This paper presents numerical solutions for the coupled radiation and natural convection heat transfer by double diffusion in a square cavity. The governing differential equations are solved by a finite-volume method, by adopting the SIMPLER algorithm for pressure–velocity coupling. The discrete ordinate method is used in modelling the radiative transfer equation. The working fluid is considered as grey, absorbing, emitting and not scattering. The walls of the enclosure are assumed to be opaque, diffuse and grey. A parametric study is performed to illustrate the influence of the Rayleigh number, the buoyancy number, the Lewis number and the optical thickness on the flow structure, the heat and mass transfer. The results obtained can be used as benchmark solutions for the validation of the codes treating the combined natural convection heat transfer by double diffusion and radiation