A specialised vapour liquid equilibrium (VLE) apparatus has been used to measure phase compositions of synthetic hydrocarbon mixtures along isochoric pathways at temperatures from (183 to 253) K and pressures from (2 to 7) MPa. Single-phase, natural gas-like mixtures were prepared gravimetrically using at least three of the following components: CH₄, C₂H₆, C₃H₈, n-C₄H₁₀, i-C₄H₁₀ and n-C₅H₁₀. These mixtures were transferred to the VLE cell at ambient temperature and then cooled at constant volume to conditions characteristic of cryogenic distillation columns in liquefied natural gas (LNG) plants. Samples of the vapour and liquid phases were acquired and analysed simultaneously. The measured mole fractions had a relative precision of 0.5 % and a relative uncertainty of about 2 %, which was the noise-floor of the gas chromatograph detector calibration. The measured VLE data were compared with several equations of state (EOS) including the multi-parameter GERG-2004 EOS and cubic EOS used in process simulation software. The deviations between the measured and calculated compositions were largest for the liquid phase and exceeded the expected uncertainty of cubic EOS tuned to binary mixture VLE data. The results of empirically tuning EOS directly to multi-component mixture data will also be presented.