

Intermediate Thermodynamics

Thermodynamic properties

Fundamentals:

Important property relations start from the first and second Tds equations:

$$T ds - P dv = du \quad (1)$$

$$T ds + v dP = dh \quad (2)$$

We define now two additional properties, the *Helmholtz function* a and the *Gibbs function* g :

$$a \equiv u - T s \quad (3)$$

$$g \equiv h - T s \quad (4)$$

Taking differentials in Eqs. (3) and (4) and using expressions (1) and (2) we can write:

$$da = -P dv - s dT \quad (5)$$

$$dg = v dP - s dT \quad (6)$$

Eqs. (1), (2), (5) and (6) are called *gibbsian equations*. If we apply the test for exactness to these equations we obtain the *Maxwell relations*:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad (7)$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \quad (8)$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (9)$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \quad (10)$$

Generalized relations

The differential change in entropy can be written as a function of T and v as:

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv \quad (11)$$

The next step is to represent ds as a function only of measurables, that is P , v , T , c_v and c_p . We can obtain the desired expression by taking the differential of u also in terms of v and T :

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv = c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \quad (12)$$

and using (1) we obtain:

$$ds = c_v \frac{dT}{T} + \frac{1}{T} \left[\left(\frac{\partial u}{\partial v} \right)_T + P \right] dv \quad (13)$$

thus, combining Eq. (11) with Eq. (13) and using Maxwell relation Eq. (9) we can write:

$$ds = c_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_v dv \quad (14)$$

Eq. (14) gives a relation between measurable quantities and the entropy. It is a *generalized relation* in the sense that are valid for any substance or phase. A second expression for the entropy can be derived similarly to obtain:

$$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_P dP \quad (15)$$

Similarly, a generalized relation for the internal energy can be obtained from Eqs. (1) and (14):

$$du = c_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv \quad (16)$$

For the enthalpy, using Eq. (15) and the second Tds relation Eq. (2) we obtain:

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP \quad (17)$$

The change of the specific heat with pressure and volume is also of interest. If we apply the test for exactness to Eqs. (14) and (15) we can write:

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_v \quad (18)$$

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P \quad (19)$$

and from (19) we can obtain the constant pressure specific heat as:

$$c_p - c_{p,0} = -T \int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP \quad (20)$$

with $c_{p,0}$ the specific heat at zero pressure, which is a relatively easy measurable quantity. The difference $c_p - c_v$ is also a quantity of interest, since either c_p or c_v can be easier to measure depending on the substance and the range of pressures. Using Eqs. (14) and (15) we obtain:

$$(c_p - c_v) \frac{dT}{T} = \left(\frac{\partial P}{\partial T}\right)_v dv + \left(\frac{\partial v}{\partial T}\right)_P dP \quad (21)$$

that after differentiating with respect to pressure at constant volume and rearrangement yields:

$$c_p - c_v = T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P \quad (22)$$

or, using $(\partial P/\partial T)_v = -(\partial v/\partial T)_P (\partial P/\partial v)_T$

$$c_p - c_v = -T \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2 \quad (23)$$

Notice from Eq. (23) that $(\partial P/\partial v)_T$ is always negative, which means that $c_p - c_v$ is either positive or zero. Is zero at the absolute zero temperature, or if $(\partial v/\partial T)_P$ is zero, as in water at 4 °C. Also, for nearly incompressible substances (most liquids and solids), $c_p - c_v$ will be small and is usually taken as zero and c_p is used. In addition, comparison of Eq. (11) with (14) leads to:

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad (24)$$

and using Eq. (15) and the exact differential for ds in terms of dT and dP we get:

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_P \quad (25)$$

which means that isobars have steeper slopes than constant volume lines in a T - s diagram.

Two important derived (and easily measurable) properties are the volumetric expansion coefficient β and the isothermal coefficient of compressibility K_T . These are defined as:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P, \quad K_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad (26)$$

Upon substitution into Eq. (23) we obtain:

$$c_p - c_v = \frac{vT\beta^2}{K_T} \quad (27)$$

In liquids and solids β and K_T are essentially constant over wide ranges of temperature and pressure, thus its use is very convenient.

Residual property functions

We define the residual function y^R as the difference between the actual value of the property y at the (P, T) state and the ideal gas property y^* :

$$y^R = y - y^* \quad (28)$$

The change in the enthalpy between two states can be calculated as:

$$h_2 - h_1 = (h_2 - h_2^*) - (h_1 - h_1^*) + h_{P_2, T_2}^* - h_{P_1, T_1}^* \quad (29)$$

that can be evaluated known the residual enthalpy and the ideal gas variation of c_p with temperature (at zero pressure so the ideal gas model is valid):

$$h_2 - h_1 = h_2^R - h_1^R + \int_{T_1}^{T_2} c_{p,0} dT \quad (30)$$

Similarly, entropy changes can be evaluated from:

$$s_2 - s_1 = s_2^R - s_1^R + \int_{T_1}^{T_2} \frac{c_{p,0}}{T} dT - R \ln \frac{P_2}{P_1} \quad (31)$$

Departure functions

Departure functions are defined in reference to a zero pressure point with the same temperature of the fluid:

$$y^D = y(T, P) - y_0^*(T) \quad (32)$$

The enthalpy can then be calculated in terms of the enthalpy departure functions as:

$$h_2 - h_1 = h_2^D - h_1^D + h_{T_2}^* - h_{T_1}^* \quad (33)$$

Using Eq. (17) we can write:

$$\left(\frac{\partial h}{\partial P} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_P \quad (34)$$

that upon integration at constant temperature leads to:

$$h(T, P) - h(T, P') = \int_{P'}^P v - T \left(\frac{\partial v}{\partial T} \right)_P dP \quad (35)$$

where the reference pressure P' can in particular be zero, in which case the enthalpy reduces to the ideal gas enthalpy at T :

$$h(T, P) - h^*(T) = h^D = \int_0^P v - T \left(\frac{\partial v}{\partial T} \right)_P dP \quad (36)$$

In terms of the compressibility factor we can write the derivative inside the integral in Eq. (35) as:

$$\left(\frac{\partial v}{\partial T}\right)_P = \left(\frac{\partial ZRT/v}{\partial T}\right)_P = \frac{RZ}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T}\right)_P \quad (37)$$

and consequently we can write the integrand in Eq. (36) in terms of Z :

$$v - T \left(\frac{\partial v}{\partial T}\right)_P = \frac{ZRT}{v} - T \left[\frac{RZ}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T}\right)_P \right] = -\frac{RT^2}{P} \left(\frac{\partial Z}{\partial T}\right)_P \quad (38)$$

thus, in terms of reduced properties:

$$v - T \left(\frac{\partial v}{\partial T}\right)_P = -\frac{RT_c}{P_c} \frac{T_R^2}{P_R} \left(\frac{\partial Z}{\partial T_R}\right)_{P_R} \quad (39)$$

and so we can write the enthalpy departure in Eq. (36) as:

$$\frac{h(T, P) - h^*(T)}{RT_c} = \frac{h^D}{RT_c} = -T_R^2 \int_0^P \frac{1}{P_R} \left(\frac{\partial Z}{\partial T_R}\right)_{P_R} dP \quad (40)$$

Eq. (40) can be evaluated for a generalized equation of state and the correction to the ideal gas enthalpy readily obtained. Also, the enthalpy departure is available in tabular form. Fig. 1 shows a chart that gives the departure function on a per-mole basis and can be alternatively employed. Thus the net enthalpy change is evaluated from Eq. (33) and an appropriate method to estimate the enthalpy departure.

In a similar fashion, the entropy change can be evaluated from:

$$s_2 - s_1 = s_2^D - s_1^D + s_{T_2}^* - s_{T_1}^* \quad (41)$$

Using Maxwell relation Eq. (10), $(\partial s / \partial P)_T = -(\partial v / \partial T)_P$, we can write the change in entropy between two states with the same temperature and different pressures:

$$s(T, P) - s(T, P') = - \int_{P'}^P \left(\frac{\partial v}{\partial T}\right)_P dP \quad (42)$$

For the case of an ideal gas we can calculate Eq. (42) using $(\partial v / \partial T)_P = R / P$:

$$s^*(T, P) - s^*(T, P') = - \int_{P'}^P \frac{R}{P} dP \quad (43)$$

and subtracting Eq.(43) from (42) we get:

$$\left[s(T, P) - s^*(T, P) \right] + \left[s(T, P') - s^*(T, P') \right] = \int_{P'}^P \frac{R}{P} - \left(\frac{\partial v}{\partial T} \right)_P dP \quad (44)$$

that, as P' goes to zero (where the real gas behaves as an ideal gas) gives the final result for the entropy departure:

$$s(T, P) - s^*(T, P) = s^D = \int_0^P \left[\frac{R}{P} - \left(\frac{\partial v}{\partial T} \right)_P \right] dP \quad (45)$$

The Z factor can be also introduced in Eq. (45). The integrand can be expressed, in terms of Z and reduced properties:

$$\frac{R}{P} - \left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P_c P_R} \left[(1 - Z) - T_R \left(\frac{\partial Z}{\partial T_R} \right)_{P_R} \right] \quad (46)$$

and replacing into Eq. (45) and using Eq. (40) we obtain the entropy departure:

$$\frac{s(T, P) - s^*(T)}{R} = \frac{s^D}{R} = \frac{h^D}{RT_R T_c} + \int_0^{P_R} \frac{(1 - Z)}{P_R} dP_R \quad (47)$$

The entropy departure for the two-parameter corresponding states principle Z charts is depicted in Fig.2.

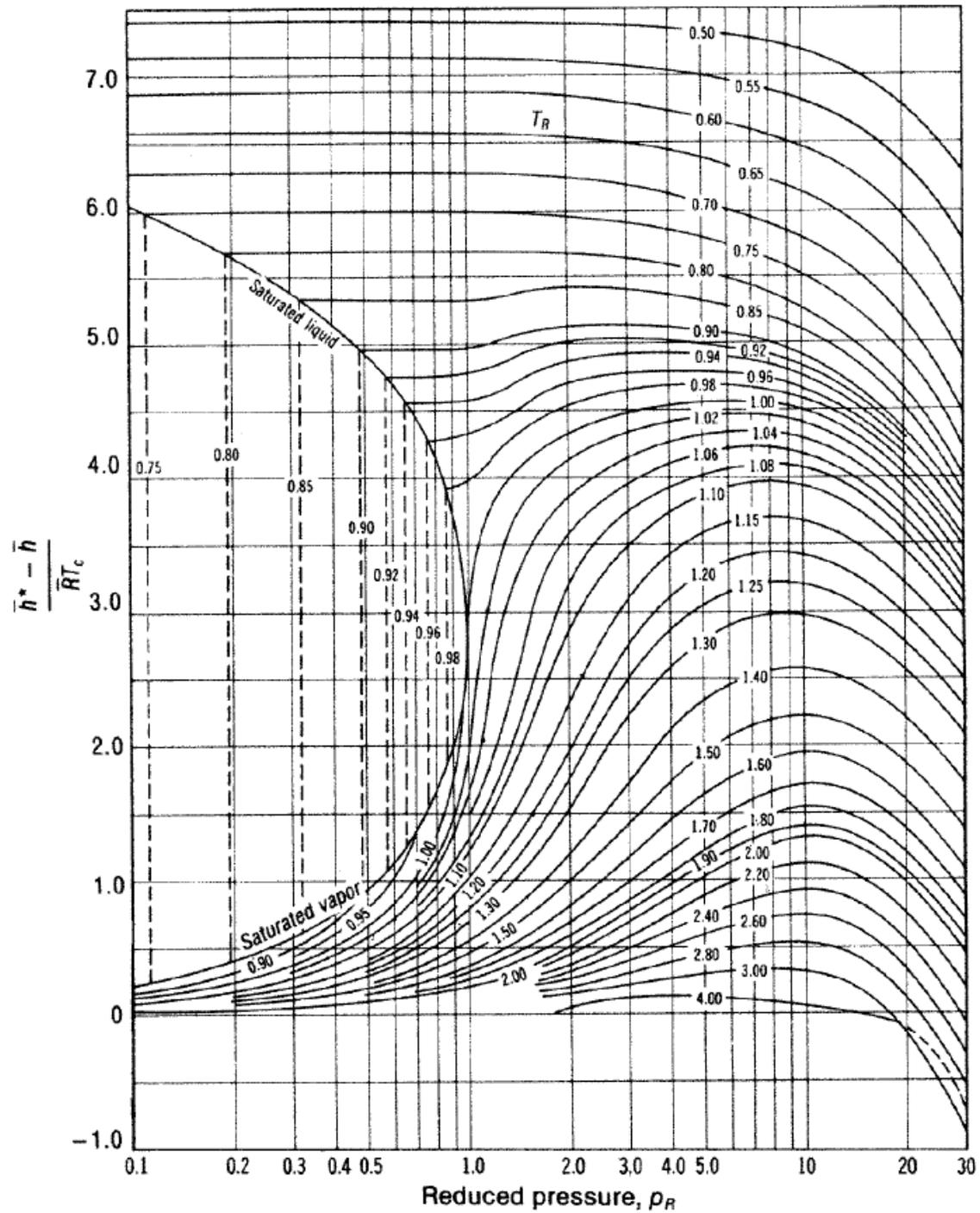


Figure 1: Enthalpy departure chart (from Moran & Shapiro)

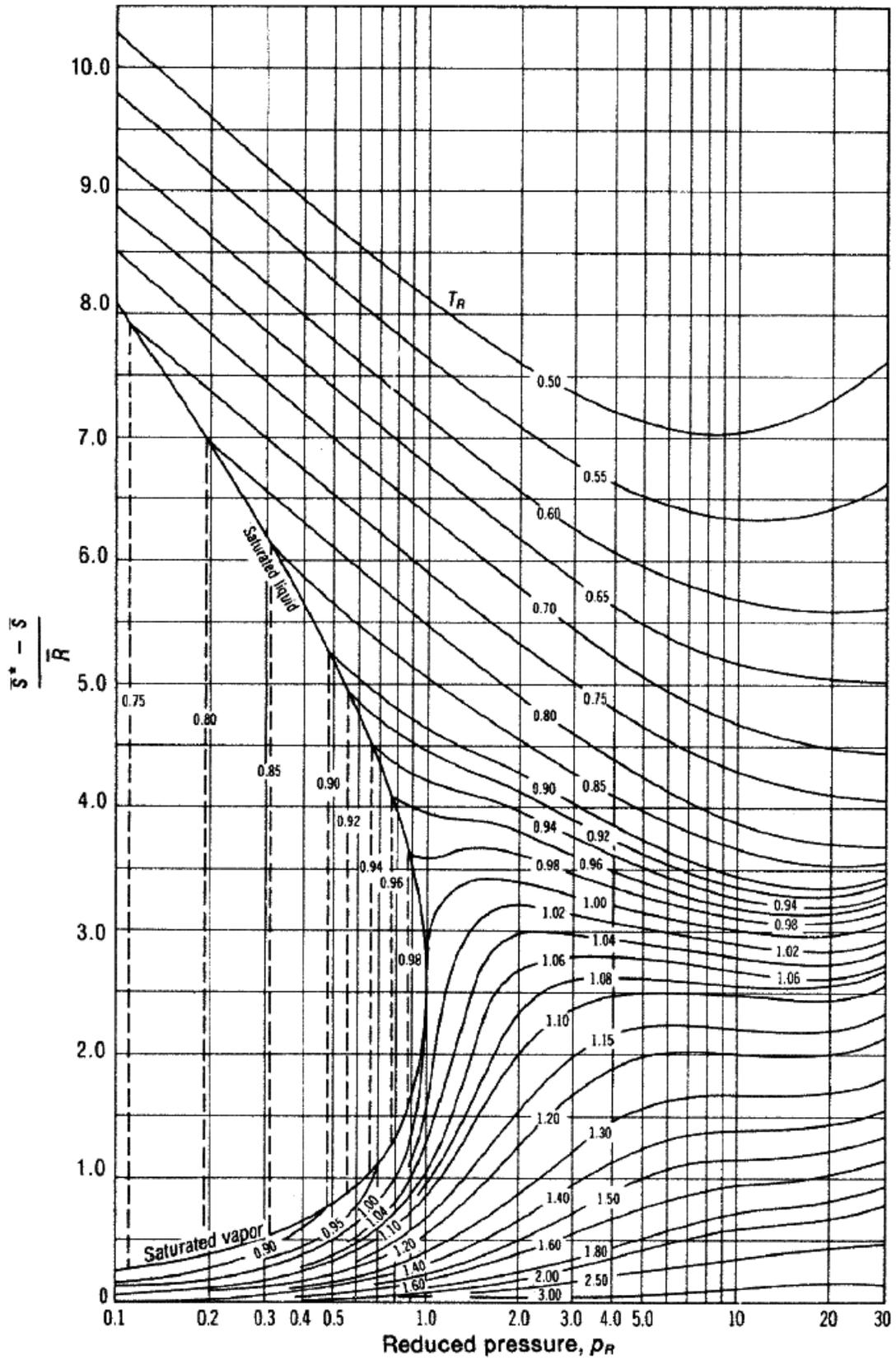


Figure 2: Entropy departure chart (from Moran & Shapiro)

Properties of the Saturation State

We are interested now in analyzing the property behavior in the saturation state of a pure substance. The case we will study is that of liquid-vapor phase change.

The phase transitions (vaporization, melting and sublimation) have a common characteristic: during phase change, the temperature and pressure remain constant. In addition, energy is required to change phases, usually called *latent heat*. If heat is used to promote vaporization, we can write for a simple compressible system:

$$Q_{vap} = \Delta u + p\Delta v = \Delta h \quad (48)$$

$$\Delta s = \frac{\Delta h}{T} \quad (49)$$

Combining the two preceding equations we can write:

$$\Delta h - T\Delta s = 0 \quad (50)$$

As $g \equiv h - Ts$, at constant temperature Eq. (50) states that the Gibbs function is constant in a phase change:

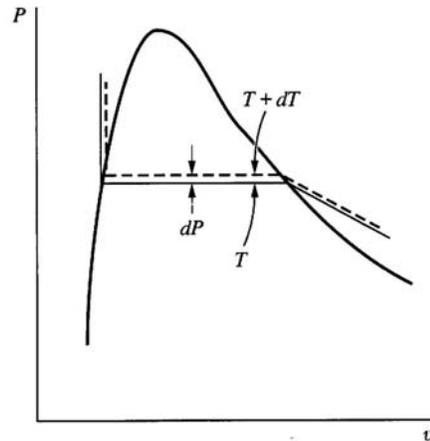
$$g^\alpha = g^\beta \quad (\text{saturation state}) \quad (51)$$

with α and β any two phases in saturation state. Though P and T do not change during phase transitions, both s and v change. Let's restrict our analysis to liquid/vapor systems. From Eq. (6), $dg = v dP - s dT$, thus:

$$v = \left(\frac{\partial g}{\partial P} \right)_T \quad s = - \left(\frac{\partial g}{\partial T} \right)_P \quad (52)$$

As the specific volume and the entropy change discontinuously during a phase change, the Gibbs function will change discontinuously on the first derivative. This is called a *phase change of first order*. Fig. 3 illustrates this. Notice that c_p goes to infinity on the two-phase mixture (see Eq. 25).

Let's consider the case of a change in temperature dT and pressure following the saturation line, as shown in the diagram. The Gibbs function on the initial state will satisfy $g_i^l = g_i^v$ on the saturated liquid and vapor phases. The final state will satisfy



$g_i^l + dg^l = g_i^v + dg^v$, thus:

$$dg^l = dg^v \quad (53)$$

Using Eq. (6), we can rewrite this equation as:

$$v^l dP - s^l dT = v^v dP - s^v dT \quad (54)$$

which leads to the relation:

$$\left. \frac{dP}{dT} \right|_{sat} = \frac{s^v - s^l}{v^v - v^l} \quad (55)$$

that in combination with Eq. (50) results in the *Clapeyron equation*:

$$\left. \frac{dP}{dT} \right|_{sat} = \frac{\Delta h}{T \Delta v} = \frac{h_{fg}}{T v_{fg}} \quad (56)$$

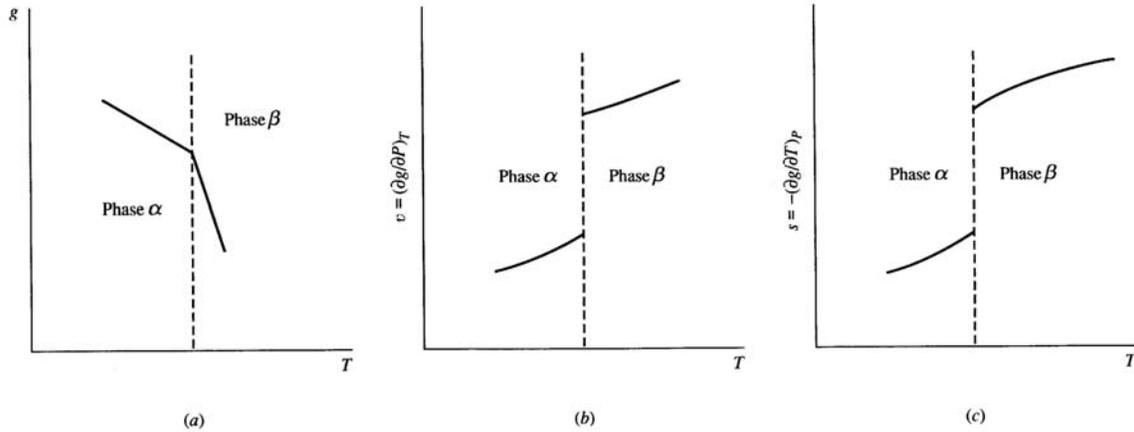


Figure 3: A first order phase change (from Wark)

In Eq. (56) the phase change enthalpy, in this case evaporation enthalpy h_{fg} and the phase change specific volume v_{fg} are related to the slope of the saturation line in a P - T diagram. The enthalpy and volume of vaporization are measured for many substances under wide ranges of conditions, since are important parameters and relatively easy to measure. For the case of evaporation and sublimation, under the ideal gas assumption, the change in volume can be approximated by $\Delta v \cong RT/P$, thus Eq. (56) reduces to:

$$\left. \frac{dP}{P} \right|_{sat} = \frac{\Delta h dT}{RT^2} \quad (57)$$

or

$$d \ln P^{sat} = -\frac{\Delta h}{R} d 1/T \quad (58)$$

Eqs. (57) and (58) are different expressions of the *Clausius-Clapeyron equation*, that relates vapor-pressure data with the enthalpy of phase change.

Eq. (58) can be integrated assuming that the enthalpy of phase change is constant, resulting in:

$$\ln P^{sat} = -\frac{\Delta h}{RT} + const \quad (59)$$

that suggests that a straight line should result in a plot of $\ln P^{sat}$ versus $1/T$. This is actually the experimental finding, though the line extends from the triple point to the critical point, even though the evaporation enthalpy h_{fg} has a strong variation on this range. The reason for this unexpected behavior lies in that the errors of assuming ideal gas and constant enthalpy of phase-change actually cancel out. A more adequate equation would be $\Delta v = (Z_g - Z_f)RT/P = \Delta Z RT/P$, which results in the modified Clausius-Clapeyron equation:

$$d \ln P^{sat} = -\frac{\Delta h}{R \Delta Z} d 1/T \quad (60)$$

where the ratio $\Delta h / \Delta Z$ remains essentially constant for most simple fluids, resulting in a straight line. Close inspection to the accurate line reveals that the actual behavior has a S-shape in a $\ln P^{sat}$ versus $1/T$ plot.

As a consequence of the previous discussion, Eq. (59) suggests that a good correlation for many fluids would be of the form:

$$\ln P^{sat} = A - \frac{B}{T} \quad (61)$$

where the constants A and B can be easily obtained from two easily measurable points. The first is the normal boiling, defined by the boiling temperature T_b at atmospheric pressure. The second is the critical point. After solving for A and B in Eq. (61) we get:

$$\ln P^{sat} = \frac{T_c \ln P_c}{T_c - T_b} \left(1 - \frac{T_b}{T} \right) \quad (62)$$

where pressures are in bar and temperatures in Kelvin. Eq. (62) is fairly accurate over a wide range of temperatures. Other more accurate correlations are available, though no much additional data is usually available, and therefore not too many variables can be adjusted. A typical more complete correlation is:

$$\ln P^{sat} = A + \frac{B}{T} + CT + DT^2 + E \ln T \quad (63)$$

where the term in natural logarithm of the temperature appears after assuming a linear dependence of h_{fg} with the temperature.

We can express Eq. (61) in terms of the reduced pressure and temperature to obtain a two-parameter format of the corresponding states principle:

$$\ln P_R^{sat} = A' \left(1 - \frac{1}{T_R^{sat}} \right) \quad (64)$$

that predicts that on reduced coordinates, all the fluids follow a line with the same slope. This slope is experimentally found to be 5.3 for simple fluids (see Fig. 3 in the chapter on Equations of State). For general fluids the accuracy of Eq. (64) is poor, as expected, and more complex equations, including a third parameter like the acentric factor can be used.

The Joule-Thompson Coefficient

To achieve a reduction in the temperature required in refrigeration systems, we can undergo basically an adiabatic expansion (as happens typically on a turbine). A second method to accomplish a reduction in temperature is to use an expansion valve. This is a simple throttling device in which a significant pressure drop occurs, thus the enthalpy remains constant if the device is well insulated and kinetic and potential energy changes can be neglected.

The Joule-Thompson coefficient relates the change in temperature with pressure of a throttling process, i. e. :

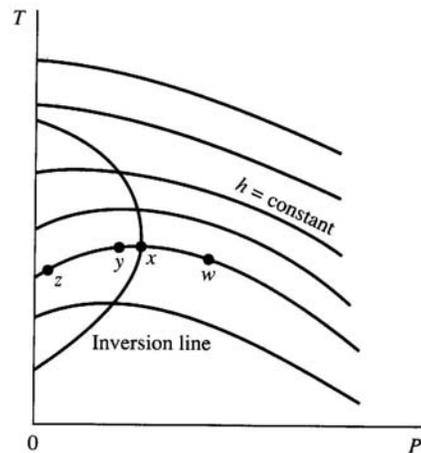


Figure 4: throttling process in a P - T diagram

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_h \quad (65)$$

We note that from Eq. (65) the temperature will increase if the Joule-Thompson coefficient is negative and will decrease if μ_{JT} is positive. Fig. 4 shows a typical P - T diagram of a throttling process, in which lines of constant h are shown. Also shown is the inversion line, defined as the line joining the points in which the h =const curves have zero slope, equivalent to $\mu_{JT} = 0$.

In a typical throttling process, we can have the inlet fluid, before the expansion valve, at a state w . After the throttling device the pressure has been reduced, to either of states x , y or z . At state x the temperature is higher than the original temperature, since the average Joule-Thompson coefficient is negative. The opposite occurs at state z . As the inversion line has two temperatures for each pressure, we refer to those temperatures as upper and lower inversion temperatures.

Figure 5 shows the Joule-Thompson coefficient for air at different temperatures and pressures. Note that in air μ_{JT} is positive at normal pressure and temperature. Other fluids, like hydrogen and helium, have positive μ_{JT} only at very low temperatures.

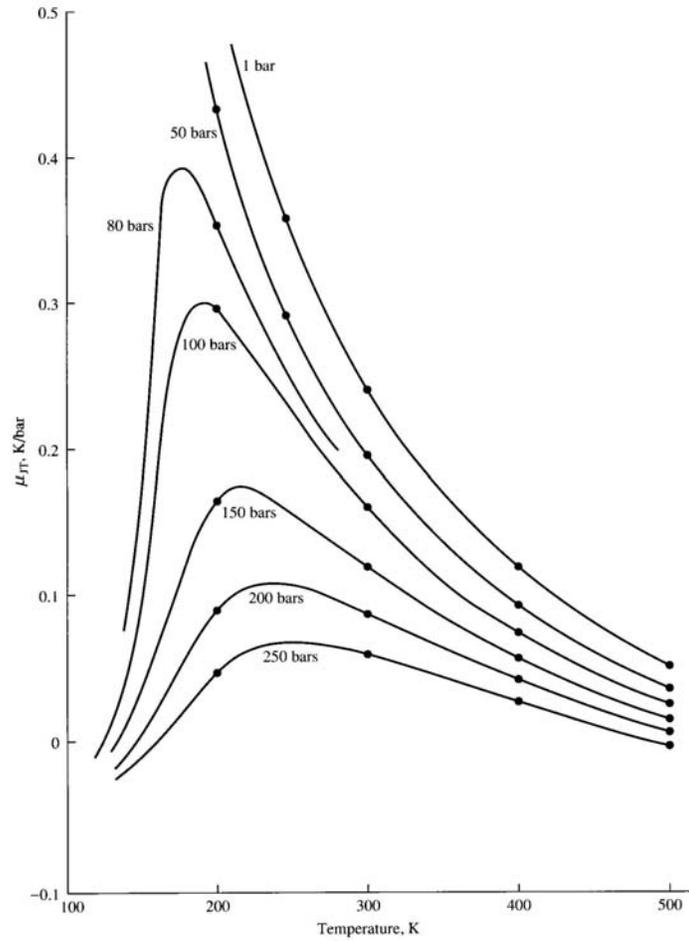


Figure 5: Joule-Thompson coefficient in air.
(from Wark)

As the Joule-Thompson coefficient is defined only in terms of properties (see Eq. 65), then is a property. We can write, using the cyclic relation and the definition of c_p :

$$\left(\frac{\partial h}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_P \left(\frac{\partial P}{\partial h} \right)_P = -1 \quad (66)$$

$$\mu_{JT} \equiv -\frac{1}{c_p} \left(\frac{\partial h}{\partial P} \right)_T \quad (67)$$

and using Eq. (17) we can express the Joule-Thompson coefficient as:

$$\mu_{JT} = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right] \quad (68)$$

Using an equation of state, we can evaluate the Joule-Thompson coefficient over a wide range of temperatures and pressures. Using the generalized equation of state $Pv = ZRT$ we obtain:

$$\mu_{JT} = \frac{RT^2}{Pc_p} \left(\frac{\partial Z}{\partial T} \right)_P \quad (69)$$

therefore μ_{JT} is positive if $\partial Z/\partial T$ is positive. An analysis of the compressibility chart shows that this happens for reduced pressures below 10 and for reduced temperatures below 5. Fig. 6 shows a diagram based on experimental data of the Joule-Thompson coefficient as a function of reduced pressure and temperature, showing that the Z-chart has the right general trend.

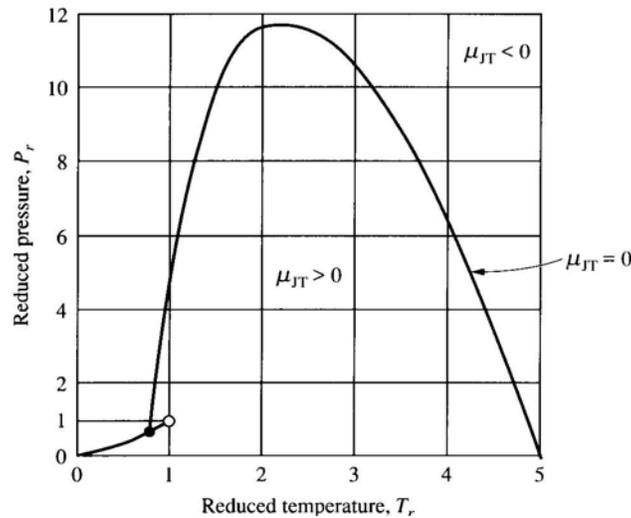


Figure 6: Inversion curve on reduced coordinates.

The Third Law of Thermodynamics

The entropy as defined as a corollary of the Second Law of Thermodynamics states that:

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{int rev}} ; \quad \Delta s = \int_1^2 \left(\frac{\delta q}{T} \right)_{\text{int rev}} \quad (70)$$

and for a simple compressible substance we use the second Tds relation, Eq. (2), to obtain:

$$\Delta s = \int_1^2 \frac{dh}{T} - \int_1^2 \frac{v dP}{T} \quad (71)$$

In a general real substance, the evaluation of the entropy changes requires the measurement of P , v , T , c_p and the enthalpies of phase change, and then the integrals in Eq. (71) can be evaluated. Let's consider for example the substance shown in Fig. 7, undergoing a process at constant pressure that we want to use to measure the entropy change at that given pressure. The substance undergoes a phase change between solid phase α and solid phase β , then at a higher temperature solid phase β melts in a phase change to liquid, finally a third phase change occurs from liquid to gas. During these phase changes, the change in entropy can be evaluated as:

$$\Delta s = \frac{\Delta h_{ab}}{T} \quad (72)$$

since during a phase change the process is isothermal.

The change in entropy on the single-phase regions solid, liquid and gas can be written as a function of the specific heat at constant pressure, since $c_p = (\partial h / \partial T)_P$:

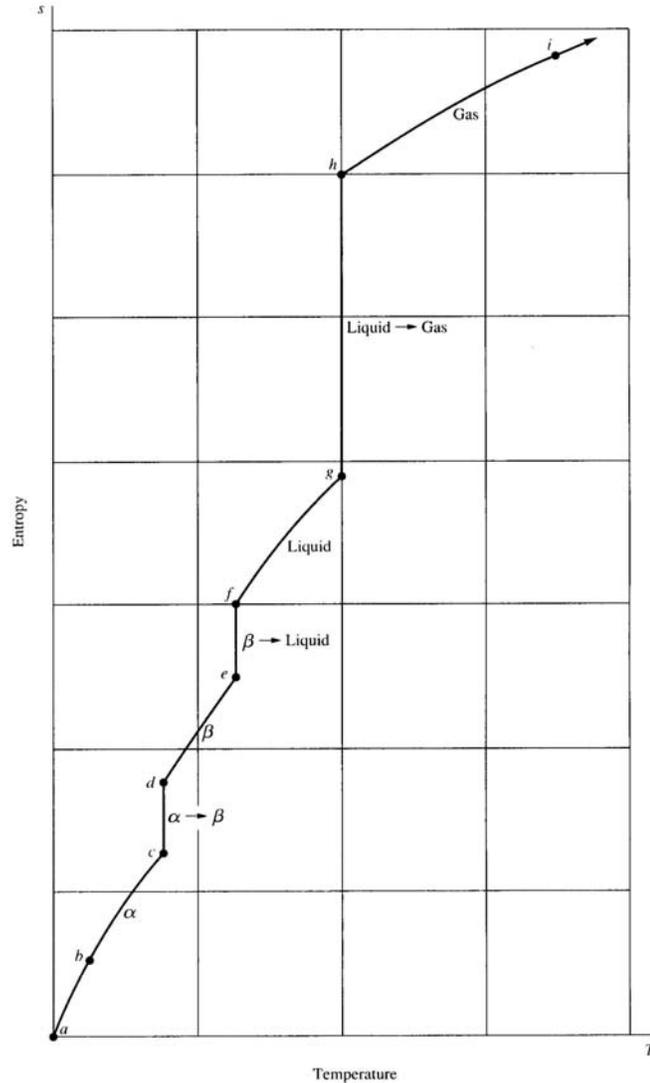


Figure 7: change in entropy at constant pressure.

$$\Delta s = \int_{T_1}^{T_2} \frac{dh}{T} = \int_{T_1}^{T_2} c_p \frac{dT}{T} \quad (73)$$

Consequently, the entropy value at some state is given by:

$$s = s_0 + \sum_j \int_j c_p \frac{dT}{T} + \sum_k \frac{\Delta h_k}{T} \quad (74)$$

where s_0 is the entropy at absolute zero temperature. The Third Law of Thermodynamics states that $s_0=0$, which allows us to define an absolute entropy scale. Since we don't know how to calculate s_0 from the First Law and the Second Law of Thermodynamics, the reference point set equal to zero is a new first principle and is called the Third Law.

The reference value of the entropy at zero absolute temperature has been initially suggested by Plank. Nernst & Simon statement of the Third Law is:

$$\lim_{T \rightarrow 0} \Delta s_T = 0 \quad (75)$$

which means that the change of the entropy tends to zero as the temperature tends to absolute zero. This has been verified by a number of experiments, including phase changes at very low temperature in He⁴, where it was found that:

$$\lim_{T \rightarrow 0} \frac{dP}{dT} = \lim_{T \rightarrow 0} \frac{\Delta s}{\Delta v} = 0 \quad (76)$$

which implies that the entropy change tends to zero since the volume is finite. Measurements on the coefficient of volumetric expansion have shown that:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \left(\frac{\partial s}{\partial P} \right)_T \quad (77)$$

tends to zero as we approach the absolute zero temperature.

Einstein and Debye Theories

Read the notes on Thermodynamics Properties from previous years.

Homework

1.- Nitrogen gas is compressed isothermically at 250 K from 1 bar to 150 bar. Determine the enthalpy change for the process, in kJ/kmol, by:

- a) employing the truncated virial equation: $Pv = RT + bP$, where
$$b = 39.5 - 10^4/T - 1.084 \cdot 10^6/T^2 \text{ cm}^3/\text{gmol}, \quad T \text{ in K.}$$
- b) using a two-parameter generalized enthalpy chart.
- c) using tabular data.

2.- He⁴ boils at 4.22 K at 1 bar, with an enthalpy of vaporization of 82.3 kJ/kmol. Reducing the pressure on the liquid phase, the fluid boils at a lower temperature. Estimate the pressure, in millibars, necessary to produce a temperature of 2 K.