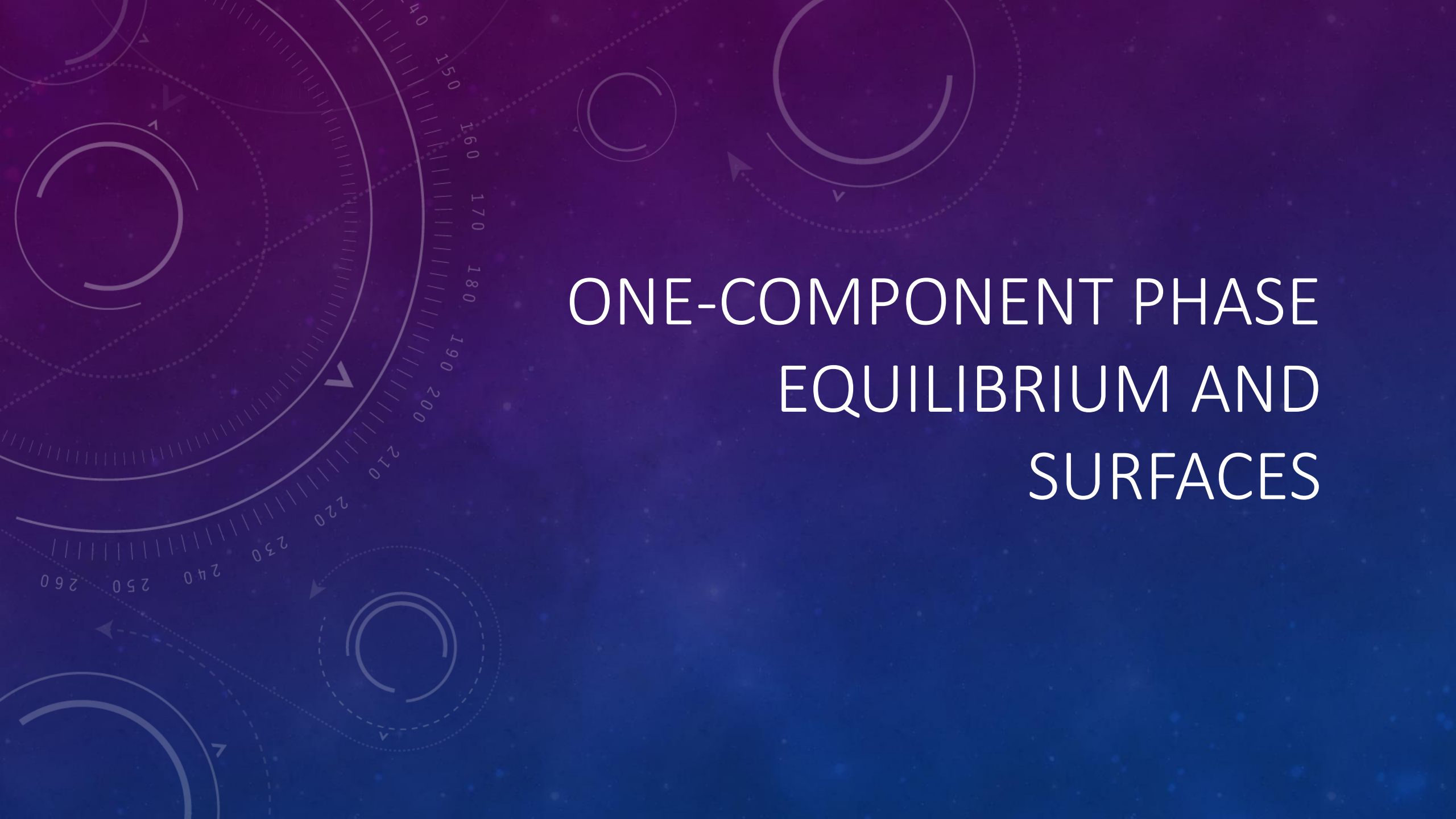


The background is a dark blue gradient with a subtle pattern of white dots. Overlaid on the left side are several concentric circular patterns. One large circle has a scale from 140 to 260 in increments of 10, with tick marks. Other circles of varying sizes are scattered around, some with arrows indicating a clockwise direction. The text is positioned on the right side of the image.

ONE-COMPONENT PHASE EQUILIBRIUM AND SURFACES

PHASE RULE

- A PHASE is a homogeneous portion of a system. A system may have several solid phases and several liquid phases but usually has at most one gas phase.
- To describe the equilibrium state of a system with several phases and several chemical species, we can specify the mole numbers of each species in each phase and the temperature and pressure, T and P; as intensive variables (some are not independent var).
- The number of degrees of freedom (or the variance) f of an equilibrium system is defined as the number of independent intensive variables needed to specify its intensive state.
- We initially make two assumptions, which will later be eliminated:
- (1) No chemical reactions occur and (2) Every chemical species is present in every phase.
- In the equation below, c = # of chemical species; p = # of phases; f = degrees of freedom

$$f = c - p + 2 \quad \text{no reactions}$$

EXERCISE

Find f for a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose.

The system has two chemical species (water and sucrose), so $c = 2$. The system has two phases (the saturated solution and the solid sucrose), so $p = 2$. Hence

$$f = c - p + 2 = 2 - 2 + 2 = 2$$

Two degrees of freedom make sense, since once T and P are specified, the equilibrium mole fraction (or concentration) of sucrose in the saturated solution is fixed.

Sucrose (s) and Sucrose (aq) are identical chemical species. They just differ in their phases.

THE PHASE RULE IN SYSTEMS WITH REACTIONS

Each independent chemical reaction provides one relation between the chemical potentials and can be used to eliminate one variable from T , P , and the mole fractions. If the number of independent chemical reactions is r and the number of additional restrictions a , then the number of independent intensive variables is reduced by r and a the phase rule becomes:

$$f = c - p + 2 - r - a$$

By independent chemical reactions, we mean that no reaction can be written as a combination of the others. We can preserve the simple form for the phase rule by defining the number of independent components c_{ind} as:

$$f = c_{ind} - p + 2$$

EXERCISE

For an aqueous solution of the weak acid HCN, write the reaction equilibrium conditions and find f and c_{ind} .

The system has the five chemical species H_2O , HCN , H^+ , OH^- , and CN^- , so $c = 5$. The two independent chemical reactions $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ and $\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$ give two equilibrium conditions: $\mu_{\text{H}_2\text{O}} = \mu_{\text{H}^+} + \mu_{\text{OH}^-}$ and $\mu_{\text{HCN}} = \mu_{\text{H}^+} + \mu_{\text{CN}^-}$. The system has $r = 2$. In addition, there is the electroneutrality condition $n_{\text{H}^+} = n_{\text{CN}^-} + n_{\text{OH}^-}$; division by n_{tot} gives the mole-fraction relation $x_{\text{H}^+} = x_{\text{CN}^-} + x_{\text{OH}^-}$. (See also Prob. 7.6.) Thus, $a = 1$. The phase rule (7.9) gives

$$f = c - p + 2 - r - a = 5 - 1 + 2 - 2 - 1 = 3$$

$$c_{ind} = c - r - a = 5 - 2 - 1 = 2$$

EXERCISE

Find f in a system consisting of $\text{CaCO}_3(s)$, $\text{CaO}(s)$, and $\text{CO}_2(g)$, where all the CaO and CO_2 come from the reaction $\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$.

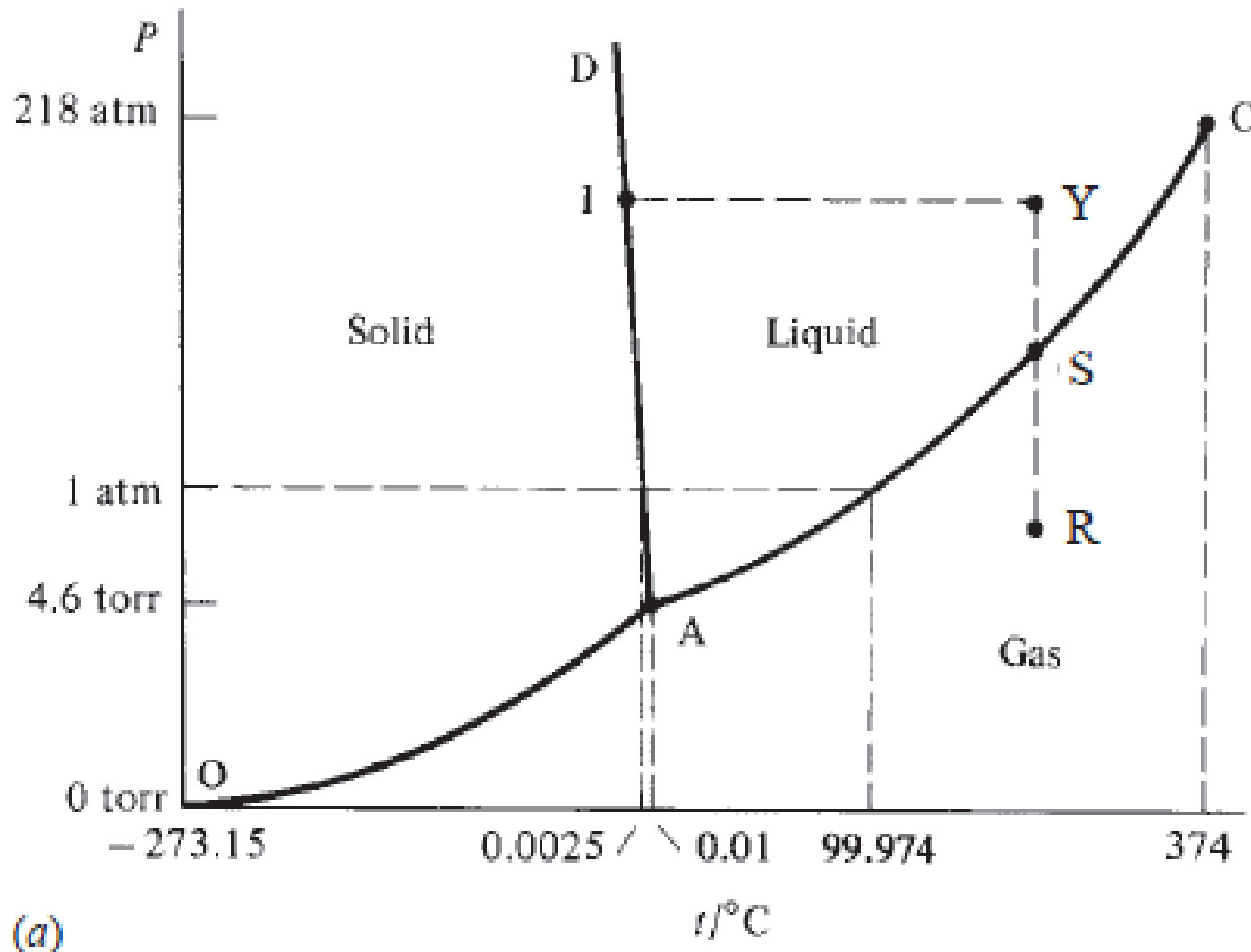
A phase is a homogeneous portion of a system, and this system has three phases: $\text{CaCO}_3(s)$, $\text{CaO}(s)$, and $\text{CO}_2(g)$. The system has three chemical species. There is one reaction-equilibrium condition, $\mu_{\text{CaCO}_3(s)} = \mu_{\text{CaO}(s)} + \mu_{\text{CO}_2(g)}$, so $r = 1$. Are there any additional restrictions on the mole fractions? It is true that the number of moles of $\text{CaO}(s)$ must equal the number of CO_2 moles: $n_{\text{CaO}(s)} = n_{\text{CO}_2(g)}$. However, this equation cannot be converted into a relation between the mole fractions in each phase, and it does not provide an additional relation between intensive variables. Hence

$$c_{\text{ind}} = c - r - a = 3 - 1 - 0 = 2$$

$$f = c_{\text{ind}} - p + 2 = 2 - 3 + 2 = 1$$

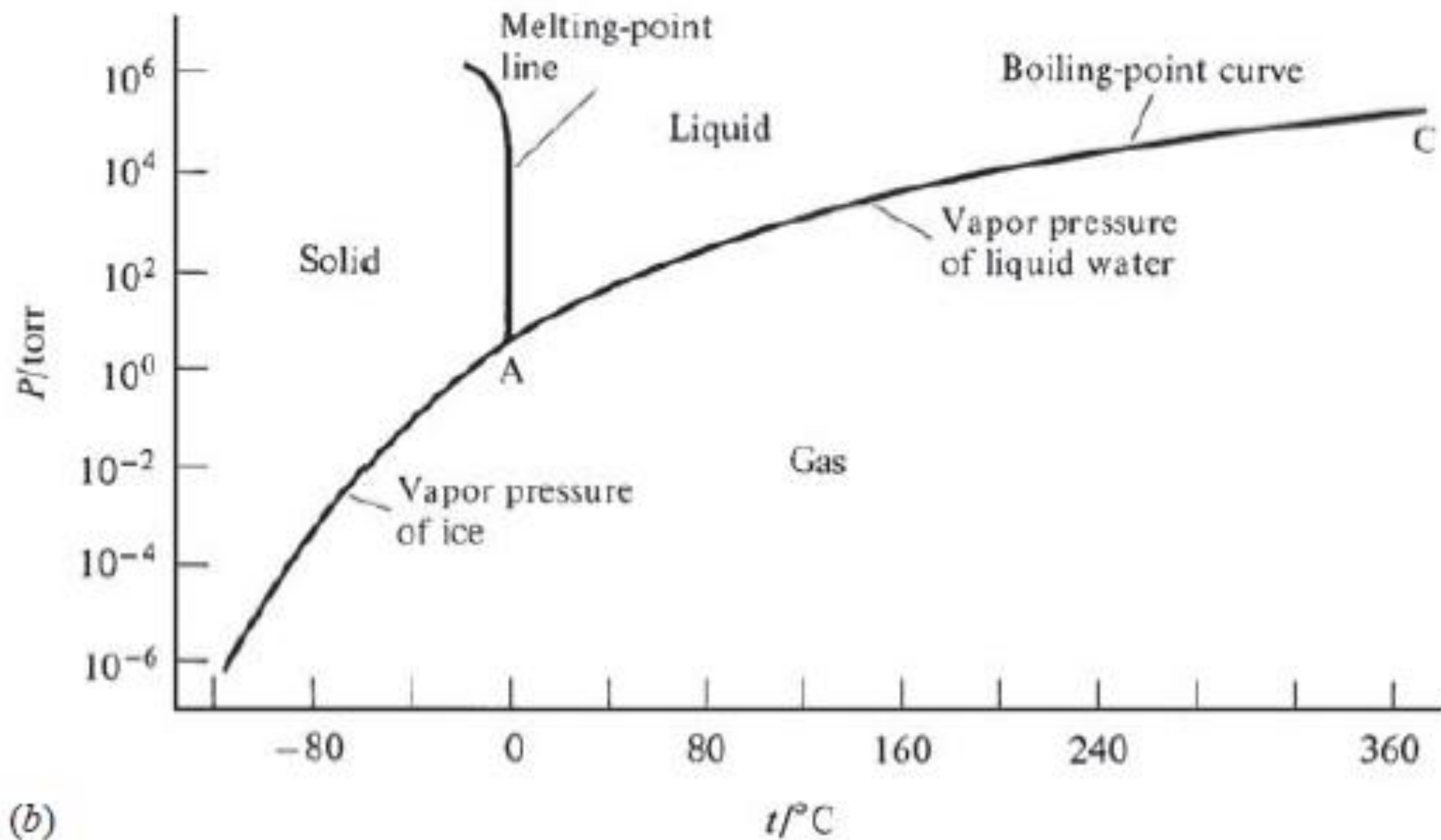
The value $f = 1$ makes sense, since once T is fixed the pressure of CO_2 gas in equilibrium with the CaCO_3 is fixed by the reaction-equilibrium condition, and so P of the system is fixed.

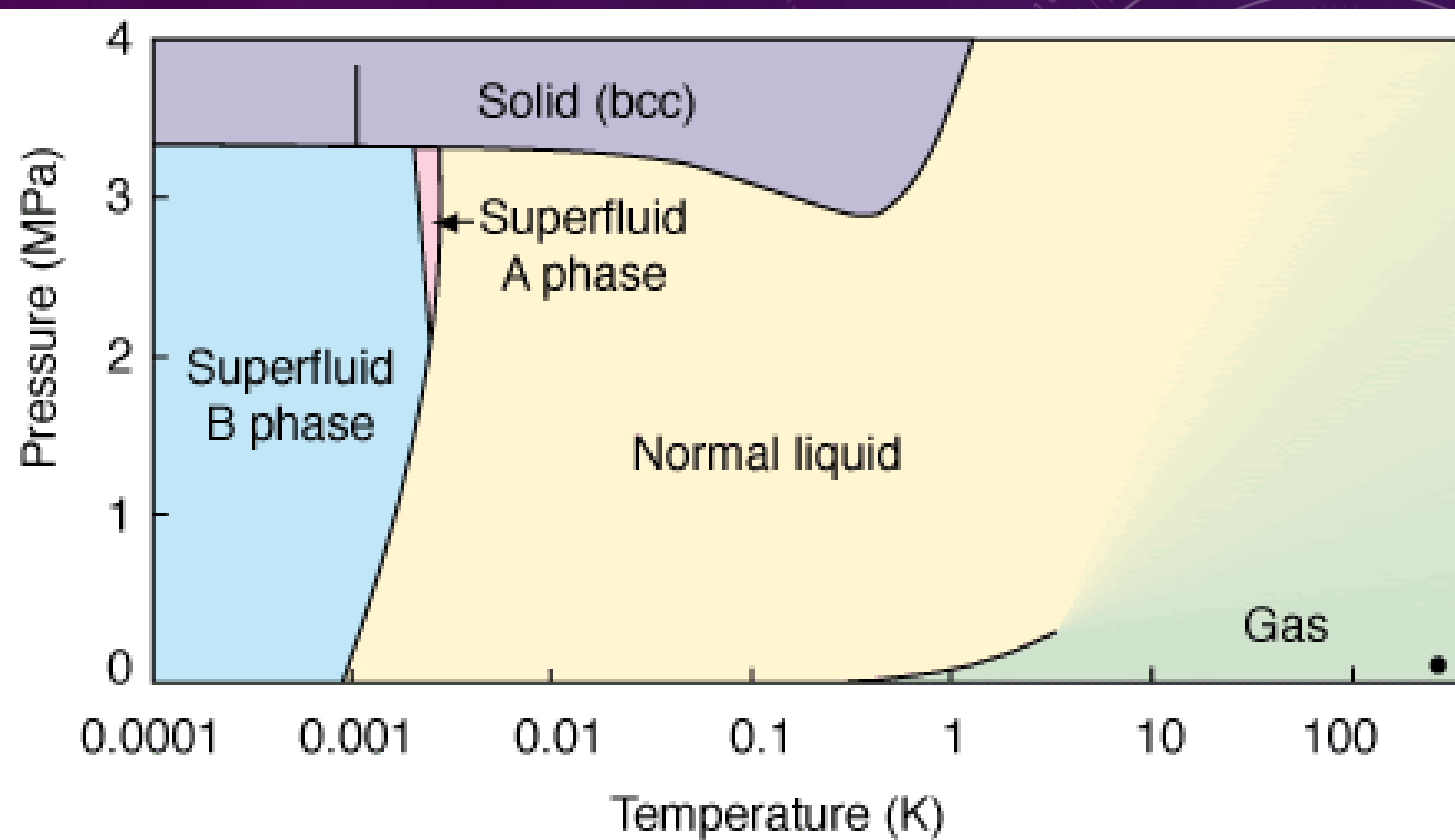
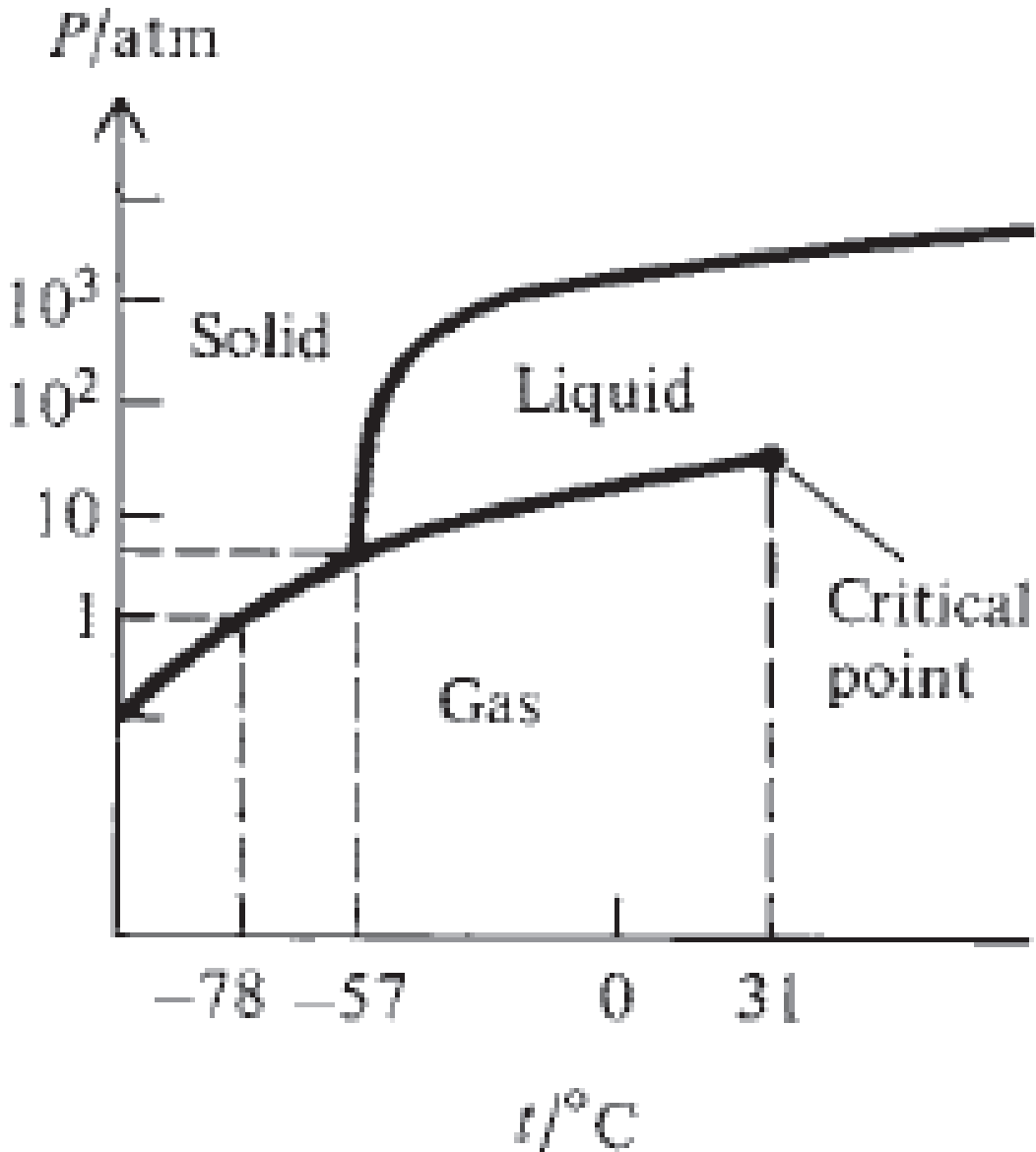
PHASE DIAGRAM



H_2O

We can represent any intensive state of a one-component system by a point on a two-dimensional P-versus-T diagram, where each point corresponds to a definite T and P. Such a diagram is a ***phase diagram***.





Supercritical Fluid - A point where distinct liquid and gas phases do not exist

Superfluid - Superfluidity is the characteristic property of a fluid with zero viscosity which therefore flows without any loss of kinetic energy. When stirred, a superfluid forms vortices that continue to rotate indefinitely.

PHASE CHANGE AND THE ENERGY ASSOCIATED IN IT

Enthalpies and Entropies of Fusion and Vaporization^a

Substance	T_{nmp} K	$\Delta_{\text{fus}}H_{\text{m}}$ kJ/mol	$\Delta_{\text{fus}}S_{\text{m}}$ J/(mol K)	T_{nbp} K	$\Delta_{\text{vap}}H_{\text{m}}$ kJ/mol	$\Delta_{\text{vap}}S_{\text{m}}$ J/(mol K)	$\Delta_{\text{vap}}S_{\text{m}}^{\text{THE}}$ J/(mol K)
Ne	24.5	0.335	13.6	27.1	1.76	65.0	64.8
N ₂	63.3	0.72	11.4	77.4	5.58	72.1	73.6
Ar	83.8	1.21	14.4	87.3	6.53	74.8	74.6
C ₂ H ₆	89.9	2.86	31.8	184.5	14.71	79.7	80.8
(C ₂ H ₅) ₂ O	156.9	7.27	46.4	307.7	26.7	86.8	85.1
NH ₃	195.4	5.65	28.9	239.7	23.3	97.4	83.0
CCl ₄	250.	2.47	9.9	349.7	30.0	85.8	86.1
H ₂ O	273.2	6.01	22.0	373.1	40.66	109.0	86.7
I ₂	386.8	15.5	40.1	457.5	41.8	91.4	88.3
Zn	693.	7.38	10.7	1184.	115.6	97.6	96.3
NaCl	1074.	28.2	26.2	1738.	171.	98.4	99.4

^a $\Delta_{\text{fus}}H_{\text{m}}$ and $\Delta_{\text{fus}}S_{\text{m}}$ are at the normal melting point (nmp). $\Delta_{\text{vap}}H_{\text{m}}$ and $\Delta_{\text{vap}}S_{\text{m}}$ are at the normal boiling point (nbp). $\Delta_{\text{vap}}S_{\text{m}}^{\text{THE}}$ is the normal-boiling-point $\Delta_{\text{vap}}S_{\text{m}}$ value predicted by the Trouton–Hildebrand–Everett rule.

A phase change at constant T and P is generally accompanied by an enthalpy change, often called the (latent) heat of the transition. (Certain special phase changes have $\Delta H=0$) One has enthalpies or heats of fusion (solid $\rightarrow$ liquid), sublimation (solid $\rightarrow$ gas), vaporization (liquid $\rightarrow$ gas), and transition (solid $\rightarrow$ solid).

THE CLAPEYRON EQUATION

The Clapeyron equation (a.k.a. Clausius Clapeyron Equation) gives the slope dP/dT of a two-phase equilibrium line on a P-T phase diagram of a one-component system and it is derived using this principle: For any point on the a-b equilibrium line. The molar Gibbs energies of one-component phases in equilibrium are equal.

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m} = \frac{\Delta H}{T \Delta V} \quad \text{one component two-phase equilib.}$$

$$dP/dT \approx P \Delta H_m / RT^2$$

$$\frac{d \ln P}{dT} \approx \frac{\Delta H_m}{RT^2} \quad \text{solid-gas or liq.-gas equilib. not near } T_c$$

EXERCISES

The normal boiling point of ethanol is 78.3°C , and at this temperature $\Delta_{\text{vap}}H_{\text{m}}$ is 38.9 kJ/mol . To what value must P be reduced if we want to boil ethanol at 25.0°C in a vacuum distillation?

The boiling point is the temperature at which the liquid's vapor pressure equals the applied pressure P on the liquid. The desired value of the applied pressure P is thus the vapor pressure of ethanol at 25°C . To solve the problem, we must find the vapor pressure of ethanol at 25°C . We know that the vapor pressure at the normal boiling point is 760 torr. The variation of vapor pressure with temperature is given by the approximate form (7.19) of the Clapeyron equation: $d \ln P/dT \approx \Delta H_{\text{m}}/RT^2$. If the temperature variation of $\Delta_{\text{vap}}H_{\text{m}}$ is neglected, integration gives [Eq. (7.21)]

$$\ln \frac{P_2}{P_1} \approx -\frac{\Delta H_{\text{m}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Let state 2 be the normal-boiling-point state with $T_2 = (78.3 + 273.2) \text{ K} = 351.5 \text{ K}$ and $P_2 = 760 \text{ torr}$. We have $T_1 = (25.0 + 273.2) \text{ K} = 298.2 \text{ K}$ and

$$\ln \frac{760 \text{ torr}}{P_1} \approx - \frac{38.9 \times 10^3 \text{ J/mol}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{351.5 \text{ K}} - \frac{1}{298.2 \text{ K}} \right) = 2.38$$

$$760 \text{ torr}/P_1 \approx 10.8, \quad P_1 \approx 70 \text{ torr}$$

The experimental vapor pressure of ethanol at 25°C is 59 torr. The substantial error in our result is due to nonideality of the vapor (which results mainly from hydrogen-bonding forces between vapor molecules) and to the temperature variation of $\Delta_{\text{vap}}H_{\text{m}}$; at 25°C , $\Delta_{\text{vap}}H_{\text{m}}$ of ethanol is 42.5 kJ/mol, substantially higher than its 78.3°C value. For an improved calculation, see Prob. 7.25.

EXERCISES

Find the melting point of ice at 100 atm.

$$P_2 - P_1 \approx \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \ln \frac{T_2}{T_1} \quad \text{solid-liq. eq., } T_2 - T_1 \text{ small}$$

Since this is a solid–liquid equilibrium, Eq. (7.24) applies. [*A frequent student error is to apply Eq. (7.19) to solid–liquid equilibria.*] For 1 g of ice, $\Delta_{\text{fus}}H = 333.6 \text{ J}$ and the densities give $\Delta_{\text{fus}}V \equiv V_{\text{liq}} - V_{\text{solid}} = 1.000 \text{ cm}^3 - 1.091 \text{ cm}^3 = -0.091 \text{ cm}^3$. Let state 1 be the normal melting point. Then $P_2 - P_1 = 100 \text{ atm} - 1 \text{ atm} = 99 \text{ atm}$, and (7.24) becomes

$$99 \text{ atm} \approx \frac{333.6 \text{ J}}{(273.15 \text{ K})(-0.091 \text{ cm}^3)} \Delta T$$
$$\Delta T = -7.38 \text{ K cm}^3 \text{ atm/J}$$

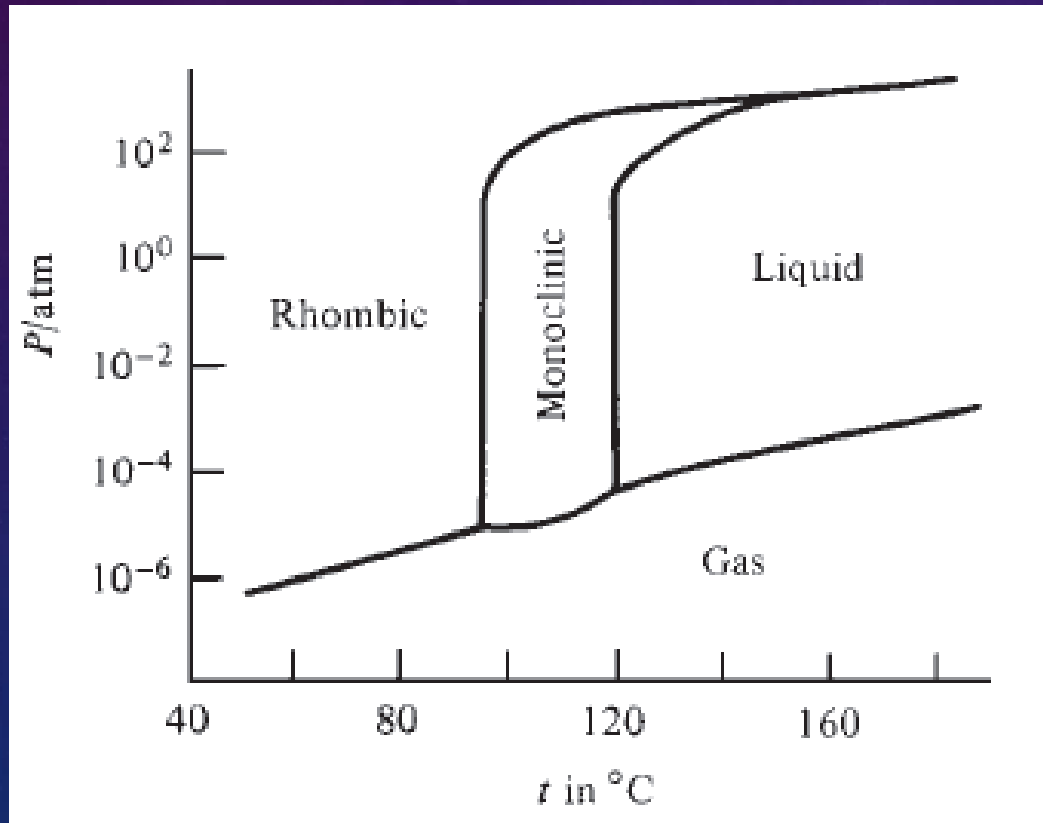
We now use two values of R to convert $\text{cm}^3 \text{ atm}$ to joules, so as to eliminate $\text{cm}^3 \text{ atm/J}$.

$$\Delta T = -7.38 \text{ K} \frac{\text{cm}^3 \text{ atm}}{\text{J}} \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}} = -0.75 \text{ K}$$

Hence, $T_2 = 273.15 \text{ K} - 0.75 \text{ K} = 272.40 \text{ K}$. The pressure increase of 99 atm has lowered the melting point by only 0.75 K to -0.75°C .

SOLID-SOLID PHASE TRANSITIONS

Many substances have more than one solid form. Each such form has a different crystal structure and is thermodynamically stable over certain ranges of T and P . This phenomenon is called *polymorphism*. Polymorphism in elements is called *allotropy*.



Part of the phase diagram for sulfur

Metastability – the lower the molar Gibbs value, the more stable the phase.

Another example of metastability besides orthorhombic sulfur is diamond.

OTHERS

Other examples are liquids cooled below their freezing points (supercooled liquids) or heated above their boiling points (superheated liquids) and gases cooled below their condensation temperatures (supersaturated vapors). One can supercool water to -40°C and superheat it to 280°C at 1 atm.

A solid usually cannot be superheated above its melting point. Computer simulations of solids indicate that the surface of a solid begins to melt below the melting point to give a thin liquidlike surface film whose properties are intermediate between those of the solid and those of the liquid, and whose thickness increases as the melting point is approached.

CAPILLARY-RISE METHOD

The capillary rise method is a test conducted to determine the surface tension of a liquid or the contact angle of liquid with soil or pipe material. Capillary rise is the rise in a liquid above zero pressure level caused by net upward force that is produced by the attraction of water molecules to a solid surface.

$$\gamma = \frac{1}{2}(\rho_{\beta} - \rho_{\alpha})ghr \quad \text{for } \theta = 0$$

$$\gamma = \frac{1}{2}(\rho_{\beta} - \rho_{\alpha})ghr / \cos \theta.$$

At the right is the formula for calculating surface tension

Where; ρ – density

g – gravity constant

r – radius

h – height

EXERCISES

For a water–air interface at 25°C and 1 atm, calculate the capillary rise in a glass capillary tube with inside diameter 0.200 mm. The surface tension of water at 25°C is 72.0 mN/m. The densities of air and water at 25°C and 1 atm are 0.001 g/cm³ and 0.997 g/cm³.

Substitution in (7.37) gives

$$0.0720 \text{ N/m} = \frac{1}{2} (0.996) (10^{-3} \text{ kg}/10^{-6} \text{ m}^3) (9.81 \text{ m/s}^2) h (0.000100 \text{ m})$$

$$h = 0.147 \text{ m} = 14.7 \text{ cm}$$

since 1 N = 1 kg m/s². The substantial value of h is due to the tiny diameter of the capillary tube.

FOOD FOR THOUGHT: VACUUM DECAY

Some physicists have speculated that the universe might currently exist in a metastable high-energy false-vacuum state that is separated by an energy barrier from the lower energy true vacuum state. If this is so, there is a slight probability for the universe to spontaneously undergo a phase transition to the true vacuum state. The transition would start at a particular location and would propagate throughout the universe at nearly the speed of light.

“Vacuum decay is the ultimate ecological catastrophe . . . after vacuum decay . . . life as we know it [is] impossible” [S. Coleman and F. DeLuccia, *Phys. Rev. D*, **21**, 3305 (1980)]

READING ASSIGNMENT

Chapter 7.9 – COLLOIDS

Write a brief review of the chapter using these parameters:

Introductory Paragraph

Function and Applications

Personal Conclusion/Recommendations

REFERENCES

- Physical Chemistry 6th Edition – Ira N. Levine
- chem.libretexts.org
- wikipedia.org
- khanacademy.org

Other chemistry websites that can be found using google search.

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THAT IS ALL FOR TODAY!

- Do you have any questions, clarifications or violent reactions?

