STATISTICAL MOLECULAR THERMODYNAMICS

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Video 9.8

Review of Module 9

CRITICAL CONCEPTS FROM MODULE 9

- A phase diagram indicates the state of matter adopted by a pure substance as a function of temperature and pressure.
- Up to 3 phases may be present simultaneously (3 happens only at the triple point); the Gibbs phase rule for a pure substance specifies that freedom to choose temperature and/or pressure is reduced by one for each phase beyond 1 present in a system.
- Water's negative volume of fusion at low pressures is highly unusual and responsible for ice floating on liquid water.
- At the critical temperature, the densities of liquid and gas phases become identical and an enthalpy of fusion is no longer observed.

CRITICAL CONCEPTS FROM MODULE 9

- Free energy of a substance varies with temperature in a fashion that permits the identification of phases and their molar entropies. Free energy of a substance varies with pressure in a fashion that permits the identification of phases and their molar volumes.
- The chemical potential is defined as

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

- At equilibrium, all chemical potentials are equal. Out of equilibrium matter flows from the higher to the lower chemical potential.
- The Clapeyron equation relates points on the solid-liquid coexistence curve to one another.

CRITICAL CONCEPTS FROM MODULE 9

- The Clausius-Clapeyron equation relates points on either solid-gas or liquid-gas coexistence curves to one another to permit estimation of variations in sublimation and vaporization behavior, respectively.
- Both the Clapeyron and Clausius-Clapeyron equations are limited in their application by the assumption of a temperature (or pressure) independent enthalpy of phase transition. Improved performance can be achieved using temperature dependent formulations for this quantity.
- The chemical potential is expressed in a standard-state formulation as

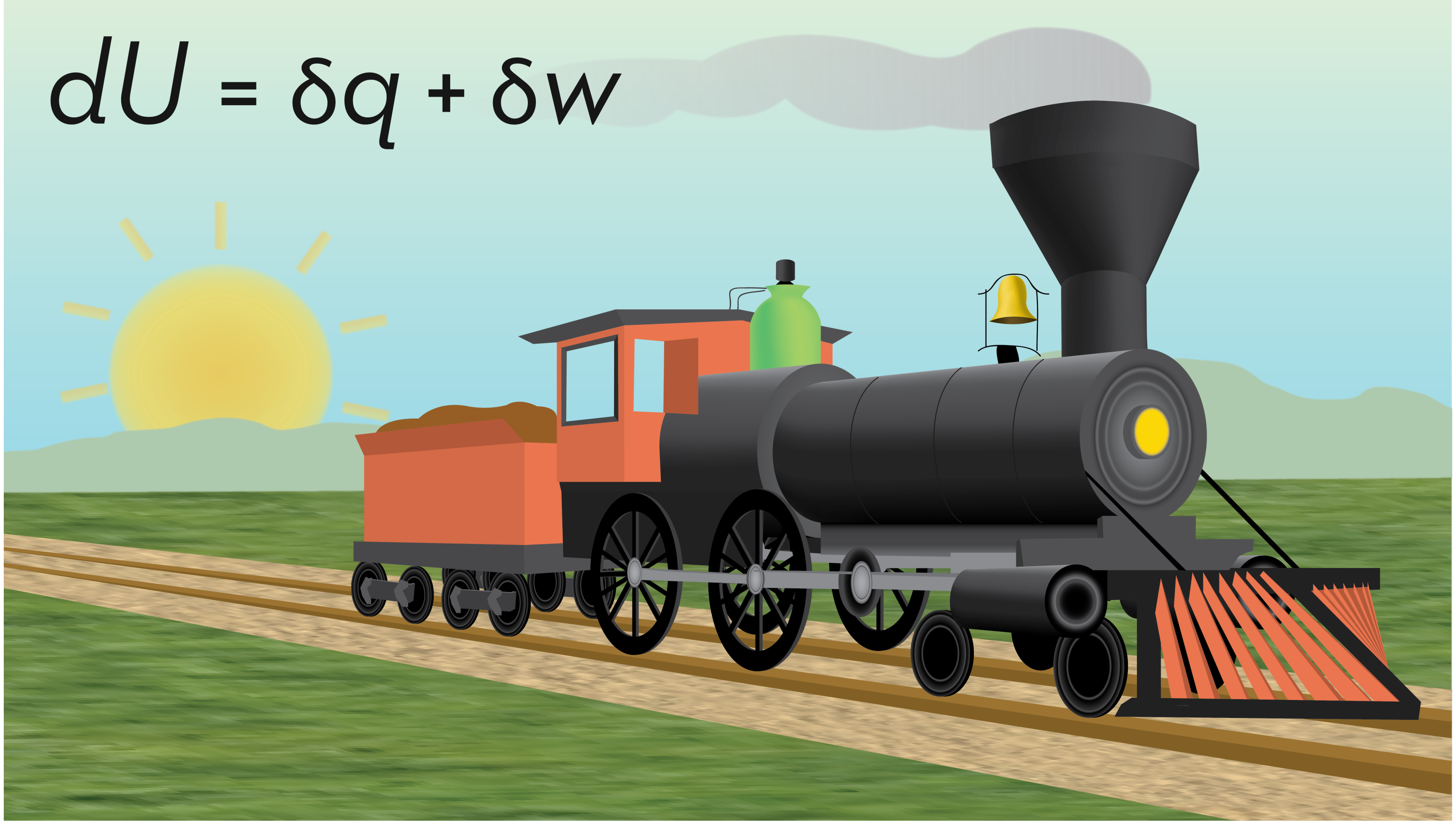
$$\mu(T,P) = \mu^{\circ}(T) + RT\ln\left(\frac{P}{P^{\circ}}\right)$$

CRITICAL CONCEPTS FROM MODULE 9

- For a given substance, the standard-state chemical potential can be computed directly from the partition function using

$$\mu^\circ(T) = -RT\ln\left[\left(\frac{q}{V}\right)\frac{k_\mathrm{B}T}{P^\circ}\right]$$

- Ideal gas behavior provides a way to compute the chemical potential of any gas directly from *q* and measurement of its vapor pressure; by the equality of chemical potentials at equilibrium, that same chemical potential applies to all other phases present in addition to the gas.



Next: Module 10