point, the flow is approximately frictionless because the fluid mates with the turbine blades smoothly. Away from the operating point, the fluid splashes onto the blades and mechanical energy is dissipated by friction in viscous eddies. The fluid moves through the turbine so fast that very little heat flows from it: so the process is approximately adiabatic. Thus the process overall is approximately isentropic. A process which repeats itself periodically is known as a cycle. For example, fluid coming out of a boiler in a steam plant moves next through the turbine and then through a condenser and then through a pump and finally again through the boiler. So, the state of the fluid returns periodically to what it was in the past.

PROPERTIES OF SYSTEMS

Each system has volume and mass. Its volume per unit mass can vary throughout the system. This is known as the specific volume v. It has SI units m^3/kg. The reciprocal of specific volume is density ρ. It has SI units kg/m^3.

Pressure p is a force intensity that acts normal to the surface of bodies that are in a fluid. It has SI units N/m^2 or Pascals. In a gas, pressure results from the recoil force of molecules : in a liquid, intermolecular forces also contribute to pressure.

Temperature T is a measure of molecular kinetic energy. It has SI units K or ^{o}C. In gases, temperature results mainly from translational and rotational motions of molecules. In liquids and solids, intermolecular forces are significant. These forces are spring like. Because of this, molecules tend to vibrate relative to each other. This vibrational motion contributes to temperature.

Internal energy u is a measure of kinetic and potential energy at the microscopic level: kinetic energy results from molecular motion while potential energy results from intermolecular forces. It has SI units kJ/kg. In a gas, intermolecular forces are insignificant so u is due only to kinetic energy: this implies that in a gas internal energy is a function of temperature only.

Systems can also have observable kinetic and potential energies. These are $ke=C^2/2$ where C is a flow speed and $pe=gz$ where g is the acceleration due to gravity.

For many thermodynamic devices, flow or pv work is important. This work has units of energy and appears in equations next to internal energy u as follows $u+pv$. For convenience, we define a new property called enthalpy h which is the sum of internal energy and flow work.

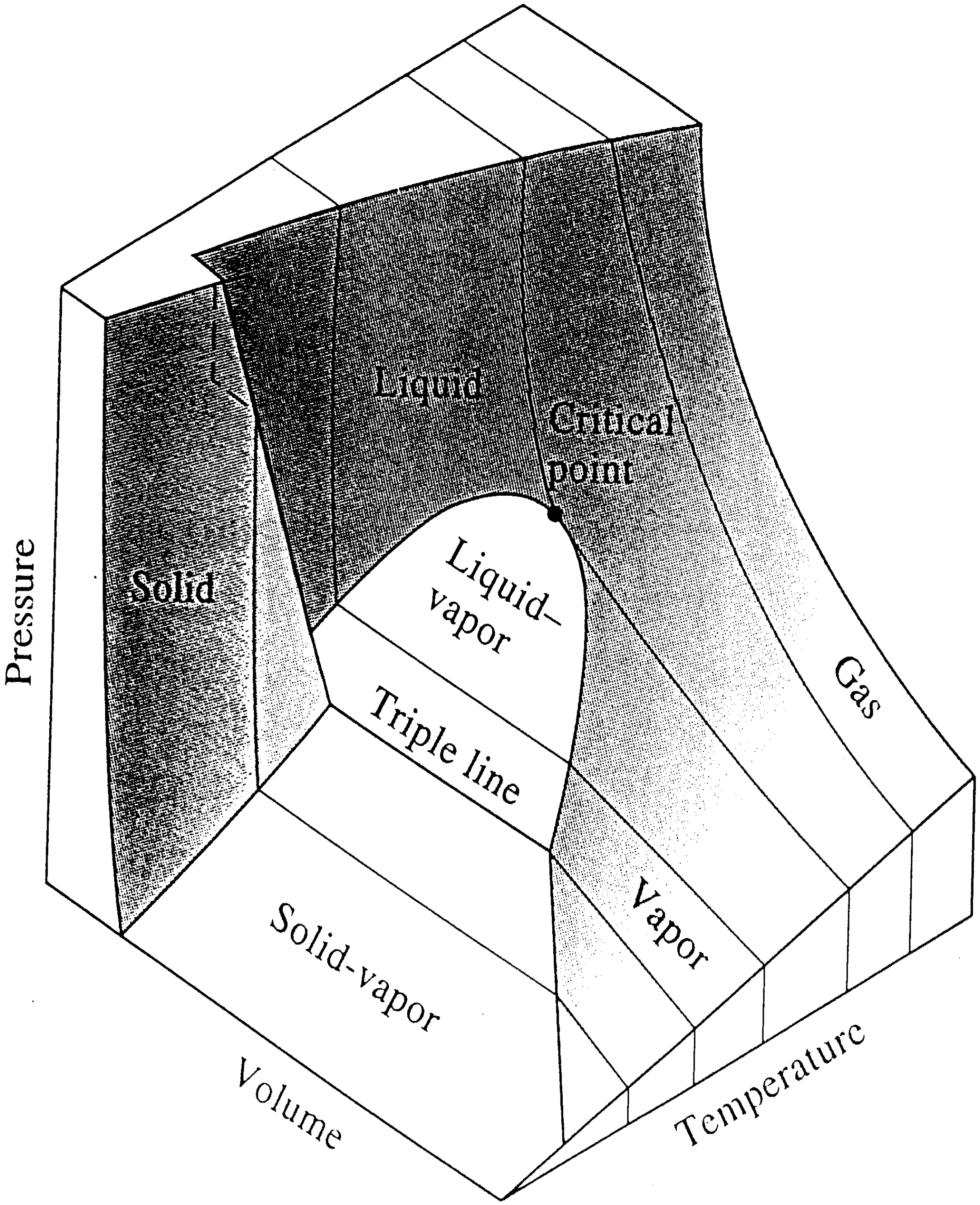
Entropy s is a property used to examine the efficiency of thermodynamic devices. It has units of heat divided by temperature. So it has SI units [kJ/kg]/K.

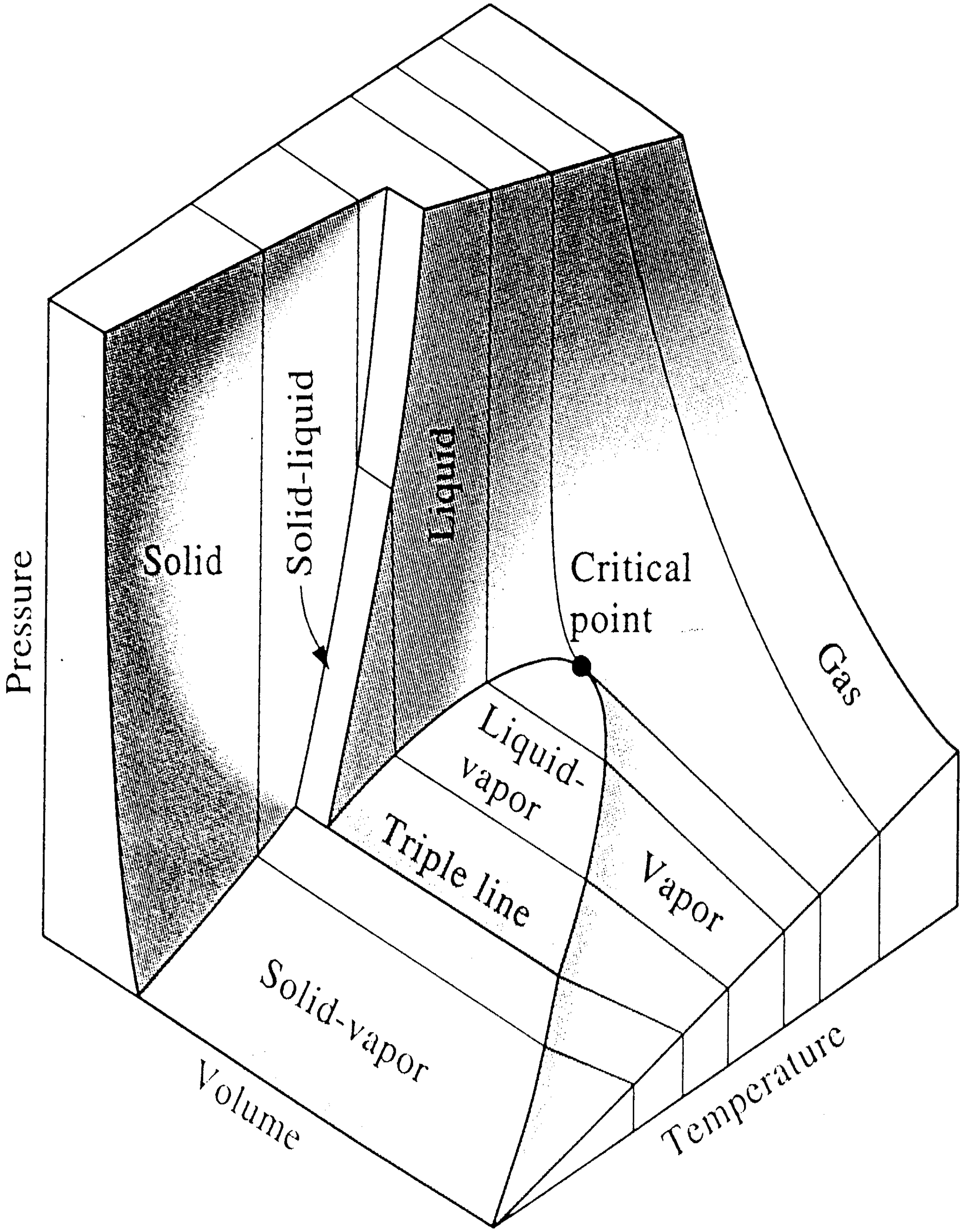
SOLID/LIQUID/VAPOR PHASE EQUILIBRIUM

Matter can exist in a single phase or as a multiphase mixture. Only 2 independent properties are needed to fix a state. We can show the interrelationship between properties in phase diagrams. These are often used when solving thermodynamics problems. They are very much like the free body diagrams used for solving mechanics problems.

A pvT plot for a substance like water that expands upon freezing is shown two pages over. This is followed by a pvT plot for a substance like carbon dioxide that contracts upon freezing. We will focus here on the plot for water. Note that the plot has regions where water exists as a single phase. It also has a region where it exists as a solid/liquid mixture and a region where it exists as a liquid/vapor mixture. There is also a region where it exists as a solid/vapor mixture. A dividing line separating these regions is known as the triple line. All 3 phases are present on this line. Above a certain pressure, the distinction between liquids and vapors disappears and we say we are dealing with a fluid. The pressure where this occurs is known as the critical pressure. Generally, we deal with liquid/vapor mixtures or pure vapors or pure liquids.

Liquid/vapor mixtures are known as saturated mixtures. The enthalpy or energy needed to go across a saturation region along a constant pressure and temperature line is known as a Latent Heat. It is the energy associated with a complete phase change. For liquid/vapor mixtures, it is known as the Latent Heat of Evaporation or Condensation. For solid/vapor mixtures, it is known as the Latent Heat of Sublimation or Solidification. For solid/liquid mixtures, it is known as the Latent Heat of Melting or Freezing. Pure vapors are known as superheated or expanded vapors while pure liquids are known as subcooled or compressed liquids. For example, in a steam plant water exists as a superheated vapor when it enters the turbine. It exists as subcooled liquid when it exits the condenser. Often, it exists as a liquid/vapor mixture when it leaves the turbine. Usually, the quality is high meaning it is almost a pure vapor. If the quality was low, water droplets in the mixture could damage the turbine blades. For most substances, experiments must be used to get data such as pvT plot data. However, for low pressure gases, it has been found that pvT behavior is governed approximately by the simple equation : $pv=pV/m=RT$ where R is the gas constant. This is known as the Ideal Gas Law.


Liquid
Critical point
Solid
Liquid-vapor
Triple line
Gas
Vapor
Solid-vapor
Pressure
Volume
Temperature


Pressure
Solid
Solid-liquid
Liquid
Critical
point
Gas
Liquid-
vapor
Triple line
Vapor
Solid-vapor
Volume
Temperature

NOTES ON PVT PLOTS

PVT plots are plots of experimental data. They can be obtained from constant volume experiments or constant pressure experiments or constant temperature experiments.

The State Postulate tells us that only two independent properties are needed to fix the state of a system. In a single phase region, these can be p and T. However, in a mixture region, p and T are not independent. So, we need another property with p or T to fix the state.

At high specific volume v or volume per unit mass, substances exist as vapors. High v means large distances between molecules: so the vapor state is not surprising. For a set high v, p is a linear function of T: $pv=RT$ where R is a gas constant. This equation is known as the Ideal Gas Law. In the ideal gas region: (1) $\Delta u=C_v\Delta T$ (2) $\Delta h=C_p\Delta T$ (3) $\Delta s=[\Delta u+p\Delta v]/T$ (4) $\Delta s=[\Delta h-v\Delta p]/T$.

As v decreases with T fixed, pressure rises. The pressure rise is steeper for solids. Solids are more difficult to compress than liquids: so the steeper rise is not surprising. Intermolecular repulsive forces are stronger in solids than in liquids.

As you heat a liquid/vapor mixture and move from saturated liquid to saturated vapor along a constant pressure line, temperature does not change. Heat turns liquid into vapor: it does not change the properties of any vapor or liquid already there. The energy per unit mass needed to change from one saturated state to another is known as a latent heat. A latent heat is a change in enthalpy: it involves a change in internal energy and a volume change work due to change in v at constant p.

For substances that expand on freezing like water, increasing pressure at constant T causes the solid phase to melt. This is what happens when a skate blade moves over an ice sheet. The surrounding ice makes the process approximately constant temperature. The blade pressure melts the ice, and the blade rides on a liquid film.

For a constant volume process with v less than the critical point v, a mixture turns into a liquid when heated. When its constant v is greater than the critical point v, a mixture turns into a vapor when heated.

The mass of vapor in a mixture divided by the mixture total mass is known as the mixture quality x.

PROPERTY DATA

The only properties we can easily measure are volume and mass and pressure and temperature. Obviously, there must be a way we can relate these to other properties such as internal energy u and enthalpy h and entropy s. The state postulate shows that only two independent properties are needed to fix a state. We could let u be a function of T and v. Differentiation gives:

$$du = \partial u/\partial T \; dT + \partial u/\partial v \; dv \quad .$$

For a constant volume process, this reduces to $du=C_v dT$ where C_v is known as the constant volume specific heat. We could let h be a function of T and p. In this case, differentiation gives

$$dh = \partial h/\partial T\ dT + \partial h/\partial p\ dp \quad .$$

For a constant pressure process, this reduces to $dh=C_p dT$ where C_p is known as the constant pressure specific heat. Integration of du and dh equations gives u and h data. Specific heats for various substances have been obtained from special experiments and statistical thermodynamics. Conservation of energy for a closed system is:

$$\delta q - \delta w = du$$

where δq and δw indicate heat and work respectively. For closed systems, one can show that $\delta q = Tds$ and $\delta w = pdv$. Substitution into energy gives the Tds relation:

$$Tds = du + pdv \quad .$$

Conservation of energy can be rewritten as:

$$\delta q - \delta w = d(h-pv) \ .$$

Substitution into this gives the Tds relation:

$$Tds = dh - vdp \quad .$$

Dividing the Tds relations by T gives ds equations. Integration of these equations gives s data.

SECOND LAW PHENOMENA

HEAT ENGINES AND HEAT PUMPS

The Second Law of Thermodynamics follows from the fact that heat has never been observed to flow spontaneously from a cold body in thermal contact with a warm body. Instead the spontaneous flow is always from warm to cold. There are two statements of the second law for cycles. One for heat engines is known as the Kelvin-Planck statement. One for heat pumps is known as the Clausius statement. A heat engine is a device that operates in a cycle and does work on its surroundings while extracting heat from a high temperature thermal source and rejecting heat to a low temperature thermal sink. A heat pump is a device that operates in a cycle and receives work from its surroundings while extracting heat from a low temperature thermal source and rejecting heat to a high temperature thermal sink. A thermal reservoir is a very large reservoir of thermal energy. When a system extracts energy from such a reservoir it is known as a thermal source. When a system rejects energy to such a reservoir it is known as a thermal sink. Because it is very large interactions with a system do not change its temperature. According to the Kelvin-Planck statement of the second law it is impossible to construct a heat engine that does work on its surroundings while extracting heat from a single thermal reservoir in its surroundings. According to the Clausius statement it is impossible to construct a heat pump that operates without work input. Both statements are equivalent. The efficiency of any device is gain divided by cost: in other words what you get divided by what you give. For a heat engine it is net work output per cycle divided by heat supplied Q_H per cycle. The net work output is Q_H-Q_L. So the efficiency is: $(Q_H-Q_L)/Q_H$ or $1-Q_L/Q_H$. For a heat pump the efficiency is the heat supplied to the warm space Q_H per cycle divided by the work input per cycle. Again the net work input is Q_H-Q_L. So the efficiency is: $Q_H/(Q_H-Q_L)$ or $1/(1-Q_L/Q_H)$. For a refrigerator the efficiency is the heat extracted from the cold space Q_L divided by the work input. Again the net work input is Q_H-Q_L. So the efficiency is $Q_L/(Q_H-Q_L)$ or $1/(Q_H/Q_L-1)$. Devices that operate on a Carnot cycle have the highest possible efficiency. Carnot cycle devices use infinitely large thermal reservoirs. Every process in these devices is reversible. It can be shown that for such devices $Q_H/Q_L=T_H/T_L$. This implies that for a Carnot heat engine the efficiency is $1-T_L/T_H$. Also for a Carnot heat pump the efficiency is $1/(1-T_L/T_H)$ while for a Carnot refrigerator it is $1/(T_H/T_L-1)$.

CARNOT HEAT ENGINES

We will consider a Piston Cylinder Carnot Heat Engine. Fluid within such an engine undergoes four reversible processes. First the engine fluid picks up heat Q_H from a thermal source with temperature T_H in an isothermal expansion process. The temperature of the fluid is infinitesimally below T_H. The infinitesimal temperature difference between the source and the fluid is needed to make the process reversible. Textbooks generally do not explain why this is so. To pick up a finite amount of heat through such a process requires that the physical contact between the source and the fluid must be infinitely large and the contact time must be infinitely long. Obviously this is not practical. Amazingly the temperature of the fluid does not change when it picks up heat. The engine fluid then undergoes an adiabatic frictionless expansion process. Here the engine does work on its surroundings. The process lowers the temperature of the fluid so that it is infinitesimally above that of a thermal sink with temperature T_L. Next the engine fluid rejects heat Q_L to the thermal sink in an isothermal compression process. Again the infinitesimal temperature difference is needed to make the process reversible. The engine fluid then undergoes an adiabatic frictionless compression process. Here the surroundings does work on the engine. The process increases the temperature of the fluid so that it infinitesimally below that of the thermal source. The engine fluid is now ready to begin another cycle. One corollary of the second law for cycles states that for given T_L and T_H a Real Heat Engine is less efficient than a Carnot Heat Engine. Another corollary states that for given T_L and T_H all Carnot Heat Engines have the same efficiency and this is dependent only on the reservoir temperatures. This efficiency is $1-T_L/T_H$. The physical makeup of the engine and the working fluid are arbitrary. Extrapolation of data from experiments on Real Engines can be used to estimate the efficiency of a Carnot

Engine. For engines operating between the ice and steam points of water they give $0.268=1-T_L/T_H$. But the ice and steam points of water differ by 100 : $T_H-T_L=100$. This gives two equations in two unknowns and allows us to define an absolute temperature scale K=°C+273.15 which is the SI temperature scale. We could also consider a Power Plant Carnot Heat Engine. In this case we would deal with heat transfer rates and work rates. The efficiency of the engine would again depend only on T_L and T_H.

ENTROPY

The property entropy allows us to deal with the Second Law of Thermodynamics in a quantitative way. It allows us to determine how inefficient real devices are relative to ideal devices. We will develop the concept for Heat Engines. For Ideal Heat Engines taking heat Q_H from a thermal source with temperature T_H and rejecting heat Q_L to a thermal sink with temperature T_L Lord Kelvin postulated that $Q_H/Q_L=T_H/T_L$: this implies that $Q_H/T_H=Q_L/T_L$. Now consider the cyclic integral:

$$\delta Q/T = Q_H/T_H - Q_L/T_L \quad .$$

Substitution into this shows that for an Ideal Engine the cyclic integral is zero. For a Real Engine with the same Q_H T_H T_L as the Ideal Engine we know that its Q_L would be greater than that of the Ideal Engine. In this case the cyclic integral would be less than zero.

Now consider an arbitrary Ideal Engine cycle made up of two parts: state 1 to state 2 along one path and then state 2 back to state 1 along another path. If the state 1 to state 2 path is fixed but the state 2 to state 1 path is arbitrary manipulation of the cyclic integral shows that the integral of $\delta Q/T$ along the return path is independent of path. The return integral is the same for all path. Path independence suggests that the integrand must be the differential of some property: we call this property entropy and give it the symbol S.

$$dS = \delta Q/T \quad .$$

Now consider a Real Engine that is ideal from state 1 to state 2 path but real from state 2 to state 1. Let its state 1 to state 2 path be the same as that of the Ideal Engine. Manipulation of the cyclic integral shows that the integral of $\delta Q/T$ or dS along the ideal return path is greater than the integral of $\delta Q/T$ along the real return path. This suggests that for real processes

$$dS > \delta Q/T \quad .$$

Note that for an isolated system δQ is zero. This suggests that for an ideal isolated system the change in entropy within the system is zero while for a real isolated system it is greater than zero. So for a real isolated system like the Universe entropy grows: this in known as the Increase in Entropy Principle.

IDEAL GAS BEHAVIOR

It has been found that behavior of low density gases is governed approximately by the simple equation:

$$pv=pV/m=RT$$

where R is a gas constant. This is known as the Ideal Gas Law. The gas constant R can be obtained from a Universal Gas Constant **R** if the molecular weight M of the gas is known:

R=**R**/M. For air M=28.97 : for water M=18.015. In SI units, the Universal Gas Constant **R** is 8314.

Differential changes in internal energy are:

$$du=C_v dT+\partial u/\partial v dv$$

while changes in enthalpy are:

$$dh=C_p dT+\partial h/\partial p dp$$

where h=u+pv. For an ideal gas u is a function of T only and h=u+RT which implies h is also a function of T only. In this case the du and dh equations reduce to:

$$du=C_v dT \quad dh=C_p dT \quad .$$

In most cases C_v and C_p are approximately constant. Then

$$\Delta u=C_v \Delta T \quad \Delta h=C_p \Delta T \quad .$$

Substitution into dh=du+RdT shows that $R=C_p-C_v$.

For any substance changes in entropy can be obtained from one of the Tds equations:

$$Tds=du+pdv \qquad Tds=dh-vdp \quad .$$

For an ideal gas substitution into these equations give:

$$ds=C_v dT/T+Rdv/v \qquad ds=C_p dT/T-Rdp/p \quad .$$

Integration of these equations from one state to another state gives:

$$s_2 - s_1 = \Delta s = C_v \ln(T_2/T_1) + R \ln(v_2/v_1)$$
$$s_2 - s_1 = \Delta s = C_p \ln(T_2/T_1) - R \ln(p_2/p_1) \quad .$$

For an isentropic process $s_2=s_1$. In this case manipulation of the Δs equations gives:

$$p_2/p_1 = [v_1/v_2]^k$$

where $k=C_p/C_v$. This implies that pvk must be constant.

HVAC systems often contain mixtures of air and water vapor. It is customary to model both the air and the water as ideal gases. There are two ways to show how much water is in the air. One is called the Specific Humidity ω: it is mass of water divided by mass of dry air:

$$\omega = m_w/ma = ([p_wV_w]/[R_wT_w]) / ([p_aV_a]/[R_aT_a])$$

$$= [R_a/R_w][p_w/p_a] = 0.622 [p_w/p_a] = 0.622p_w/[p-p_w].$$

Another measure of water content is known as the Relative Humidity φ. This is actual mass of water divided by mass of water that would be present if air was saturated:

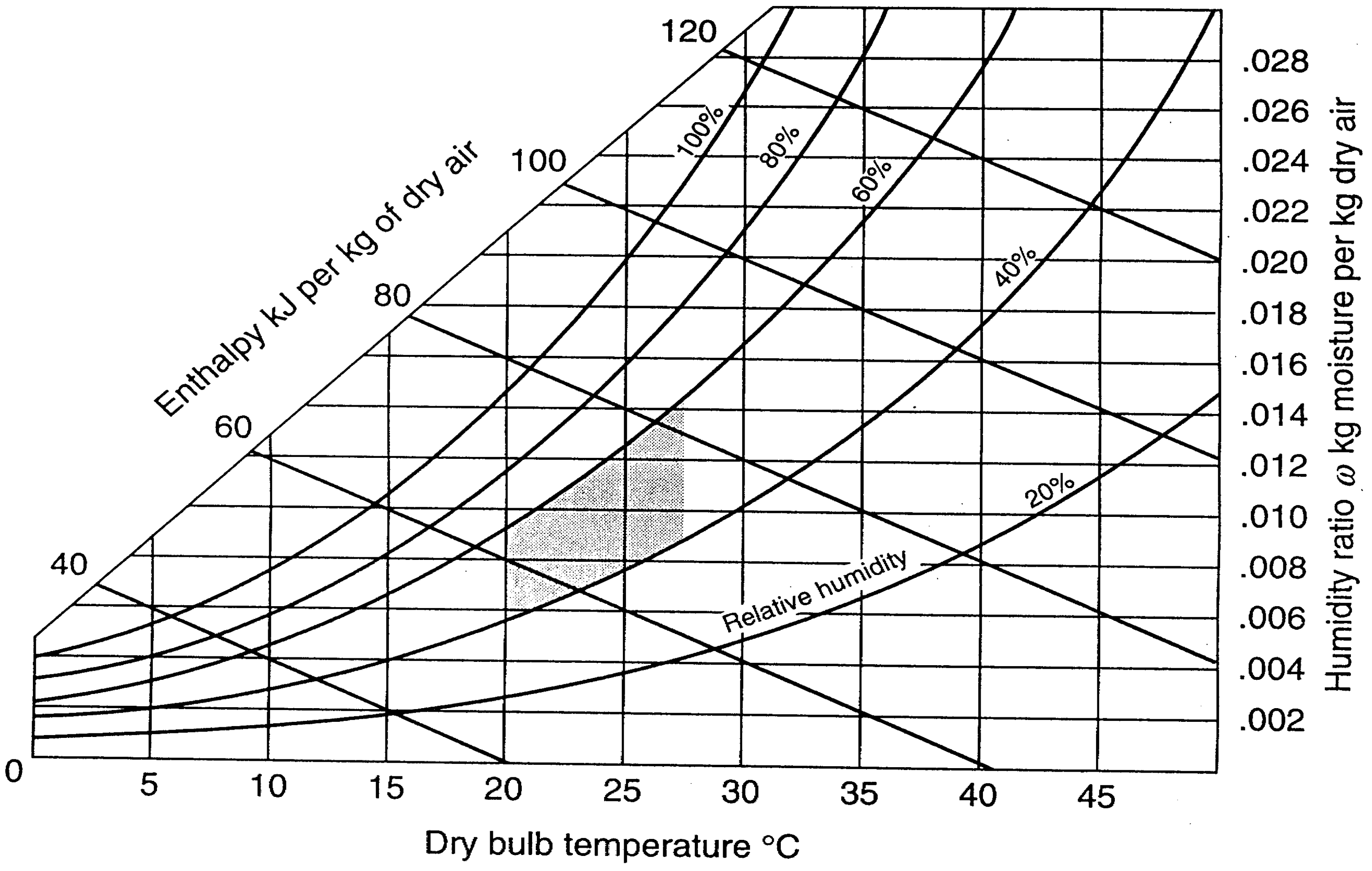
$$\varphi = ([p_wV_w]/[R_wT_w]) / ([p_sV_s]/[R_sT_s]) = p_w/p_s \quad .$$

Manipulations shows that:

$$\varphi = \omega p/[0.622+\omega]p_s \qquad \omega = 0.622\varphi p_s/[p-\varphi p_s] \quad .$$

The total enthalpy in an air/water mixture is: $H=H_a+H_w$. It is customary to express specific enthalpy per unit mass of dry air not total mass. Dividing through by mass of dry air gives : $h = h_a+\omega h_w = h_a+\omega h_s = C_pT+\omega h_s$.

HVAC systems generally operate at around 1 bar pressure. If we set pressure then only 2 other properties are needed to fix the state of an air water mixture. If we know mixture temperature T then all we would need is ω. There are now electronic devices that can give us ω. Such devices did not exist a few years ago. In the past we had to use devices such as the sling psychrometer that gave us wet and dry bulb temperatures. Thermodynamics took these temperatures and gave us ω. HVAC data are often obtained from a psychrometric chart such as that on the next page. This is for 1 bar pressure. It is a plot of dry bulb or normal temperature T on a horizontal axis versus specific humidity ω on a vertical axis on the right and enthalpy h on a slanted axis on the left. Note that the chart contains lines of constant relative humidity φ. Some charts also contain lines of constant wet bulb temperature. Note that on the chart simple heating or cooling operations where water content remains constant show up as horizontal lines whereas humidification or dehumidification operations where water content changes show up as slanted lines.


Enthalpy kJ per kg of dry air
40
60
80
100
120
100%
80%
60%
40%
20%
Relative humidity
.028
.026
.024
.022
.020
.018
.016
.014
.012
.010
.008
.006
.004
.002
Humidity ratio ω kg moisture per kg dry air
0
5
10
15
20
25
30
35
40
45
Dry bulb temperature °C